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CURE ANALYSIS OF PROMOTED POLYESTER AND VINYLESTER REINFORCED COMPOSITES AND HEAT TRANSFER IN RTM MOLDS

Azizeh YOUSEFI-MOSHIRABAD
DÉPARTEMENT DE GÉNIE CHIMIQUE
ÉCOLE POLYTECHNIQUE DE MONTRÉAL

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Cette thèse intitulée:

CURE ANALYSIS OF PROMOTED POLYESTER AND VINYLESTER REINFORCED COMPOSITES AND HEAT TRANSFER IN RTM MOLDS

présentée par: YOUSEFI-MOSHIRABAD Azizeh
en vue de l'obtention du diplôme de : Philosophiae Doctor
a été dûment acceptée par le jury d'examen constitué de:

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M. LAFLEUR Pierre G., Ph.D., membre et directeur de recherche

M. GAUVIN Raymond, Ph.D., membre et co-directeur de recherche

M. BOUKHILI Rachid, Ph.D., membre

M. KAMAL Musa R., Ph.D., membre

To my husband
Manouchehr
for his patience and encouragement
and to
my parents, sisters and brothers
who inspired me in so many ways

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RÉSUMÉ

À l'heure actuelle, le délai requis pour la chauffe et la polymérisation de la résine constitue le principal facteur limitant la réduction des temps de production dans les procédés de fabrication des polyméres composites. Cependant, le temps de réticulation d'une pièce composite dépend fortement de la formulation de la résine utilisée. Les résines contiennent plusieurs additifs; la compréhension de l'influence de ces additifs sur la cinétique de réaction revêt donc une importance capitale dans les procédés de fabrication. Dans le présent travail, un modèle phénoménologique de la cinétique autocatalytique a été utilisé pour décrire les réactions de réticulation d'une résine polyester et d'une résine vinylester, contenant un promoteur à base de cobalt. Les modifications à la réticulation des systèmes contenant un promoteur, résultant de l'incorporation de fibres de verre coupées, ont également été étudiées. Pour établir un modèle cinétique de la réticulation, une série d'essais isothermes a été réalisée sur le DSC à différentes températures. Une nouvelle procédure a été développée pour compenser la perte d'information liée à la partie de la réticulation ayant lieu pendant la période de stabilisation du calorimètre, celle-ci n'étant pas considérée par l'appareil comme faisant partie du test. Cette procédure permet de déterminer un facteur de correction applicable à la quantité totale de chaleur dégagée, et ce pour différentes températures.

En dépit du fait que les résines polyester ne contenant pas de promoteur montrent des paramètres cinétiques constants, une dépendance de ces paramètres envers la température

a été posée pour les polyesters contenant un promoteur, afin de prendre en compte la complexité du mécanisme de réticulation dans ce cas. L'effet principal de la présence de fibres de verre dans la résine polyester contenant un promoteur est une diminution du taux de réaction global à basse température. Les fibres se comportent comme des puits de chaleur, et absorbent une partie de la chaleur de réaction; une nouvelle cinétique de réaction isotherme en résulte. Les résultats ainsi obtenus indiquent également que la somme des exposants de la réaction n'est pas une constante; les fluctuations des caractéristiques de la réticulation sont causées par la présence du promoteur. De plus, pour une température donneé, la chaleur totale dégagée lors de la réaction isotherme est demeurée essentiellement identique pour les systèmes contenant un promoteur, avec ou sans fibres de verre.

Les effects du promoteur et des fibres de verre sur la cinétique de réticulation du vinylester ont été étudiés par calorimétrie différentielle (DSC), par une série de mesures isothermes, sur la plage comprise entre 25 et 90 °C. Le principal effet du promoteur est d'introduire une déviation significative des taux isothermes de réaction, comparativement à la courbe classique, en forme de cloche. Pour prendre en compte cette déviation, un modèle cinétique existant, contenant 5 paramètres, a été utilisé. Les paramètres cinétiques estimés pour la résine vinylester additionnée d'un promoteur ont montré une dépendance envers la température, sur la plage étudiée dans le cadre du présent travail. Il a également été observé que l'ajout de fibres de verre aux résines diminue fortement la vitesse de réticulation en fin de cuisson isotherme. Puisque l'application d'agents de surface convenablement choisis peut vaincre l'inhibition de la réaction causée par les surfaces contenant des oxides pour les composites renforcés de fibres de verre, l'inhibition observée a été attribuée à la présence d'un agent de surface formulé pour une utilisation avec une résine polyester. Afin d'évaluer les variations de la viscosité pendant la progression de la réaction, des mesures rhéologiques ont été effectuées sur la résine vinylester contenant un promoteur, à l'aide d'un viscosimètre à plaques parallèles. Il en a été déduit que ce second modèle, caractérisé par une énergie d'activation dépendante du degré de conversion, pouvait représenter correctement l'évolution de la viscosité d'un système contenant un promoteur.

Le programme informatique développé dans ce travail permet de solutionner les équations de la conduction transitoire et du taux de réaction. La méthode de Galerkin a été utilisée. Les modèles cinétiques développés à cette fin nous ont permis de prédire l'influence de l'incorporation d'un renfort sur les variables du procédé, notamment le temps de gel et le temps de démoulage, ainsi que sur les distributions de la température et sur le degré de réticulation selon la normale à l'écoulement, pour les deux résines étudiées. Une analyse de sensibilité, basée sur la variation de la chaleur de réaction isotherme totale, a été réalisée dans le cadre de ce travail. Il a été démontré qu'une faible variation de la chaleur isotherme peut causer une différence notable sur l'estimation de la température et sur le degré de réticulation, notamment au moment ou les maxima sont atteints. Une comparaision a été faite entre les résultats numériques et les données expérimentales, pour le cas d'une pièce polyester réticulée dans un moule chauffant. La différence entre les conclusions théoriques et expérimentales a été attribuée aux incertitudes associées à l'estimation des paramètres cinétiques aux températures élevées, ainsi qu'aux délais de réponse aux changements soudains de température induits par les thermocouples.

ABSTRACT

Experimental works have shown that the time required to heat and cure the resin system is a major factor inhibiting further reduction in the cycle time of the composite manufacturing processes. Since the cure time of a composite part is mainly determined by the resin formulation, and thermosetting resins generally contain a variety of additives, a good understanding of the influence of different additives on the kinetics of cure is of great importance in composite manufacturing processes. In the present work, a phenomenological autocatalytic kinetic model was used to describe the cure reactions of a polyester and a vinylester resin containing a cobalt-based promoter. The changes in the curing characteristics of the promoted systems caused by incorporation of chopped glass fibers were also investigated. To establish a kinetic model for the cure reactions, isothermal DSC experiments were performed at different temperatures. In the present work, a new procedure was developed to compensate for the unrecorded extent of cure during the stabilization period of the calorimeter in isothermal DSC measurements. This procedure enabled us to define a correction factor related to the total isothermal heat of cure at different isothermal cure temperatures.

In spite of the fact that nonpromoted polyester resins show constant kinetic parameters, in the case of the promoted polyester resin kinetic parameters were considered temperature dependent to account for the complexity of the cure mechanism in the presence of the promoter. The primary effect of the glass fibers on the curing behavior of promoted polyester resin was a decrease in the overall reaction rate at low cure temperatures. Acting as heat sinks, glass fibers absorbed the heat of reaction, and yielded a different cure behavior in the isothermal cure. The obtained results also indicated that the sum of reaction exponents was not a constant value due to the changes caused by the promoter in the cure characteristics of the polyester system. Moreover, for a given temperature, the total isothermal heat of reaction was almost identical for both filled and unfilled systems.

The effects of promoter and glass fibers on the curing kinetics of vinylester resin at 25-90°C were studied by isothermal DSC measurements. The major effect of the promoter was a significant deviation of the rate exotherms from bell-shaped profile. To take into account this deviation, an existing kinetic model with five kinetic parameters was used. The estimated kinetic parameters for the cure system of the promoted vinylester resin had a temperature dependent characteristic within the temperature range studied in this work. This characteristic was attributed to the different cure mechanisms governing in different temperature ranges. It was also found that the addition of glass fibers to the cure formulation caused a severe deceleration of the cure reactions at the end of the isothermal cure period. Since a proper selection of surface treating agents can overcome the inhibition of cure caused by oxide surfaces in the case of glass fiber reinforced composites, the inhibition was mostly attributed to the sizing agent of the reinforcement which was formulated for a polyester resin. To evaluate the variation of viscosity during the cure reactions, rheological measurements were conducted on the promoted vinylester resin in steady shear mode using a set of parallel plates. It was inferred that a chemorheological model with conversion dependent activation energy was able to represent adequately the chemoviscosity of a promoted system.

In the program developed in this work, transient heat conduction and rate of cure equations were solved as a coupled system of equations. The Galerkin finite element method was applied to solve the problem. The specialized kinetic models enabled us to predict the influence of the incorporated reinforcement on the process variables, e.g. gel time and demold time, and on the distributions of temperature and extent of cure in through-the-thickness direction of the polyester and vinylester composites. As expected, the peak temperature decreased with increasing glass fiber content, and it is delayed because the thermal conductivity of the polymer was smaller than that of glass fibers. A sensitivity analysis based on the variation of the total isothermal heat of cure was performed in the present work. It was shown that a small variation on the isothermal heat of cure may cause a considerable difference on the estimation of temperature and extent of cure particularly at the peak time. A comparison was made between numerical results and experimental data for a reinforced polyester part cured in a heated mold. The discrepancy between the theoretical and experimental results was attributed to the uncertainties associated with the estimation of kinetic parameters at high cure temperatures, as well as to the delay time of thermocouples in response to sudden temperature changes.

CONDENSÉ EN FRANÇAIS

La production par moulage RTM (moulage par transfert de résine - Resin Transfer Molding) de composites à matrices polymères thermodurcissables renforcés de fibres continues, suscite un intérêt grandissant de la part de l'industrie, notamment au niveau des fabricants de l'industrie automobile. Les pièces ainsi fabriquées présentent de bonnes propriétés mécaniques et de faibles densités; de plus, leur coût de production est relativement bas. À l'heure actuelle, le délai requis pour la chauffe et la polymérisation de la résine constitue le principal facteur limitant la réduction des temps de production.

Le calcul des temps de réaction des résines, appliqué à différents procédés de fabrication, a fait l'objet de nombreux travaux de recherche. L'approche généralement retenue consiste à coupler les équations de la conduction en régime transitoire à celles de la génération de chaleur à l'intérieur de la pièce produite. La combinaison de ce modèle thermique à un modèle de l'écoulement permet ensuite de prévoir l'évolution des températures pour le cycle complet. Cependant, le temps de réticulation d'une pièce composite dépend fortement de la formulation de la résine utilisée. Les résines contiennent plusieurs additifs; la compréhension de l'influence de ces additifs sur la cinétique de réaction revêt donc une importance capitale pour la modélisation des procédés de fabrication.

La température de décomposition de la majorité des initiateurs (ou amorceurs) est relativement élevée; à la plupart des résines commerciales est donc ajouté un promoteur (ou accélérateur), permettant la production de pièces à température ambiante. Le promoteur permet de hausser la vitesse de la réaction en initiant celle-ci. De plus, l'addition de promoteur force la réaction à démarrer à des températures plus basses, prévenant ainsi la dégradation du centre des pièces qui est souvent observé lorsque celles-ci sont moulées à haute température. La principale difficulté associée à l'utilisation d'un promoteur réside dans la plus grande complexité du mécanisme de réticulation. En général, la conversion des résines conçues pour une utilisation à basse température n'est que partielle, en raison du phénomène de vitrification. Dans ce cas, le modèle autocatalytique ne s'applique pas à la totalité de la réaction.

Les polymères thermodurcissables réticulés présentent, en général, des propriétés physiques moyennes. De plus, une hausse marquée des températures se produit généralement lors de la réaction exothermique des résines, en raison de leurs faibles conductivités thermiques. De cette hausse peut résulter une sévère diminution des propriétés mécaniques des pièces, voire même leur endommagement. L'ajout de renforts présente deux avantages importants: d'une part, les propriétés mécaniques peuvent être grandement améliorées, notamment les modules et la résistance à l'impact. D'autre part, les renforts font office de puits thermiques, réduisant ainsi la température de moulage et le risque de bris.

Les fibres de verre, généralement utilisées en production, peuvent fortement inhiber la réticulation des résines, particulièrement à basse température. L'existence d'une relation entre le caractère de donneur d'éléctron des oxides et l'abaissement des pics exothermiques de réticulation des résines par ces mêmes oxides, a été démontrée. L'activité de donneur d'éléctron des oxides formés en présence de verre peut être classée comme suit:

$$MgO > ZnO > Al_2O_3 > TiO_2 > SiO_2$$

Les fibres de verre E, qui sont courrament utilisées pour les pièces de performance moyenne, peuvent également diminuer le caractère exothermique de la réaction si un traitement de surface approprié ne leur est pas appliqué. En conséquence, la considération de l'effet inhibiteur du renfort est un aspect essentiel de la modélisation des profils de température et de la cinétique de réticulation des pièces composites.

Dans le présent travail, un modèle phénoménologique de la cinétique autocatalytique a été utilisé pour décrire les réactions de réticulation d'une résine polyester et d'une résine vinylester, contenant un promoteur à base de cobalt. Les modifications à la réticulation des systèmes contenant un promoteur, résultant de l'incorporation de fibres de verre coupées, ont également été étudiées.

La calorimétrie dynamique différentielle (DSC - Dynamic Differential Scanning Calorimetry) a été utilisée pour l'étude des résines polyester contenant un promoteur mais exemptes de renfort; les taux de chauffe considérés sont de 5, 10, 15, et 20 °C/min. Un second échauffement a été effectué sur les échantillons réticulés, de facon à déterminer leurs lignes de base. La présente étude montre que l'augmentation du taux de chauffe résulte en une augmentation de la température d'initiation de la réticulation et de la température maximale atteinte lors de la réaction. Par contre la chaleur totale dégagée lors de la réaction, estimée par l'aire de l'exotherme, montre une tendance inverse. Selon la littérature, il est possible d'atteindre la réticulation complète d'une résine en y ajoutant une quantité suffisante d'initiateur, et en réalisant la réticulation dynamique à une vitesse de chauffe très faible. Dans le cadre de ce travail, la chaleur de réaction dégagée par une conversion complète du monomère a été obtenue par extrapolation à vitesse de chauffe nulle.

Pour établir un modèle cinétique de la réticulation, une série d'essais isothermes, donnant le degré de conversion en fonction du temps, a été réalisée sur le DSC à différentes températures. Dans le cas de la résine polyester, une partie significative de la réaction se produit alors que le calorimètre est en période de stabilisation, aux températures supérieures à 75 °C. Les résultats obtenus dans cette plage de température n'ont donc pas été considérés dans l'analyse.

Une nouvelle procédure a été développée pour compenser la perte d'information liée à la partie de la réticulation ayant lieu pendant la période de stabilisation du calorimètre, celle-ci n'étant pas considérée par l'appareil comme faisant partie du test. Cette procédure permet de déterminer un facteur de correction applicable à la quantité totale de chaleur dégagée, et ce pour différentes températures. Il a été démontré que le facteur de correction peut également être appliqué aux cas de réticulations à faibles températures, puisque les taux de génération de chaleur prennent alors des valeurs tombant sous le seuil de sensibilité de l'appareil; la fiabilité des données ainsi obtenues peut être remise en cause.

En dépit du fait que les résines polyester ne contenant pas de promoteur montrent des paramètres cinétiques constants, une dépendance de ces paramètres envers la température a été posée pour les polyesters contenant un promoteur, afin de prendre en compte la complexité du mécanisme de réticulation dans ce cas. Il a été observé que cette complexité résulte de la présence du promoteur, qui induit chimiquement la réaction à basse température. L'effet principal de la présence de fibres de verre dans la résine polyester contenant un promoteur est une diminution du taux de réaction global à basse température. Les fibres se comportent comme des puits de chaleur, et absorbent une partie de la chaleur de réaction; une nouvelle cinétique de réaction isotherme en résulte. Sur la base de paramètres cinétiques estimés, deux domaines de température, différenciés par leurs caractéristiques de réticulation, ont été observés:

1. Aux températures inférieures à 60°C, où l'influence de l'agent promoteur est plus prononcée, le rôle essentiel du promoteur est d'augmenter la vitesse globale de réaction via le facteur de fréquence d'Arrhenius. L'exposant de l'équation décrivant la réaction

a également été modifié, et ce sur tout le domaine de température. L'ajout de fibres de verre a donné lieu à une diminution de la vitesse de réticulation, à travers le facteur de fréquence d'Arrhenius; ce dernier effet a été observé aux températures inférieures à 45 °C . La cause de la décélération de la réaction a pu être identifiée; il s'agit de la fonctionnalité inadéquate des radicaux libres inorganiques produits en présence des fibres de verre. L'incorporation de fibres de verre dans la résine polyester a également résulté en un allongement de la période d'induction de la réaction, aux températures inférieures à 60 °C. En absorbant la chaleur de réaction, les fibres de verre se comportent en puits de chaleur; leur présence résulte en un taux de réaction réduit et affecte la réticulation de manière défavorable. Contrairement au promoteur, les fibres de verre n'ont pas affecté les exposants de la réaction de facon appréciable.

2. Aux températures supérieures à 60 °C, une diminution significative de la constante du taux de réaction de la résine polyester contenant un promoteur a été observée, à partir des changements du facteur d'Arrhenius et de l'énergie d'activation de la réticulation. La même tendance a été observée pour les exposants de la réaction, m et n; ceux-ci s'approchent asymptotiquement des valeurs publiées pour les résines polyester ne contenant pas de promoteur. Ces résultats indiquent que l'effet du promoteur est moins significatif aux températures supérieures à 60 °C. Pour les échantillons contenant des fibres de verre, une augmentation de la constante de réaction a été observée aux températures supérieures à 45°C . Cette augmentation a été attribuée aux radicaux

libres inorganiques produits en présence de fibres de verre, dont l'activité est plus adéquate aux températures de réticulation élevées.

Les résultats ainsi obtenus indiqent également que la somme des exposants de la réaction n'est pas une constante; les fluctuations des caractéristiques de la réticulation sont causées par la présence du promoteur. De plus, la chaleur totale dégagée lors de la réaction isotherme est demeurée essentiellement identique pour les systèmes contenant un promoteur, avec ou sans fibres de verre. Il a été observé que les valeurs assignées aux paramètres cinétiques résultent en une prédiction théorique concordant bien avec les résultats expérimentaux obtenus des essais de calorimétrie isothermes.

Les effects du promoteur et des fibres de verre sur la cinétique de réticulation du vinylester ont été étudiés par calorimétrie différentielle (DSC), par une série de mesures isothermes, sur la plage comprise entre 25 et 90 °C . Il a été trouvé qu'en présence d'un promoteur à base de cobalt, la cinétique de réaction est trop complexe pour pouvoir être représentée de facon satisfaisante par un modèle autocatalytique simple. Le principal effet du promoteur est d'introduire une déviation significative des taux isothermes de réaction, comparativement à la courbe classique, en forme de cloche. Pour prendre en compte cette déviation, un modèle cinétique existant, contenant 5 paramètres, a été utilisé; la déviation a été liée à un exposant additionnel. En dépit d'une bonne approximation des taux de réticulation, ce modèle avait le désavantage de donner des valeurs de paramètres cinétiques ne correspondant pas à l'ordre de grandeur habituel.

En corrélant les données expérimentales recueillies à l'équation du taux de réaction, les changements dans la cinétique induits par l'agent promoteur on pu être investigués. Les paramètres cinétiques estimés pour la résine vinylester additionnée d'un promoteur ont montré une dépendance envers la température, sur la plage étudiée dans le cadre du présent travail. Ce comportement a été attribué aux relatives prépondérances que prennent les divers mécanismes de réticulation à différentes températures. Il a été observé que l'effet du promoteur est plus prononcé aux faibles températures, lorsque les réactions sont induites chimiquement.

Des mesures de calorimétrie dynamique ont été conduites aux taux de chauffe de 5, 10, 15, et 20 °C/min sur toutes les résines contenant un promoteur, incluant les mélanges additionnés de fibres de verre. Une différence marquée a pu être observée entre les valeurs de la chaleur dynamique de réaction, obtenues à différents taux de chauffe, à partir des échantillons contenant des fibres de verre d'une part et ceux n'en contenant pas d'autre part. Il a également été observé que l'ajout de fibres de verre aux résines diminue fortement la vitesse de réticulation en fin de cuisson isotherme. En conséquence, une diminution significative du taux de conversion et de la chaleur de réaction finale a pu être observée dans le cas des échantillons contenant des fibres de verre. Également à noter, des périodes d'induction de la réticulation plus longues ont aussi été observées en présence de fibres de verre, aux températures de réaction isotherme inférieures à 60 °C.

L'inhibition de la réticulation en présence de fibres de verre a été attribuée aux propriétés supérieures de mouillage et d'adhésion à ces fibres des molécules de résine vinylester; ceci est dû à la présence de groupes hydroxyles secondaires sur ces molécules. Conséquemment, un nombre élevé de radicaux inorganiques produits dans le médium réactif a été identifié comme étant la cause de la diminution du degré de conversion observée en présence de fibres de verre. Règle générale, l'activité de ces radicaux n'est pas suffisament élevée pour initier d'autres radicaux libres à basse température. Puisque l'application d'agents de surface convenablement choisis peut vaincre l'inhibition de la réaction causée par les surfaces contenant des oxides pour les composites renforcés de fibres de verre, l'inhibition observée a été attribuée à la présence d'un agent de surface formulé pour une utilisation avec une résine polyester.

Dans le cas de la résine vinylester contenant un promoteur mais exempte de fibres, la dépendance des exposants de la réaction envers la température a été représentée par des fonctions de correlation en forme de cloche. En dépit d'un comportement relativement complexe des exposants de la réaction, les valeurs prises par ces expressions approchent asymptotiquement celles des systèmes vinylester exempts de promoteur, aux températures élevées. L'exposant de la réaction autocatalytique de la résine vinylester contenant des fibres de verre a conservé une valeur constante, indépendamment de la température.

Afin d'évaluer les variations de la viscosité pendant la progression de la réaction, des mesures rhéologiques ont été effectuées sur la résine vinylester contenant un promoteur, à l'aide d'un viscosimètre à plaques parallèles. Puisqu'un modèle chimico-rhéologique simple, défini par une seule valeur d'énergie d'activation, ne s'est pas montré apte à représenter le comportement rhéologique des échantillons vinylester additionnés de promoteur, un modèle chimico-rhéologique modifié, prenant en compte l'effet du promoteur, a été introduit. Conséquemment, deux ensembles différents de valeurs ont été assignés aux paramètres rhéologiques, à partir de l'amorce de la réaction, jusqu'à l'atteinte du point de gel. Il en a été déduit que ce second modèle, caractérisé par une énergie d'activation dépendante du degré de conversion, pouvait représenter correctement l'évolution de la viscosité d'un système contenant un promoteur.

À partir d'une estimation des paramètres cinétiques des résines polyester et vinylester additionnées de promoteur, la période du procédé RTM suivant immédiatement le remplissage a été analysée par la méthode des éléments finis. Les modèles cinétiques développés à cette fin nous ont permis de prédire l'influence de l'incorporation d'un renfort sur les variables du procédé, notamment le temps de gel et le temps de démoulage, ainsi que sur les distributions de la température et sur le degré de réticulation selon la normale à l'écoulement, pour les deux résines étudiées.

Le programme informatique développé dans ce travail permet de solutionner les équations de la conduction transitoire et du taux de réaction. La méthode de Galerkin a été utilisée. Il a également été démontré que dans le cas de la résine vinylester, l'incorporation de fibres de verre donne lieu à de plus faibles températures d'exothermes, en raison de la présence de radicaux inorganiques produits dans la résine. Nous avons observé que l'effet inhibiteur du renfort de verre pour les résines à base de polyester était moindre; le délai d'atteinte de la température maximale a été principalement attribué aux effets thermiques induits par la présence des fibres de verre. Ces derniers effets deviennent importants si une différence appréciable existe entre les conductivités thermiques de la résine et du renfort. Les fibres font office de puits de chaleur, et causent certaines modifications aux profils de températures observables à l'intérieur de la pièce moulée.

L'effet de la quantité de renfort sur la température atteinte au centre des pièces faites de résine polyester ou vinylester a été analysé à partir du programme informatique développé. Comme il fallait s'y attendre, la température maximale a montré une diminution avec l'augmentation de la quantité de renfort; l'atteinte de ce maximum a été retardé, puisque la conductivité thermique du polymère est inférieure à celle des fibres de verre. Dans le cas de pièces de vinylester renforcées de verre, les exothermes observés lors de la réticulation étaient plus élevés au départ, comparativement aux pièces non renforcées. Cependant, en fin de réaction, nous avons pu observer un degré de réaction plus élevé pour les pièces vinylester non renforcées.

L'étude de l'influence de l'épaisseur des pièces moulées et de la température des parois sur l'évolution des températures au centre des pièces renforcées a indiqué qu'une augmentation de l'épaisseur résulte en une température maximale au centre plus élevée. De plus, la température maximale atteinte au centre de la pièce augmente avec la température des parois. Ce maximum est atteint plus rapidement lorsque la température des parois est haussée. Ceci résutle en des taux de réticulation plus élevés, et donc en des degrés de conversion rehaussés.

L'influence de l'épaisseur des pièces et de la température des parois sur les variables du procédé telles que le temps de gel et le temps de démoulage a également été étudiée. Le temps de gel des résines vinylester renforcées montre une tendance à la hausse lorsque le taux de verre est augmenté, et une tendance à la baisse lorsque les températures des parois ou l'épaisseur de la pièce sont augmentées. Dans le cas de pièces vinylester non renforcées, le temps de gel observé était exceptionellement élevé, particulièrement à proximité des parois du moule. Exception faite de la zone située près des parois, le temps de gel ne varie à peu près pas avec la position, le long de l'épaisseur de la pièce. La variation soudaine du temps de gel à proximité des parois du moule est dûe à la faible conductivité de la matrice polymère.

Le temps de démoulage a été défini comme étant le délai requis pour l'atteinte d'un degré de conversion minimal de 70% en tout point de la pièce. Pour les pièces les plus épaisses, le temps de démoulage était à peu près constant à proximité du plan central, et augmentait fortement à l'approche des parois du moule; ce phénomène est dû à une accumulation de chaleur dans l'environnement du plan central, et causé par la faible conductivité de la matrice polymère. La diminution du temps de démoulage avec l'augmentation des températures de paroi pour les pièces de polyester était importante pour toutes les pièces renforcées, mais était plus prononcée encore dans le cas des pièces non renforcées.

Une analyse de sensitivité, basée sur la variation de la chaleur de réaction isotherme totale, a été réalisée dans le cadre de ce travail. Il a été démontré qu'une faible variation de la chaleur isotherme peut causer une différence notable sur l'estimation de la température et sur le degré de réticulation, notamment au moment ou les maxima sont atteints. À partir de cette approche, l'amplitude de l'erreur résultante sur la température et sur le degré de conversion à cet instant, à travers l'épaisseur de pièces polyester et vinylester renforcées par des quantités variables de verre, a été évaluée à l'aide du programme informatique développé.

Une comparaision a été faite entre les résultats numériques et les données expérimentales, pour le cas d'une pièce polyester réticulée dans un moule chauffant. La différence entre les conclusions théoriques et expérimentales a été attribuée aux incertitudes associées à l'estimation des paramètres cinétiques aux températures élevées, ainsi qu'aux délais de réponse aux changements soudains de température induits par les thermocouples. Nous avons conclu que dans le cas de résines vinylester renforcées contenant un promoteur, les valeurs des paramètres cinétiques prenant en compte l'effet inhibiteur des fibres de verre devraient préférablement être utilisées lors de l'analyse numérique des procédés de fabrication des matériaux composites.

La procédure d'estimation des paramètres appliquée lors de ce travail s'est avérée fiable pour l'évaluation des paramètres cinétiques. Considérant les complexités impliquées lors de la réticulation des résines thermodurcissables additionnées d'un promoteur, une certaine prudence doit être recommandée dans l’expression de la dépendance des paramètres cinétiques envers la température; c'est-à-dire que ces expressions, dépendantes de température, devraient aussi donner des valeurs acceptables en dehors des plages de température sur lesquelles les données de réticulation ont été recueillies.

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NOMENCLATURE

a	surface area
C	concentration of reactive species
$[C]$	capacitance or damping matrix
$[C']$	effective capacitance or damping matrix
C_p	specific heat (J/g.°K)
$\{F\}$	forcing function
$\{F'\}$	effective forcing function
G	a value between 0 and 1 in Eq. 1.6
h	heat transfer coefficient (J/m^2.s.°K)
k	thermal conductivity (J/m.s.°K)
k_2	reaction rate constant (s^{-1})
$[K]$	permeability tensor in Eq. 1.1 and stiffness matrix in Appendix II
L	half thickness of the mold (m)
m	reaction exponent
n	number of element nodal points, and reaction exponent in Appendix II
N	shape function
p	reaction exponent
P	pressure
Q_u	ultimate enthalpy of cure (kJ/kg of resin)
$\dot{Q}$	rate of heat generation (kJ/m^3.s)
$\dot{Q}'$	dimensionless rate of heat generation
R_Ω	residual of Eq. II.13 in Ω
S_c	source term for the chemical reaction
t	time (s)
t'	dimensionless time
t_f	fill time (s)
t_z	inhibition time (s)
T	temperature (°C)
T'	dimensionless temperature
T_0	initial temperature (°C)
T_{ad}	adiabatic temperature (°C)
T_w	wall temperature (°C)
v	velocity in Chapter 1 (m/s) and volume content in Appendix II

$\bar{v}$	average velocity in Chapter 1 (m/s)
x,y	Cartesian coordinates
x'	dimensionless x coordinate
y'	dimensionless y coordinate
α	thermal diffusivity in Eqs. 1.4 and 1.5
α	cumulative conversion at a given time t
α_{max}	vitrification conversion
$d\alpha/dt$	conversion rate (s^{-1})
Γ	boundary of the region of interest
ΔH	enthalpy of reaction (kJ/kg of resin)
Δt	time step in the numerical analysis
$\Delta t'$	dimensionless time step in the numerical analysis
ϵ	fiber medium porosity
θ	an arbitrary value between 0 and 1
ρ	density (Kg/m^3)
Ω	region of interest in discritization
∇	operator nabla
λ	a coefficient in Eq. 2 (J/m^3.K)
μ	viscosity (Pa.s)

Subscripts

c	composite
f	fiber
r	resin
w	mold wall

INTRODUCTION

Thermosetting materials have a wide variety of applications due to their outstanding heat resistance and performance characteristics. During the passed two decades there have been significant developments in reactive processing, and sophisticated design and control concepts for heat transfer and reaction issues have emerged to improve the product quality and processing efficiency. The Resin Transfer Molding (RTM) process is a composite manufacturing process which has attracted much attention in recent years, particularly from the automotive industry, due to its potential for reducing manufacturing costs. In RTM process, a liquid thermosetting resin is introduced into a closed mold and impregnates the fibers, forming an interfacial bond before polymerization begins. This process is shown in schematic form in Fig. i.1.

The principal advantages of RTM compared with alternative composite manufacturing processes are the ability to produce fiber preforms in off-line process, and the use of low cost shell molds [1]. In Table i.1, Some differences between RTM and Structural Reaction Injection Molding (SRIM) are tabulated. Optimizing the composite manufacturing processes, including RTM, is a sophisticated task because it involves a large number of process variables. Since significant amount of experimental work is required to optimize the process variables through trial and error runs, the process modeling by numerical analysis offers the manufacturer the opportunity to reduce the costs and the spent time associated with developing of new formulations.

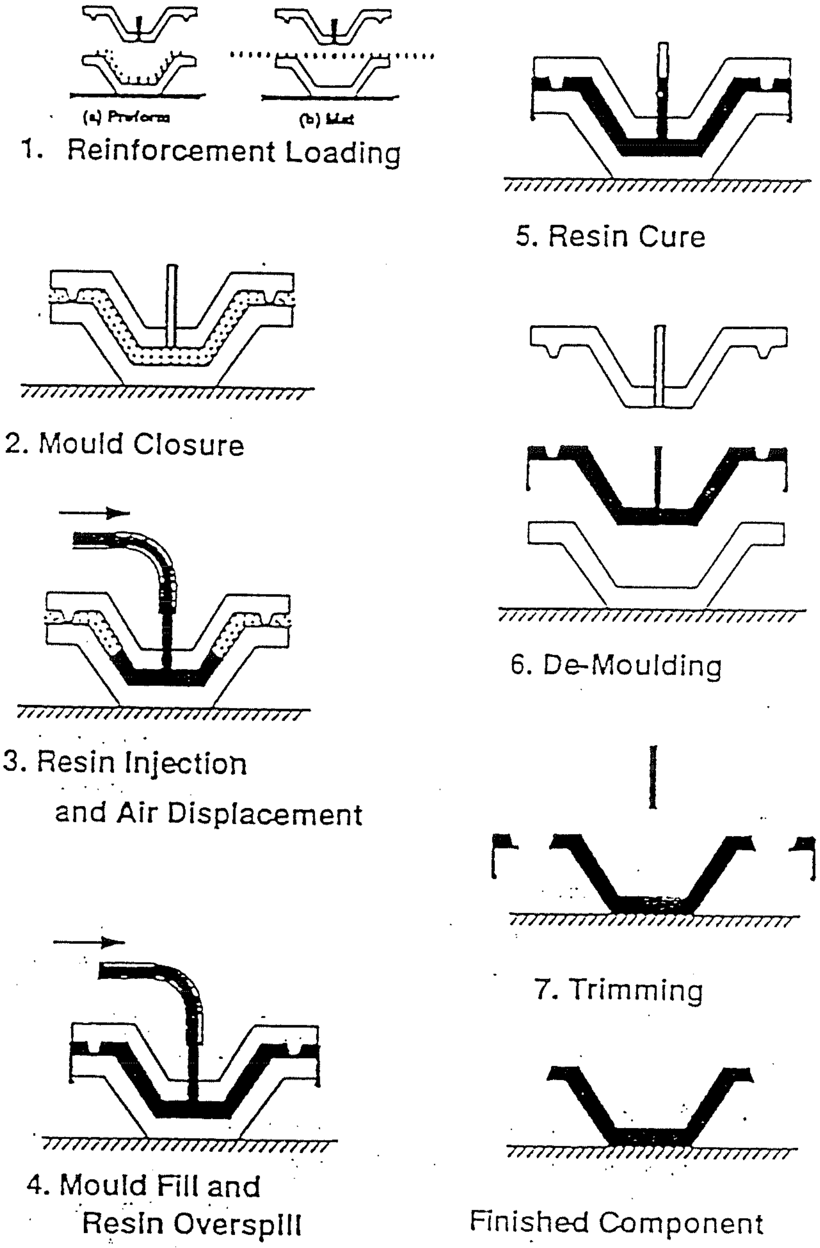

Fig. i.1. Schematic representation of the RTM process [1]

Table i.1. Comparison of S-RIM to RTM [2]

	RTM	**S-RIM**
Equipment Cost	\$30,000	\$500,000
Flow Rate (kg/min)	2.3	55
Mixing	static mixers	impingement
Mold Pressure (MPa)	0.3	2.4
Void Content (vol%)	0.1 - 0.5	0.5 - 2.0
Mold Material	epoxy	steel
Mold Temperature (°C)	25 - 40	95
Component Viscosity (MPa.s)	100 - 550	< 200
Cycle Time (min)	10 - 60	2 - 6

Unsaturated polyester resins are used in a wide variety of markets because of their ease of fabrication, low weight, high strength, corrosion resistance, and low cost. The ability to tailor the reactivity of polyester resins, by addition of promoters or inhibitors, is one of the advantages exhibited by this family of polymers. This characteristic, which allows the manufacturer to have sufficient working time followed by a rapid cure, has led to the development of many processes that specifically use unsaturated polyester resins.

The application for vinylester resins vary widely. Corrosion-resistant reinforced plastics make up the largest market for this class of thermosetting resins. The reasons why vinylester resins have increased their market for reinforced thermosetting plastics are: 1) high toughness because of their high tensile elongation; 2) high cohesive strength, and superior wetting and bonding to fibrous reinforcements; 3) providing cured polymers with chemical resistance to a wide range of chemicals, from strong acids to strong alkalies; and 4) ease of processing with a variety of catalyst systems.

In order to develop a realistic model of RTM process, it is necessary to include accurate kinetic models of cure and rheological data on the cure system under consideration. The present work attempts to estimate the kinetic parameters representing the cure characteristics of polyester and vinylester resins in the presence of a promoter and glass fiber reinforcement. Chapter 1 presents the attempts made in the literature to model the mold filling and curing phases of the reactive processing. Chapter 2 attempts to give an extensive review of the literature regarding the existing kinetic and chemorheological models as well as parameter estimation procedures, and discusses the effects of different additives on the kinetics of cure. The influence of a cobalt-based promoter and glass fiber reinforcement on the curing behavior of polyester and vinylester resins is discussed in Chapters 3 and 4. A one-dimensional numerical analysis for the post-filling phase of RTM processes is presented in Chapter 5. The kinetic parameters estimated in Chapters 3 and 4, with regard to the influence of the cobalt-based promoter and glass fiber reinforcement, are used in the mathematical modeling.

CHAPTER 1

LITERATURE REVIEW

The prediction of mold filling or impregnation phase of RTM has been considered by many investigators [3-6], and several authors have considered this problem for the isothermal case [7-9]. For some composite manufacturing processes, mathematical models have been developed to predict the cure period [10-12]. The approach which is generally used considers the problem as a transient heat conduction coupled with an internal heat generation provided by a kinetic model which simulates the cure reactions [1]. By combining the impregnation model with such a cure model, a prediction can be made for the temperature history of the entire cycle.

1.1 MODELS OF FLOW THROUGH FIBER BEDS

The flow of fluid through a fiber bed can be analyzed by either a microscopic or a macroscopic method. In the microscopic approach, the flow through the fibrous mat is studied based on the boundary conditions which account for all the fibers in the flow field. One approach is to simplify the fibrous mat as a set of parallel tubes or capillaries [13]. By solving the Navier-Stokes equation and the corresponding boundary conditions, the flow front and pressure distribution in the mold can be obtained. However, this model can be misleading because the fibrous mats are more complex than parallel tubes. In macroscopic studies, the mold filling process can be regarded as a process of flow through porous media. The equation which is widely used in modeling of flow through porous media is Darcy's law:

$$u = -\frac{1}{\mu}[K]\nabla P \tag{1.1}$$

where u is the velocity vector, μ is the viscosity of the resin, $[K]$ is the permeability tensor, and ∇p is the pressure gradient [14]. Darcy's law assumes plug flow and, therefore, does not account for any drag effects from the walls of the mold. However, if it is assumed that there is a region, in the mold cavity, large enough compared with the pore size and small enough compared with the mold dimensions, it is possible to use Darcy's law instead of the linear momentum balance [15]. The exception to this is when the mold cavity is very thin and the porosity of the reinforcement is high [13].

Patel *et al.* [16] investigated resin-fiber wetting and bonding in RTM/SRIM. They conducted some experiments to analyze the effects of flow rate and reinforcement temperature on the wetting and bonding at the resin-fiber interface. Based on their results, the wetting and bonding could be improved by using low injection pressure and high fiber mat temperature. Cai [17] presented a simplified RTM analysis based on a one-dimensional resin flow model. The results were applied to the mold design and vent arrangement in RTM process. On the basis of obtained results, it was suggested that the resin flow direction should be from larger sides to smaller sides to guarantee rapid reduction of unoccupied volume. Chan and Morgan

[18,19] analyzed resin impregnation of unidirectional and bi-directional preforms. The models were based on postulating two levels of flow during RTM; 1) flow through the larger pore spaces between fiber tows, and 2) radial flow into the small pore spaces formed among filaments within the fiber tow. The models were applied to analyze the effect of material and operating parameters on molding of unidirectional and bi-directional composites. Coulter *et al.* [20,21] studied the resin impregnation in manufacturing of composite materials. They applied a numerical analysis based on the assumption of two-dimensional isothermal flow of a viscous fluid through a porous medium. As boundary conditions, they considered a constant velocity at the mold inlet, zero velocity along all walls, and zero shear stress along the resin impregnation front. The numerical results yielded a resin front pattern which was more elongated than the one observed experimentally. Two-dimensional and three-dimensional computer simulation schemes for mold filling of RTM and SRIM under isothermal condition have also been developed by Young *et al.* [22].

Um and Lee [23] simulated the mold filling phase of RTM using the boundary element method (BEM). They claimed that BEM analysis gave accurate numerical results in relatively short computing time compared with the control volume methods, such as finite element or finite difference method. Li and Gauvin [24] studied the resin flow in RTM using the numerical generation of boundary-fitted coordinate system. They reported that the developed model was capable of handling molds of complex shapes under different manufacturing conditions. According to their work, the main difficulties encountered in simulation of RTM process were edge effects and the capillary forces which are not usually included in the developed approaches. Recently, Wu and Hourng [25] have proposed a model to explain the edge effects. The introduced model is based on the concept that an effective gap is located between the side wall and the fiber mats. Trochu and Gauvin [26] have discussed the limitations of boundary-fitted finite difference technique. Based on their discussion, this technique can not be easily implemented for molds containing interior obstacles, or for more than one injection port. Numerical stabilities can also limit the convergence of algorithm when it is applied to molds of irregular shapes in the case of a dividing front line.

1.2 MODELING OF CHEMICAL REACTION AND HEAT TRANSFER

Extensive research has been devoted in the literature to the modeling of reactive processing, including RIM, SRIM and RTM [27-39]. Tucker III [40] has discussed the modeling of heat transfer and chemical reaction in liquid composite molding processes by attempting to identify areas that deserve further attention. It is suggested to be precautious in selecting the proper mathematical model, material properties, and numerical solution methods.

Gebart [41] obtained an analytical solution for heat transfer and chemical reaction of thermosetting materials, based on a second order autocatalytic kinetic model. It was claimed that the analytical solution agreed very well with numerical results for small exotherm peaks, less than 10% of the adiabatic temperature rise, but a qualitative agreement was reported for cases with significant exotherm peaks. Ryan [42] presented a numerical simulation of the injection molding process for thermosetting resins, by taking into account the non-Newtonian behavior of the fluid, the effect of the temperature and degree of conversion on the viscosity, and the compressibility of the material. The distributions of temperature, degree of conversion, velocity, and pressure in both semicircular and rectangular mold cavities were predicted during the entire injection molding cycle. Kamal and Ryan [43] applied the mathematical modeling to the injection molding process of an epoxy resin in a semi-circular cavity. Charbonneaux and Macosko [44] developed a model for the flow of a thermosetting polymer at a constant flow rate through a straight cylindrical tube using a finite element method with moving grid. Castro [45] developed a model to predict the pressure rise during filling, and the extent of cure and temperature during the filling and curing stages of a rectangular thin mold. The developed model was experimentally verified using a polyurethane RIM system. Hayes *et al.* [46] presented a two dimensional finite element model for simulation of the advancing front in RIM. A non-mechanistic second order kinetic model was used. Rheological behavior of the thermosetting resin was expressed using the model introduced by Castro [45]. Reboredo and Rogas [47] proposed a model for the injection molding of reactive polymers into a mold containing reinforcement. They determined moldability areas for a low pressure RIM equipment, and discussed the selection of operating conditions to optimize pressure drop, cycle time, and quality of product. Gonzalez and Macosko [48] employed moldability diagrams to define the parameters necessary to meet the process requirements. In their approach, the criterion for selecting the amount of fiber reinforcement, injection time, catalyst level, and process temperature in order to optimize properties and demold time was described.

Gonzalez *et al.* [49] analyzed the influence of the glass fibers on the pressure drop, extent of reaction and temperature during mold filling and curing steps. Their model is unidirectional in either rectangular or cylindrical geometries where chemical reaction and heat transfer during mold filling can be neglected. The curing behavior of a mixing activated polyurethane system was compared with a heat activated styrene based copolymer using experimental data and model predictions. Both mechanistic and phenomenological kinetic models were employed. The observed induction period for heat activated system was attributed to the consumption of the inhibitor by the produced initiator radicals. It was reported that the maximum temperature in the curing phase decreased as porosity droped and was delayed as porosity increased, because the thermal conductivity of the polymer was smaller than that of the glass fiber. Gonzalez-Romero and Macosko [50,51] analyzed the problem of heat transfer during transient flow through the porous bed. They obtained an analytical solution for the adiabatic case by assuming no chemical reaction, no heat transfer from the mold walls, and no temperature gradients inside each fiber. Only the heat exchange between the porous solid and the flowing liquid was taken into account. On the Basis of experimental results, they reported that the heat transfer coefficient between a petroleum oil and glass fibers, h, was linear with velocity, v [51]:

$$h = \lambda v \tag{1.2}$$

with $\lambda = 44$ J/m^{3}K [15].

Kendall and Rudd [52] compared the temperature and pressure profiles in mold cavities with preplaced continuous strand mats during impregnation, heating and curing for both RTM and SRIM processes using polyester, vinylester, and polyurethane resins. The observed experimental results were related to chemical, thermal, and rheological effects. Chan and Hwang [53] considered the non-Newtonian flow through the fabric mat and heat transfer between mold, fabric mat, and flowing fluid. The model was developed for the mold filling of a carbon fiber mat with pseudoplastic polyimide solution. The numerical results provided information about the optimization of the mold filling parameters. The results showed a heavy dependence of required inlet pressure on the power-law index of the polymer solution. In another work, Chan and Hwang [54] analyzed the isothermal mold filling during RTM process. Their model took into account the anisotropic nature of fibrous reinforcement and change in the viscosity of the polymer resin as a result of chemical reaction. They claimed that their model was useful for making predictive studies of thin polymeric composites in the RTM process.

Chan and Hwang [55] simulated the non-isothermal mold filling stage of RTM and SRIM using two dimensional Darcian flow. Mass balance on the reactive species yielded the following equation:

$$\frac{\partial C}{\partial T} + \bar{v}.\nabla C = S_c \tag{1.3}$$

where S_c is a source term for the chemical reaction. Simultaneous resin reaction and heat transfer among resin, mold walls, and fibers were considered in the model. An energy balance was written separately for each of the resin and fiber phases. For the fiber phase the energy equation used was the following:

$$\frac{\partial T_f}{\partial t} - \alpha_f \nabla^2 T_f = - \frac{h_f a_f}{(1-\epsilon)\rho_f C_{pf}} (T_f - T_r) \tag{1.4}$$

where subscripts "f" and "r" denote fiber and resin phases, respectively, α is thermal diffusivity, h is heat transfer coefficient, "a" is surface area, ϵ is fiber medium porosity, ρ is density, and C_p is heat capacity. In Eq. 1.4, the second term represents heat conduction in the planar dimensions, while the right hand term accounts for heat transfer across the resin/fiber interface. The energy equation used in the model for the resin phase was:

$$\frac{\partial T_r}{\partial t} + \bar{v}\nabla T_r - \alpha_r \nabla^2 T_r = \frac{-\Delta H S_c}{C_{pr}} - \frac{h_f a_f}{\epsilon \rho_r C_{pr}}(T_r - T_f) - \frac{h_w a_w}{\epsilon \rho_r C_{pr}}(T_r - T_w) \tag{1.5}$$

where subscript "*w*" denotes the mold wall. The three terms on the right hand side represent contributions from heat generated by the resin reaction, heat transfer between resin and fibers, and heat transfer between mold walls and the resin. The heat transfer coefficient between resin and fibers, h_f, was expressed as a linear function of the fluid velocity. An estimate of h_w was obtained from the analytical solution of the energy equation for Darcian flow. A least square finite element method was used to solve the convection dominated mass and energy equations. Simulation results on polyurethane/glass fiber composites were presented without no experimental data for comparison.

To analyze the non-isothermal mold filling and curing in thin cavities with preplaced fiber mats a numerical model was developed by Lin *et al.* [56,57]. Both lumped temperature system (local thermal equilibrium between the resin and the fiber) and unlumped temperature system (thermal non-equilibrium locally) were considered. The channelling effect, fiber mat deformation during mold filling, and heat transfer through the mold walls were neglected. The viscous dissipation was considered insignificant compared with other contributions such as heat transfer between the resin and the fiber mat, or reaction exotherm. The mass diffusion rate was also considered negligible compared with chemical reaction rate. It was assumed that for thin cavities, the flow might be simplified to a two dimensional problem. However, heat transfer in three dimensions was taken into account because heat convection in planar direction and heat conduction in the gapwise direction were both significant. For simplicity, isotropic and constant thermal physical properties were assumed. To take the solidification into account, solidified sub-layers were distinguished from un-solidified sub-layers by comparing the conversion of sub-layers with gel conversion, and the effective thickness was obtained by subtracting all the solid sub-layers from the cavity thickness. It was demonstrated that the conversion distribution at the end of mold filling had a temperature like distribution since the kinetic parameters were temperature sensitive. The results obtained for lumped temperature system were considerably different with those of unlumped one. However, at lower flow rates both system gave similar results. No experimental data were presented to validate the model predictions.

In their recent publication, Lin *et al.* [58] have compared the experimental results obtained for a polyurethane/glass fiber composite with the model predictions. They applied a method different from that of Gonzalez [15] to measure the volumetric heat transfer coefficient, h_v, between the fiber mat and the resin. A modified nth order kinetic model was used for cure reaction, and a phenomenological model [59,60] was used to fit viscosity data. In SRIM, the predicted inlet pressure showed a notable difference between the un-lumped and lumped temperature models. The former gave a better prediction. In RTM, both lumped and unlumped temperature systems predicted nearly the same inlet pressure profile. Moreover, in the simulation of SRIM the resin temperature and the fiber temperature differed from each other at the end of filling for un-lumped system, while in the RTM simulation both temperatures were nearly the same. Heat transfer through the mold walls was not treated in their work.

Batch and Macosko [61] developed a mathematical model to explain the effects of initiator concentration, die temperature and line speed on curing inside a pultrusion die. The developed model featured the mechanistic kinetic equations based on the cure mechanism of polyester and vinylester resins, changing physical properties during cure, and reduced heat transfer rate due to the shrinkage. The sensitivity analysis indicated that a more realistic prediction of temperature profiles would be attained when the changes in thermal conductivity, heat capacity, and density of the resins with temperature and cure were included in the mathematical modeling. The increase in the thermal conductivity throughout the process was found more significant, about 90%. The influence of the profile shrinkage on heat transfer was modeled by decreasing the wall Nusselt number. The obtained numerical results indicated that including the profile shrinkage in the mathematical modeling caused a significant improvement in the temperature profile near the wall after the peak exotherm.

Castro [62] has derived some criteria to determine when the filling stage can be decoupled and simulated regardless of heat transfer and chemical reaction. It was stated that for usual RTM and SRIM conditions, the mold wall temperature was not much higher than the initial material temperature. Therefore, neglecting the heat transfer during flow was a good first approximation. Since the free radicals generated in the polyester-based formulations are initially inactivated by reacting with an inhibitor, for neglecting the chemical reaction in RTM process where polyester type materials are used, the following equation was recommended:

$$G = \frac{t_f}{t_z} \tag{1.6}$$

where t_f is the fill time, and t_z is the inhibition time at the mold wall temperature. Thus for the chemical reaction to be neglected, G should be less than unity.

1.3 CHANGES IN PHYSICAL PROPERTIES WITH TEMPERATURE AND CURE

A series of experiments has been conducted by Hilal *et al.* [63] to investigate the effect of temperature on thermal conductivity, thermal capacity, and thermal diffusivity of polyester resin cured with styrene. It was reported that the specific heat capacity of polyester cured with styrene slightly increased with an increase in temperature. The same trend was reported for changes of the thermal conductivity. However, the thermal diffusivity exhibited a slight decrease with increasing temperature.

In the case of a liquid epoxy resin, it is reported [64,65] that the specific heat remained constant at low degrees of cure. Similarly at high conversions, the specific heat showed little variation. However, at intermediate conversions, the specific heat varied significantly and continuously from the uncured value to the fully-cured value. Some increase in the thermal conductivity of epoxy resins is also reported with increasing crosslink density [64,65]. In general, the thermal conductivity of epoxy resin has been found to increase linearly with the extent of cure during the initial stages of the crosslinking reaction. A more pronounced increase in the thermal conductivity was reported as a result of a glass transition due to cure. For the epoxy resin system, it is reported that the thermal diffusivity increases sigmoidally with cure time, attains a maximum level and then decreases slightly to a final value [64,65].

PRESENTATION OF CHAPTER 2

In order to develop a realistic mathematical model for the RTM process, the existing approaches for modeling of the cure reactions and viscosity variation in reactive systems were extensively reviewed. Chapter 2 gives an extensive review of the literature regarding the existing mechanistic and phenomenological cure models, and discusses various aspects of the cure. The last section of this chapter is devoted to the most frequently used chemorheological models in reactive processing. Since the activation energy of flow for a reactive system is more likely to be conversion dependent, particular attention has been given in the literature to the chemorheological models featuring a conversion dependent characteristic.

Since thermal analysis by differential scanning calorimetry has the advantage of simultaneously yielding kinetic and thermal data on the reactive system, in the following chapter emphasis has been placed on this particular technique and on the parameter estimation methods suited for the cure data obtained by this technique. The influence of various factors, including fillers and additives, on the curing behavior of thermosetting resin is also discussed in Chapter 2.

CHAPTER 2

KINETIC STUDIES OF THERMOSET CURE REACTIONS - A REVIEW -

by

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2.1 INTRODUCTION

Thermosetting resins play an important role in industry today due to their high flexibility in tailoring desired ultimate properties. Since in industrial formulations, a variety of additives (*e.g.* promoting agents, fillers, etc.) is included in the cure system which results in complex cure kinetics, a good understanding of the cure process is the most important prerequisite in process optimization of composites.

The methods employed to monitor the progress of the cure, fall into two categories [1]:

1. Methods which are based on monitoring the changes in concentration of reactive groups consumed or produced in the course of reaction. These methods include chemical analysis, IR and UV spectroscopy.
2. Methods which are based on the effects of network formation on the physico-mechanical properties of the sample.

Only a few of these methods can be employed to follow the whole cure process from beginning to end.

One of the methods which are mostly used in the literature to study the kinetics of cure reactions is the thermal analysis by differential scanning calorimeter (DSC) in both isothermal and non-isothermal modes [2-10]. In the kinetic studies performed using thermal analysis, it is assumed that the rate of heat generation is proportional to the rate of the cure reactions [11,12]. Thermal analysis is a strong technique for studying the kinetics of physico-chemical processes [13]. Moreover, it is a useful technique for making time-temperature predictions, and optimization of process variables [14]. Another popular technique, which is based on the heat evolution in the course of reaction, is the adiabatic reactor method. This method requires a highly reactive polymerizing mixture at the initial temperature. The extent of conversion is related to temperature exotherms under adiabatic conditions [1]. Adiabatic temperature rise methods have been used to study the cure process of urethanes [15-23], polyureas [24], and unsaturated polyester systems [25]. Other popular techniques that are widely used in the literature are based on spectroscopic analysis [26-31], rheological measurements [32-40], electromagnetic and dielectric techniques [41-47], and volumetric Changes [48].

Lem and Han [49] have briefly compared differential thermal analysis (DTA) and differential scanning calorimetry (DSC). According to their discussion, the use of DTA to obtain quantitative information on the curing kinetics of thermosetting resins is limited because of the non-uniformity of the temperature within some reactive samples during the measurement. In DTA measurements conducted on dilute solutions, the temperature within the sample can be maintained uniform at low heating rates. However, in the solid state the difficulty arises in maintaining a uniform temperature within the sample unless an extremely small sample size is used. As a consequence, a small difference in temperature within the sample may give rise to a significant difference in the rate of reaction [49]. Another inherent drawback of DTA is the assumption of having constant heat capacities and heat transfer coefficient throughout the entire range of temperature investigated. Since, the thermal properties of thermosetting resins are dependent on both temperature and the degree of cure, the value of heat evolution determined by DTA is a relative quantity. Therefore, DSC is a more reliable technique because it directly measures the rate of heat evolution [49]. Prime [50] reported that the kinetic parameters obtained from DTA were generally in disagreement with the values determined using other techniques. Moreover, the values of activation energy obtained from the first half of the DTA curve were somewhat higher than those determined based on the variation of peak position with heating rate.

The present article attempts to review the kinetic studies carried out on thermosetting resins, by putting the emphasis on those conducted using the thermal analysis technique by DSC. In the next section, the most important kinetic models are presented, and a brief comparison is made between the existing categories. Section 3 deals with some parameter estimation techniques applied to isothermal and non-isothermal cure data. The effect of various factors on the cure process of reactive polymers is discussed in section 4, by putting the emphasis on the chemistry of unsaturated polyester system. Finally, in section 5 some popular rheological models applied to the flow process of reactive polymers are presented.

2.2 KINETIC MODELS

Many studies have been conducted so far on the kinetics of the cure reactions, and a variety of kinetic models have been used to relate the rate of the chemical reactions to the independent variables in the cure process, that is, time, temperature, and extent of cure. In general, the kinetic models fall into two main categories:

1. Phenomenological models
2. Mechanistic models

A phenomenological model is generally expressed in a relatively simple rate equation, and is developed ignoring the details of how reactive species take part in the reaction. On the other hand, mechanistic models are obtained from balances of reactive species involved in the reaction. In spite of a better prediction and interpretation offered by mechanistic models, it is not always possible to derive such models due to the complexity of cure reactions. In addition, they generally require more kinetic parameters than phenomenological models do [51]. So in most cases, phenomenological models are preferred in studying the cure processes.

2.2.1 Phenomenological models

Although several simultaneous reactions occur during the cure process, some simple models have been developed assuming that only one reaction can represent the entire cure process. The most simple model is expressed by an nth order rate equation [52]:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2.1}$$

where α is the conversion, n represents the reaction exponent and k is the rate constant obeying an Arrhenius temperature dependency:

$$k = k_0 \exp(-E/RT) \tag{2.2}$$

For the majority of cure systems, the efficiency of this model has been postulated by some workers [53-61]. However, an nth order equation cannot describe the progress of the entire reaction because several simultaneous reactions occur during the cure process. For an isothermal reaction, Eq. 2.1 predicts the maximum of reaction rate at time = 0 which is not the case for autocatalytic cure processes. On the other hand, different events (phase separation, gelation, vitrification, etc.] take place in the course of cure reactions which make the kinetics of cure more complicated. These events are briefly discussed elsewhere [62]

Kamal, *et al.* [63,64] have shown that the following model represents adequately the cure kinetics of epoxy and unsaturated polyester cure systems:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{2.3}$$

where k_1 and k_2 are rate constants with Arrhenius temperature dependency, and m and n are constants independent of temperature. This equation has been widely used in the literature to represent the curing of thermosetting resins [65-69].

The relative degree of cure, α, in Eq. 2.3 is defined by [70]:

$$\alpha = \frac{Q}{Q_u} \tag{2.4}$$

where Q is the total amount of heat generated isothermally from the beginning of the reaction up to a given time t, and Q_u is the ultimate heat of cure obtained from the total area under the scanning cure thermogram. For non-isothermal cures, a numerical procedure has been proposed to calculate conversion (α) and conversion rate ($d\alpha/dt$) during a linear temperature scan [64].

In Eq. 2.3, the reaction rate gains its maximum value at some intermediate conversion, α_p, which is given by [70]:

$$\alpha_p = \frac{m}{(m+n)} \tag{2.5}$$

In an autocatalyzed cure system, the maximum rate of heat evolution generally occurs at 30-40% conversion [71].

In general, thermosetting materials exhibit the vitrification phenomenon which stops the reaction before complete conversion is achieved (see section 4.3). After vitrification, the cure process exhibits a diffusion controlled mechanism and as a consequence, the experimental conversion and conversion rate are lower than those predicted by Eq. 2.3 [71]. Therefore, Eq. 2.3 does not satisfy the observed zero rate condition at the end of the cure where the reaction terminates before a complete conversion is achieved ($\alpha < 1.0$). To remove this deficiency, a new fractional conversion, x, was defined [63,70]:

$$x = \frac{Q}{Q_M} \tag{2.6}$$

where Q_M is a temperature dependent quantity described by :

$$Q_M = C_1 + C_2 T + C_3 T^2 \tag{2.7}$$

here C_1, C_2, and C_3 are constants.

To fulfil the condition of zero reaction rate at the vitrification conversion, which approximates the final extent of cure α_{max} [72], some reaction rate expressions were introduced. Gonzalez-Romero and Casillas [51] used the following equation to include the vitrification phenomenon:

$$\frac{d\alpha}{dt} = A\exp(-E/RT)(\alpha_{\max} - \alpha)^n g(\alpha) \tag{2.8}$$

where by an empirical fit, $g(\alpha)$ was expressed in the following form:

$$g(\alpha) = \exp(m\alpha) \tag{2.9}$$

In these equations, the terms have the usual definitions.

Batch and Macosko [72] used an existing model developed on the variation of T_g with conversion, and extended it to the vitrification conversion:

$$\alpha_{\max} = \frac{1}{a}\left(\frac{1}{T_0} - \frac{1}{T_{cure}}\right) \tag{2.10}$$

where "a" is a fitting parameter, T_{cure} is the cure temperature, and T_0 (in degrees Kelvin) is the theoretical temperature where no cure reactions could occur ($\alpha_{max} = 0$). In Eq. 2.10, the upper bound of α_{max} at high cure temperatures is unity.

An alternative kinetic model was presented by Lam, *et al.* [73] for autocatalytic curing of styrene-based thermoset resins. By introducing one more kinetic parameter, namely the total ultimate conversion, α_u, and taking $k_1 = 0$ in Eq. 2.3 for styrene - based resins the following equation was obtained:

$$\frac{d\alpha}{dt} = k\alpha^m(\alpha_u - \alpha)^n \tag{2.11}$$

It was claimed that by applying the integral form of Eq. 2.11 in the following form:

$$\alpha = \frac{\alpha_u[k.t.\alpha_u.(n-1)]^{1/n-1}}{1+[k.t.\alpha_u.(n-1)]^{1/n-1}} \tag{2.12}$$

and introducing α_u in the autocatalytic kinetic model, a better fit was observed between the model and the experimental cure data.

To take into account the diffusion controlling step of the cure process, some attempts have been made to assign a more general form to the rate constants of the cure reactions. According to Chern and Poehlein [74], diffusion becomes controlling when the degree of cure reaches a critical value α_c. Consequently, the rate constant, k_d, was defined as:

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \tag{2.13}$$

where k_c is the rate constant for the chemical reaction and C is a constant.

Since the onset of diffusion controlling step approaches gradually, there is a region where both chemical and diffusion factors are controlling [71]. As a consequence, the overall effective rate constant, k_e, can be defined as [71]:

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \tag{2.14}$$

where k_d and k_c are rate constants.

Khanna and Chanda [71] defined a diffusion factor, $f(\alpha)$, with combining Eqs. 2.13 and 2.14:

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp\left[C(\alpha - \alpha_c)\right]} \tag{2.15}$$

For $\alpha \ll \alpha_c$, $f(\alpha)$ approaches unity. The effective reaction rate at a given conversion was represented as the product of chemical reaction rate and $f(\alpha)$.

2.2.2 Mechanistic models

Mechanistic models have some advantages over empirical ones. For instance, without conducting laborious and time consuming cure experiments, one can treat separately the influence of the type, concentration or number of initiators on the overall reaction rate. The fundamentals of free radical polymerization have been extensively discussed by Flory [75], and the mechanism of free radical copolymerization with inhibition has been analyzed by Stevenson [76-78]. The model developed by Stevenson [77] is suitable for multiple initiators, inhibition and copolymerization assuming that concentration and reaction rate ratios are equal. Moreover, in this model it is assumed that the chain termination reactions are negligible. According to Stevenson, after complete consumption of inhibitor, polymer chains are initiated by build up of free radical concentration.

To date, several workers have attempted to model the cure process of thermosetting resins using the concept of free radical polymerization [79-84]. Kamal and Sourour described the autocatalytic reactions of epoxy-aromatic diamine systems up to the diffusion-controlled step by a mechanistic model [85]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1-\alpha)(B-\alpha) \tag{2.16}$$

where α is the fraction of epoxide reacted at a given time t, and B is the initial ratio of amine to epoxide functional groups. When $B = 1$, Eq. 2.16 becomes equivalent to Eq. 2.3.

With some simplifying assumptions, Gonzalez [1] applied mechanistic kinetic models to both isothermal and non-isothermal conditions. Under isothermal conditions, the following equation was obtained:

$$\frac{d\alpha}{dt} = 2 f k_d I_0 k_p (1-\alpha)(t-t_z) \tag{2.17}$$

where α is the fractional conversion of reactive group, f represents the initiator efficiency, I_0 stands for the initial initiator concentration, k_d and k_p are the rate constants of initiation and propagation, respectively, and t_z is the inhibition time. This equation implies that plotting $(d\alpha/dt)/(1-\alpha)$ *vs.* time will result in a straight line after consumption of the inhibitor. It was reported that during the polymerization three different zones, namely inhibition, transition and chain growth zone, might be observed. A good agreement was reported between model predictions and experimental results for styrene-dimethacrylate copolymer system.

Han and Lee [79] developed a kinetic model for curing of unsaturated polyester resin with no assumption on the magnitude of the rate constants of the inhibition and termination reactions. Consequently, the propagation and termination rate constants, k_p and k_t, were defined as follows:

$$k_p = A_0 \exp(-E_p/RT)[1-(\alpha/\alpha_f)]^m \tag{2.18}$$

$$k_t = B_0 \exp(-E_t/RT)[1-(\alpha/\alpha_f)]^n \tag{2.19}$$

where α_f denotes the final degree of conversion, and m and n are constants. According to their work, the cure reactions begin only when the inhibitor is completely consumed in the cure system, and the inhibition reaction is followed by the curing reactions. This conclusion is consistent with the findings of Stevenson, and was found acceptable for polyester/styrene cure systems due to the large ratio of inhibition to propagation rate constant in these systems. A good agreement was reported between the conversion rate and degree of conversion computed by the developed model, and those obtained experimentally. Based on this mechanistic model, Han and Lee [80] studied the cure process of unsaturated polyester resin with mixed initiators. It was demonstrated that mixed initiators could have a higher efficiency than a single initiator in the cure system of unsaturated polyester. A better agreement was reported between the predicted rate profiles and experimental results provided that the efficiencies of the individual initiators changed when two initiators were mixed together. It was claimed that this kinetic model was capable of predicting the effectiveness of various combinations of different initiators.

By applying a mechanistic kinetic model [79], Lee and Han [81] compared the reactivity of three unsaturated polyester resins, by evaluating the rate constant and activation energy of the propagation reaction. It was assumed that the termination reaction was small compared to the propagation reaction, and that the initial efficiency of initiator for the three polyester systems is identical. The theoretical model was also used to predict the effect of the concentration of initiator on the curing behavior of the unsaturated polyester resin. The model predictions were found to be satisfactory except for the resin formulation that had a high, 2 wt%, initiator concentration.

A mechanistic kinetic model, accounting for diffusion controlled reactions, was presented by Ng and Manas-Zloczower [82] for the curing of unsaturated polyester system. The rate equation was given by:

$$\frac{dC^*}{dt} = 2fA_p \exp\left(-\frac{E_p}{RT}\right)(I_0 - I)(1 - C^*)\left(1 - \frac{C^*}{C_f^*}\right)^n \qquad (2.20)$$

where C^* is the degree of cure, C_f^* represents the final conversion attained at the end of cure, I is the initiator concentration at a given time t, I_0 stands for the initiator concentration at the beginning of the cure and after the complete consumption of the inhibitor in the system, f represents the efficiency of the initiator, A_p and E_p are the frequency factor and activation energy of the propagation reaction, respectively, R is the universal gas constant, T denotes the absolute temperature and $(n + 1)$ is a pseudo order of reaction. This model was developed for the systems with single initiator and inhibitor. It was assumed that the polymerization reaction did not start until the inhibition reaction completed. The developed model was used to estimate the kinetic parameters from nonisothermal DSC thermograms. It was claimed that an excellent agreement was observed between the experimental and predicted values of conversion.

Batch and Macosko [72] proposed a mechanistic model by taking into account the diffusion limitations at high conversions, and the effect of temperature and concentration of initiator and inhibitor on the rate of cure. In their model, the decrease in initiator efficiency and the onset of radical trapping were considered. However, bimolecular termination was assumed to be negligible. It was reported that model predictions agreed well with isothermal cure data of divinyl benzene and vinylester resins at various temperatures, and initiator and inhibitor concentrations. This model was mostly recommended for the optimization of temperature, and the concentrations of initiator and inhibitor in the cure process.

2.3 PARAMETER ESTIMATION TECHNIQUES

2.3.1 Isothermal measurements

The non-linear least squares method is one of the mostly used techniques in estimation of the kinetic parameters from isothermal kinetic data. However, some other estimation techniques are also applied in the literature. Scott and Saad [86] introduced an estimation procedure on the basis of the Box-Kanemasu method [87] to evaluate the kinetic parameters of the model represented by Eq. 2.3. Experimental data were provided by DSC and dielectric measurements, and a sensitivity study was performed to evaluate the degree of correlation between the estimated parameters. The proposed estimation procedure was not found appropriate for evaluation of kinetic parameters from dynamic experiments because the sensitivity study indicated that the parameters estimated from these data would be correlated. It was claimed that the procedure provided a more accurate estimation of the kinetic parameters than the linear regression, and allowed a direct estimation of the

Arrhenius constants. They stated that assuming α as the dependent variable, and applying the Box-Kanemasu based procedure provided the best estimation of the kinetic parameters of the autocatalytic kinetic model represented by Eq. 2.3 [86,88].

A graphic-analytical method was presented by Kenny [89] to compute the parameters of Eq. 2.3. This method does not presume the overall reaction order, and is mostly recommended when a controversy was noticed between the predicted values of the overall reaction order by mechanistic and empirical models (for instance, $m + n = 3$ for $B = 1$ in Eq. 2.16, and $m + n = 2$ in Eq. 2.3).

Keenan [90] proposed an estimation method based on isothermal DSC measurements for the materials which exhibit autocatalytic cure behavior with zero initial cure rate. Ryan and Dutta [91] developed an estimation technique to evaluate the order of reaction and rate constants from isothermal DSC data using the initial and peak degree of cure. Arrhenius constants were subsequently estimated from the rate constants using linear regression. In spite of the simplicity of this procedure, experimental errors can introduce a considerable inaccuracy in the estimation of the kinetic parameters since only two experimental data points are used in the estimation procedure [86].

Lam, *et al.* [73] reported that the reaction exponents of the unsaturated polyester estimated from the integrated equation (Eq. 2.12) were somewhat smaller than those evaluated using the differential equation (Eq. 2.11). The opposite result was reported about the vinylester. The integrated equation also yielded smaller estimates of reaction rate constant.

2.3.2 Dynamic measurements

Isothermal DSC measurements have the drawback of being time-consuming. It is also pointed out by Peyser and Bascom [92] that the major weakness of the isothermal DSC measurements stems from the fact that the initial 10 percent of the isothermal cure data are not sufficiently accurate, specially when the sample must be heated quickly to the test temperature. Furthermore, at low cure temperatures, reaction rate is too low to be detected accurately by DSC. So, considering the shortcomings associated with isothermal DSC cure data, it is sometimes difficult to evaluate the temperature dependency of reaction rate constants from isothermal DSC thermograms [1]. By conducting non-isothermal DSC measurements, one can overcome these deficiencies making dynamic measurements attractive for the quality control in industrial and research applications [49].

Many attempts have been made to estimate the kinetic parameters using dynamic DSC data, and a variety of techniques have been introduced. In general these estimation techniques are appropriate for nth order kinetic models. Kissinger [93,94] was one of the first who evaluated the kinetic parameters of chemical reaction from the DTA exotherms using the peak temperature-heating rate data, regardless of the reaction order, with the following equation [93,94]:

$$\frac{d\left[\ln \frac{\varphi}{T_m^2}\right]}{d\left[\frac{1}{T_m}\right]} = -\frac{E}{R} \tag{2.21}$$

where $\varphi = dT/dt$ denotes the heating rate, and T_m is the peak temperature.

Ozawa [95] introduced two methods for estimating the kinetic parameters from dynamic measurements. In the first method, he utilized the linear relation between peak temperature and heating rate. This method provides the evaluation of the activation energy, and does not require any information about the cure mechanism. Since in Dynamic DSC measurements, due to the presence of an additional minor reaction specially at elevated temperatures, integration of the reaction rate profile is not always equal to the degree of conversion [95], the second method proposed by Ozawa would be applicable when the effect of the minor side reaction can be neglected. The latter method requires the information about both the conversion and conversion rate versus temperature, and kinetic mechanism is assumed *a priori*. It is reported that the method proposed by Ozawa provided more accurate estimation of the activation energy than Eq. 2.21 [56,100].

Using the relation between the heating rate and peak temperature the kinetic parameters may be calculated by applying the following equation [96]:

$$\log \varphi = -\frac{E_a}{2.303\,T_m} + B \tag{2.22}$$

which is similar to that proposed by Ozawa [95]. In this expression, B is a constant related to the Arrhenius frequency factor.

An alternative method uses only one heating rate by applying the following form [96]:

$$\ln \frac{\dot{\alpha}}{(1-\alpha)^n} = -\frac{E_a}{RT} + \ln(k_0) \tag{2.23}$$

where α and $\dot{\alpha}$ are the conversion and conversion rate, respectively, T denotes the temperature, E_a is the activation energy, k_0 represents the Arrhenius frequency factor, and n is the reaction order.

Barton [97] eliminated k_0 and n in Eq. 2.23 by applying this equation to two different heating rates:

$$\ln \frac{\dot{\alpha}_i}{(1-\alpha_i)^n} = -\frac{E_a}{RT_i} + \ln(k_0) \tag{2.24}$$

where $i = 1,2$ represents two experiments conducted at different heating rates. Then, by taking the same degree of conversion in the set of the two equations ($\alpha_1 = \alpha_2$), the following form was attained:

$$\ln\frac{\dot{\alpha}_1}{\dot{\alpha}_2} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2.25}$$

Using Eq. 2.25 the activation energy can be estimated. However, this equation does not provide any information about the reaction order and Arrhenius frequency factor.

Hernandez-Sanchez and Vera-Graziano [96] eliminated k_0 in a different way by taking the same conversion rate in the two equations $(\dot{\alpha}_1 = \dot{\alpha}_2)$. The following equation was attained:

$$\ln\frac{1-\alpha_1}{1-\alpha_2} = -\frac{E_a}{nR}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2.26}$$

To calculate the reaction order, Eq. 2.24 was used for two different heating rates but the same temperature:

$$\ln\frac{\dot{\alpha}_1}{\dot{\alpha}_2} = n\ln\frac{1-\alpha_1}{1-\alpha_2} \tag{2.27}$$

It is reported that when the cure data is obtained from the same side of the bell-shaped cure thermogram, as in Barton's method, significant errors are introduced in the estimation of the activation energy [96]. In general, experiments which use the initial, pre-peak part of the DSC curve, give rise to high estimates of the kinetic parameters, whereas estimations which are based on the variation of peak position with heating rate yield low values [50].

2.3.3 Comparison of kinetic data estimated from isothermal and dynamic measurements

According to Prime [50], the kinetic parameters estimated from non-isothermal DSC measurements are frequently different from those evaluated using isothermal DSC measurements. Several workers have compared cure data obtained from isothermal and dynamic DSC experiments. Gonzalez-Romero and Casillas [51] reported that the kinetic parameters evaluated using isothermal and dynamic data were relatively close. The existing difference between these values were attributed to the weakness of the kinetic model rather than the experimental techniques. They claimed that dynamic data could be simulated from isothermal information; however, simulation of isothermal data from non-isothermal information was not found satisfactory.

Ng and Manas-Zloczower [82] estimated the kinetic parameters for cure reactions of polyester resin using non-isothermal DSC measurements. According to their findings, the kinetic parameters obtained by isothermal and non-isothermal DSC methods did not match very well; however, similar magnitude of discrepancy was reported between the parameters obtained from the same method. Patel, *et al.* [98] analyzed the DSC data by applying various methods to evaluate the kinetic parameters of a bisphenolic resin cure system. It was reported that the different methods applied to analyze the DSC data yielded consistent values of the activation energies and overall reaction order.

Several workers [50,99,100] have pointed out that different reaction rate expressions should be used for isothermal and non-isothermal conditions. Since the extent of cure depends on time and temperature, Prime [50] proposed the following equation for the rate of cure under constant heating rate conditions:

$$\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_T + \beta\left(\frac{\partial\alpha}{\partial T}\right)_t \qquad (2.28)$$

where $(\partial\alpha/\partial t)_T$ stands for the rate of reaction under isothermal conditions. There are different points of view about the validity of Eq. 2.28. Although the validity of this equation was postulated by some authors, it was found fundamentally in error by others because if one considers $\alpha = f(t,T)$ as a path function, it could not be partially differentiated [70,101,102]. Kissinger [93] has also emphasized that by fixing the time coordinate, the last term in the right hand side would be zero, because fixing the time also fixes the number and position of particles in the system.

Dutta and Ryan [99] suggested a procedure to relate the isothermal kinetic expression to the non-isothermal one. In this procedure, it was assumed that the degree of cure (α) is a function of cure time and temperature. After the partial differentiation of α with respect to time (t) and Temperature (T), it gave:

$$\frac{d\alpha}{dt} = (\frac{\partial \alpha}{\partial t})_T \{1 + \beta\,[(\frac{\partial h}{\partial T})_t - (\partial h/\partial T)_\alpha]\} \tag{2.29}$$

where:

$$h(\alpha, T) = \int \frac{1}{f(\alpha, T)} d\alpha \tag{2.30}$$

with $f(\alpha, T)$ being the isothermal conversion rate defined as:

$$f(\alpha, T) = (\frac{\partial \alpha}{\partial t})_T \tag{2.31}$$

In these equations, β is the heating rate.

2.4 INFLUENCE OF VARIOUS FACTORS ON THE CURE

2.4.1 Additives and fillers

Most of the commercially available resins are pre-promoted with a variety of promoters for room-temperature cure processing. In general, for industrial formulations the temperature of chemical decomposition of the initiator is too high. Moreover, for most thermosetting resins used in manufacturing of composite parts, a long cure time could be a limiting factor in mass production. So, most industrial formulations are cured at ambient temperature in the presence of promoters.

Performing ESR spectroscopy on unsaturated polyester resins promoted by various quantities of cobalt naphthenate promoter, Slupkowski, *et al.* [103] reported that the concentration of free radicals produced during cure reactions reached its maximum value in a shorter period when the concentration of the promoter was increased. Using DSC measurements, Salla and Ramis [104] studied the effect of tertiary amines as promoters on the curing kinetics of unsaturated polyester resin. They applied a kinetic model to predict the time, temperature, and degree of cure without assigning any forms to the experimental rate equation, $f(\alpha)$. They claimed that this method was capable of predicting the cure process outside the range of experimental data. It was stated that the activation energy could vary according to the extent of cure and effectiveness of the promoters. Moreover, the influence of both the type of promoter and the ratio of initiator/promoter was found more pronounced at the start of cure. No changes in the final degree of conversion was observed due to the presence of the promoter. Lem and Han [49] reported that in the presence of promoter, the resin/initiator mixture exhibited two major exotherm peaks in dynamic cure, but a single exotherm peak in isothermal cure. By applying adiabatic temperature rise technique, Rojas, *et al.* [25] presented an nth order kinetic model to predict the curing behavior of unsaturated polyester resins promoted by cobalt octoate. The broad range of n values, $2 \leq n \leq 4$, reported by Rojas, *et al.* [25] implies that the overall reaction order for promoted unsaturated polyester resin is temperature dependent. Assuming a 3rd order kinetic model, $n=3$, they calculated the best values of the Arrhenius frequency factor and activation energy for the promoted system. However, a considerable discrepancy was reported between theoretical and experimental values obtained in a heated mold. This discrepancy was partly attributed to the values assigned to the kinetic parameters. Huang and Leu [28] investigated the effects of temperature, initiator and promoter on the curing kinetics of unsaturated polyester resins. On the basis of a microgel kinetic model, it was reported that increasing the promoter concentration caused a higher conversion of polyester vinylene over styrene conversion from the beginning of the cure reaction up to a point beyond the start of diffusion-controlled step. It was also indicated that an increase in the promoter concentration yielded a sharper cure exotherm profile, and caused a slight increase in the final extent of cure. According to Yousefi, *et al.* [105] the cure characteristics of unsaturated polyester system is highly affected by the presence of cobalt promoters. On the basis of estimated kinetic parameters, they found that the effect of promoter could be manifested in temperature dependency of reaction exponents, as well as in significant increase in the Arrhenius frequency factor. The accelerating effect of promoter was found more pronounced at low cure temperatures up to 60°C. The efficiency of some compounds as promoters of unsaturated polyester resins was studied by Tanzi, *et al.* [106].

In general, for some promoted cure systems an ordinary autocatalytic model, *e.g.* Eq. 2.3, is not adequate to represent the whole cure process. The cure exotherm of some promoted systems may exhibit some deviation from a bell-shaped profile. To take into account the complexity of cure process in the presence of promoters, Eq. 2.3 was modified as follows [107,108]:

$$\frac{d\alpha}{dt} = k\alpha^m(\alpha_{\max} - \alpha)^n(1 - \alpha)^p \qquad (2.32)$$

where p is the third reaction exponent. The modified rate expression in Eq. 2.32 accounts for both partial conversion, through α_{max}, and deviation of the cure exotherm from a bell-shaped profile by including a third term, $(1-\alpha)^p$, in the rate expression. Mohan and Grentzer [108] applied Eq. 2.32 to the cure system of promoted vinylester resin, and estimated the kinetic parameters of the rate equation using nonlinear least squares regression. The reaction exponent, m, and vitrification conversion, α_{max}, were made temperature dependent to account for the complexity of cure reactions. Temperature dependent reaction exponents for promoted vinylester resins were also reported by Yousefi, *et al* [109].

Low profile additives are frequently used in the cure system of unsaturated polyester and vinylester resins to control the shrinkage of the manufactured part. According to Lem and Han [49] polyvinyl-acetate (PVAc) as low-profile additive decreases the rate of cure and final degree of cure. A decrease in the heat of cure was also reported by Tollens and Lee [110] for unsaturated polyester resin cured in the presence of PVAc as a low profile additive. By ESR studies they found that the major effect of PVAc was the reduction in the radical generation rate. This event was attributed to the possible role of PVAc as a radical scavenger. The effect of the chemical structure of low-profile additives on the curing of unsaturated polyester resins has been studied by Lee and Han [111].

A variety of fillers are generally used in the cure formulation to improve the curing shrinkage, hardness, modulus, and to decrease the peak isotherm by acting as a heat sink. There are some works in the literature with regard to the effect of fillers on curing of thermosetting resins [91,105,109,112-116]. Dutta and Ryan [91] attempted to find an expression to demonstrate the role of fillers in curing of epoxy resins. Consequently, the rate of cure was defined as:

$$\frac{d\alpha}{dt} = (k_1^* + k_2^* \alpha)^m (1-\alpha)^n \tag{2.33}$$

where rate constants, k_1^* and k_2^*, are functions of filler content. According to their observations, the sum of the kinetic exponents is approximately 2, independent of temperature. It was also reported that the type, and concentration of filler incorporated in cure system did not affect the overall reaction exponent, but influenced the reaction rate through the rate constants k_1^* and k_2^*. Based on their results, carbon black filler influences kinetic rate constants of epoxy cure systems by altering the Arrhenius frequency factor, whereas silica affects only the kinetic rate constant k_1^* through the activation energy. Kubota

[112] reported that the presence of a high quantity of filler in the cure system increases both the thermal conductivity and the viscosity of the resin; however, it reduced the concentration of reactive double bonds per unit volume. It was noted that while the first two factors enhanced the cure reactions, the last factor had an unfavourable effect on cure. According to his observations, with increasing filler content the cure started at a lower temperature; however, the total heat of cure decreased with increasing filler content. As a consequence, a decrease was reported in the final degree of conversion with increasing the amount of filler. Lucas and coworkers [115] reported a decrease in the induction period of the styrene /polyester system cured in the presence of $CaCO_3$ as a filler. This effect was attributed to preferential adsorption of inhibitors, including dissolved oxygen, in the filler-rich phase. Assuming that the presence of filler does not alter the reaction kinetics, McGee [114] applied a simple nth order model to demonstrate the effect of particulate fillers on the heat transfer and cure process. He reported that the gel time of polyester system increased with increasing the glass content since the rate of reaction was decreased by the modifications in the temperature profile. Ng and Manas-Zloczower [116] investigated the influence of kaolinite clay and glass fiber on the curing of a polyester resin. They reported that the total heat of reaction per unit mass of resin remained constant irrespective of the filler added, and that the presence of filler did not affect the peak temperature. Furthermore, it was found that the influence of incorporating kaolinite at different concentration, as well as the presence of glass fiber had very little effect on the progression of the cure reactions. These results were found for high temperature peroxide initiation. However, a severe inhibiting effect is

reported for glass and other fillers on room-temperature-curing of polyester system [117]. The changes in the cure characteristic of promoted polyester system caused by incorporation of chopped glass fiber were investigated by Yousefi, *et al.* [105]. On the basis of experimental results, it was indicated that the presence of glass fiber did not appreciably affect the reaction exponents; however, it resulted in some changes in the overall reaction rate of the cure system. The major effect of glass fiber was found to be the inhibition of cure process at low temperatures (below 45°C). This inhibition was mainly manifested in some decrease in the Arrhenius frequency factor. No significant changes in the ultimate heat of cure per unit mass of resin and final degree of conversion were observed in the presence of glass fiber. An opposite trend was reported about the effect of glass fiber on the curing behavior of promoted vinylester resin [109]. It was reported that the presence of glass fiber significantly decreased the ultimate heat of cure per unit mass of vinylester resin, and as a consequence the final degree of cure. This inhibition was mainly attributed to the chemical structure of the vinylester resin as well as the sizing agent of the reinforcement which was formulated for a polyester resin.

2.4.2 Chemical composition

Huang and Chen [119] studied the effect of comonomer compositions on the cure kinetics of unsaturated polyester resins at low temperatures using DSC and Infrared spectroscopy. Microgel-based reaction mechanisms was introduced to explain the curing of unsaturated polyester resin. The rate was considered as a summation of both reaction rates for intramicrogel and intermicrogel crosslinking reactions. According to their work, at the initial molar ratio of styrene to polyester C=C bonds equal to 2, the curing reactions exhibited the highest maximum reaction rate among all the molar ratios, and a near-azeotropic copolymerization prior to the peak of DSC thermogram. The azeotropic copolymerization occurs when the double bonds of styrene and unsaturated polyester are incorporated into the polymer network in the same ratio as their initial ratio [119]. It was also stated that at a molar ratio of styrene to polyester C=C bonds where the intramicrogel and intermicrogel crosslinking reaction rates are approximately the same, the azeotropic copolymerization behavior was noticed [118,120]. At higher molar ratios of styrene to polyester C=C bonds, a shoulder was observed after the peak in the isothermal DSC thermogram obtained at 40°C, and it was attributed to the grafting of styrene on C=C bonds of the polyester chain [118]. Effects of comonomer composition on curing of polyester resin at medium temperature reactions (60-100°C) were studied by Huang and Chen [120]. Rather than the shoulder reported after the peak for low temperature reactions, at medium temperature reactions a shoulder was observed in the initial DSC thermogram, when the molar ratio of styrene to polyester C=C bonds was greater than 1. At isothermal cure temperature of 75°C, an azeotropic copolymerization was reported by Lucas, *et al.* [119] for polyester/styrene cure system when the initial double bond ratio of styrene to polyester was 2.5.

The effect of the structure of unsaturated polyester resin on its isothermal cure was investigated by Lee and Han [81]. The DSC and infrared (IR) spectroscopy were used to determine the curing kinetics. Based on the experimental studies, it was reported that at the same styrene-to-fumarate molar ratio, the resin containing isophthalates exhibits a slower cure. Furthermore, a higher rate of cure was observed for the resin having a high styrene-to-fumarate ratio, and for the cure systems with higher concentration of initiator [81]. It is reported that in free radical copolymerization of styrene/unsaturated polyester system, a percentage of the polyester and styrene do not participate in the polymer network [121]. As a consequence, the expected theoretical conversion is not achieved at the end of cure process. Ramis and Salla [121] proposed two different methods to evaluate the theoretical conversion of the cure system using chemical composition of the reacting species and gel permeation chromatography technique. The presence of trapped polyester C=C bonds in the crosslink network was also indicated by Lucas, *et al.* [119]. They reported that the value of theoretical heat of cure generated at a complete conversion, was 69 kJ/mol irrespective of the initial ratio of styrene and polyester C=C bonds. The nature of propagating radicals in free radical copolymerization of styrene/unsaturated polyester system has been investigated using ESR spectroscopy by Hsu and Lee [122].

2.4.3 Gelation, vitrification, and crosslinking density

Gelation corresponds to the incipient formation of an infinite molecular network which results in a viscoelastic behavior in the macroscopic fluid [62]. With the progress of cure, the increase in the density of crosslinks gives rise to an increase in the glass transition temperature, T_g, of the cure system. Vitrification occurs when the glass transition temperature of the cure system approaches the cure temperature. Consequently, the mobility of the reacting groups is hindered and the cure mechanism changes to a diffusion controlled step [71].

Lee and Lee [123] presented the variation of glass transition temperature *versus* degree of conversion in a graphical form for the cure system of vinylester resin. The inflection point observed in the glass transition temperature was considered as the gel point of the cure system. Consequently, two sets of kinetic parameters, corresponding to the cure mechanism before and after gelation, were estimated. It was also indicated that the glass transition temperature of the fully cured samples is identical regardless of the isothermal cure condition. Hsu and Lee [124,125] divided the cure process into five stages, that is induction, microgel formation, transition with or without phase separation, macrogelation and post-gelation. Consequently, a gelation mechanism was proposed for the cure system of styrene/unsaturated polyester resin. It was indicated that the phase separation stopped after the gel point was attained. The microgelation during the cure process of unsaturated polyester resins with various chemical structures and molecular weights has been studied by Liu et al [126].

It is reported that the cure reaction of polyester fumarate with styrene monomer was accelerated about 10 to 50 times by the gel effect and this autoacceleration was more pronounced for the systems with higher crosslinking densities. It is also indicated that the final degree of conversion achieved in the isothermal cure decreased with increasing crosslinking density. Oyanguren and Williams [6] obtained a superposition of T_g *vs.* ln (time) for epoxy novalacs. They indicated that the network structure was determined exclusively by the degree of conversion achieved in the polymerization, irrespective of the selected cure temperature. As a consequence, conversion at gel point was considered constant and independent of temperature. It is also reported elsewhere [119] that T_g is very sensitive to the network structure and is affected by the initial ratio of styrene and polyester C=C bonds and final degree of conversion.

2.4.4 Experimental and process variables

It is reported that pressure has two competing effects on the cure. Since the addition polymerization usually involves a decrease of volume per mole, from a thermodynamical point of view pressure is favorable to the radical polymerization [112]. On the other hand, pressure tends to decrease the free volume, so the latter effect attempts to hinder the cure reactions. The cure is generally inhibited when the free volume effect becomes predominant [127]. Using the transition state theory, the pressure dependence of reaction rate constants, *k*, has been expressed as follows [127]:

$$\frac{d\ln(k)}{dp}=-\frac{\Delta V^*}{RT} \tag{2.34}$$

where ΔV^* is the volume of the activated complex minus the volume of the reactants, p is the pressure, T is the absolute temperature, and R is the universal gas constant. Both the rate constants of initiation by the thermal decomposition and bimolecular termination decrease by increasing pressure, whereas the rate constant of propagation increases with the pressure. Consequently, the initial rate of cure is increased by high pressures.

Kubota [112] reported that in the curing of polyester, with increasing pressure an increase in the rate of cure was resulted. Moreover, the total heat of cure was also found to be affected by pressure. So, a high molding pressure was found beneficial since it causes higher final degree of conversion, and as a consequence, shorter cycle times and higher mechanical properties. Using a high pressure DSC and an FTIR spectrometer, Yang and Lee [128] studied the reaction kinetics of Styrene-unsaturated polyester systems at elevated cure temperatures and pressures. It was reported that at high cure temperatures, the styrene reaction was enhanced more than the polyester reaction. The obtained isothermal thermograms and conversion results indicated that by increasing pressure, the reaction rate was decreased due to the increase in both the onset time and peak time. A significant increase of final extent of cure was reported when pressure applied to the cure system. According to Huang and coworkers, in the curing of unsaturated polyester resin, increasing pressure leads to a plateau of kinetic controlled region in the initial rate profile of DSC. In this region, the conversion of polyester C=C bonds exceed that of styrene, and the intramicrogel crosslinking reactions become predominant. It was indicated that the final conversion increased with pressure up to 500 psig, then decreased with further pressure increase. It was also found that increasing pressure had no effect on the gel conversion, but it prolonged the gelation time.

It is stated that the overall heat of polymerization depends strongly on both the scan speed and initial initiator concentration; however, the obtained kinetic parameters are independent of the scanning rate and initiator concentration [116]. The effect of experimental variables on evaluation of the kinetic parameters by DSC was also investigated by Van Dooren and Müller [129], and Flynn [130]. On the basis of the experimental study, it was indicated that the values of the kinetic parameters could be affected by both sample mass and particle size [129].

2.5. RHEOLOGICAL BEHAVIOR OF REACTIVE POLYMER SYSTEMS

One of the most essential properties of a polymer considering its importance in polymer processing is viscosity. The variation of viscosity caused by chemical reactions is referred to as chemoviscosity. Chemorheology is the study of chemoviscosity [131].

The rheological characterization of reactive polymers is complicated since polymer rheology depends on a variety of variables, that is, time, temperature, deformation rate, pressure, filler concentration, chemical formulation, etc. [132]. Two different possibilities exist in modelling the chemoviscosity of a reactive polymer:

1. An expression can be developed to represent the time dependency of viscosity. Consequently, the temperature dependency of parameters belonging to this expression may be evaluated.
2. An expression can be developed to represent the temperature dependency of viscosity. Afterward, the parameters of this expression related to an appropriate kinetic expression.

Some researchers, including White [133], and Tajima and Crozier [131,135], have suggested semi-empirical models to predict the variation of viscosity during the cure process. The models representing the changes of viscosity with reaction time have the following form:

$$\eta(t) = \eta_0 \exp(kt) \tag{2.35}$$

where η_0 represents the isothermal melt viscosity and k is the reaction rate constant. Roller [34,135] extended Eq. 2.35 by assuming an Arrhenius temperature dependence for η_0 and k:

$$\ln\eta(t)=\ln\eta_{\infty}+\Delta E_{\eta}/RT+tk_{\infty}\exp(\Delta E_{k}/RT) \tag{2.36}$$

where $\eta(t)$ represents viscosity as a function of time at temperature T, η_{∞} stands for calculated viscosity at $T=\infty$, ΔE_{η} is the Arrhenius activation energy for viscosity, R is the universal gas constant, T denotes absolute temperature, t is time, k_{∞} represents the kinetic analog of η_{∞} and ΔE_k is the kinetic analog of ΔE_{η}. At the early stage of cure it is generally assumed that the viscosity is Newtonian [34,60,136,137]. As it can be seen from Eq. 2.36, in this model no forms of kinetic model is assumed.

Eq. 2.36 was modified by introducing an integral form to predict the viscosity changes in non-isothermal systems [34]:

$$\ln\eta(t,T)=\ln\eta_{\infty}+E_{\eta}/RT+\int_{0}^{t}k_{\infty}\exp(\Delta E_{k}/RT)\,dt. \tag{2.37}$$

Since evaluation of the parameters in Eq. 2.37 from multiple isothermal experiments is time consuming, Eley [138] developed a technique to obtain these parameters from a single dynamic measurement. By comparing the values of steady shear viscosity, dynamic viscosity, and complex viscosity it was found that they were virtually identical at short times and low viscosities. Kamal and Ryan [139] stated that dynamic measurements had the drawback of being more dependent or sensitive to structural variations or resin chemistry; however, dynamic measurements in oscillatory shear were considered advantageous because they could be conducted even beyond the gelation point. Tungare, *et al.* [38] conducted a sensitivity analysis on parameters of Eq. 2.37. It was indicated that the four parameters in this equation had different sensitivities, and the sensitivities changed with the crosslinking reactions. It is repeatedly indicated in the literature that the flow activation energy is independent of the shear rate but may increase with progress of the cure reactions. Thus the application of Eq. 2.37 is limited since the flow activation energy is considered to be independent of the extent of cure [139].

Ryan [140] expressed the viscosity of epoxy resin as a function of temperature, shear rate, and conversion by the following form:

$$\eta = f_1(T) f_2(\dot{\gamma}) f_3(\alpha) \tag{2.38}$$

By an empirical fit, the viscosity was expressed as:

$$\eta = \eta_0 \exp\left(C' \int_{\alpha_c}^{\alpha} \frac{d\alpha}{\alpha^m (1-\alpha)^n}\right) \tag{2.39}$$

where η_0 was represented by:

$$\eta_0 = \eta^* \dot{\gamma}^{n'-1} \exp\left(\frac{E_{\dot{\gamma}}}{RT}\right) \tag{2.40}$$

where m and n are kinetic exponents, α_c represents the critical extent of cure, η^* is a constant, and n' is the power-law index.

Based on the second approach in modelling the chemoviscosity of a reactive system, the temperature dependence of viscosity may be expressed in the form of a Williams-Landel-Ferry (WLF) equation [26]:

$$\log \eta(T) = \log \eta(T_s) + \frac{a(T-T_s)}{b+(T-T_s)} \tag{2.41}$$

where η represents viscosity, T denotes temperature, T_s is a reference temperature, and a and b are constants. The parameters T_s and $\eta(T_s)$ vary with the progress of cure so they can be expressed as a function of conversion (α). Using this approach, Tajima and Crozier [131] demonstrated the variation of viscosity for epoxy resins in the course of cure reactions by the WLF equation. The "viscosity-temperature" shift factor was defined as: $a_T = \eta(T)/\eta(T_s)$. By regression analysis, a relationship was established between T_s and the amount of hardener consumed to react with the epoxy resin. Moreover, log $\eta(T_s)$ was found proportional to T_s. According to Tajima and Crozier [37], for epoxy resin T_s might be expressed as a linear function of α^2, and log $\eta(T_s)$ as a linear function of α.

Lee and Han [142] applied the WLF equation to unsaturated polyester cure system. They expressed both activation energy of flow, E_η, and frequency factor, A, in terms of extent of cure, α. By establishing relationships between the reference temperature T_s and the extent of cure, as well as between log $\eta(T_s)$ and T_s, the following form was obtained:

$$\log\eta(T,\alpha) = (a_1 + b_1\alpha) - \frac{a_2(b_2 + T - c_2\alpha)}{a_3 + T - c_2\alpha} \tag{2.42}$$

where a_1, b_1, a_2, b_2, c_2, and a_3 are parameters.

Lee and Han [142] applied a WLF equation to model the chemorheology of polyester resin:

$$\log\eta(T) = \log\eta(T_g) - \frac{a(T - T_g)}{51.6 + T - T_g} \tag{2.43}$$

where "a" is a free volume parameter, and T_g is the glass transition temperature of the resin. The main difference between Eq. 2.41 and Eq. 2.43 is that the former treats T_s as an unknown parameter, whereas the latter considers T_g as a physical property of the cured resin. On the basis of experimental data obtained from partially cured samples, T_g was related to the extent of cure, α. Log $\eta(T_g)$, and free volume parameter "a" were also expressed in terms of α, using least squares analysis. They claimed that the theoretical predictions showed a good agreement with experimental data at low extent of cure.

One of the most extensively used viscosity-conversion expressions was suggested by Castro [18], and Wang, *et al.* [40]:

$$\eta/\eta_0 = [\frac{\alpha_g}{\alpha_g - \alpha}]^{f(\alpha,T)} \tag{2.44}$$

where $\eta_0 = \eta(\alpha = 0, T) = A_\eta Exp(\Delta E_\eta /RT)$, α is conversion, and α_g is the gel point conversion. For a fast curing resin used in the Reaction Injection Molding (RIM) process, Gonzalez [1] applied a similar expression to represent dependency of viscosity on degree of cure:

$$\eta/\eta_m = (1 - g)^{-f_\eta(g)} \tag{2.45}$$

where η_m denotes the monomer viscosity, α_g represents the gel point conversion, $g = \alpha/\alpha_g$, and $f_\eta\ (g)$ is a linear function of g. Eqs. 2.44 and 2.45 have been widely used in the literature for fast curing RIM resins [143-146].

Kim and Kim [147] represented the variation of viscosity during the polymerization of unsaturated polyester resin in the following form:

$$\eta = \eta_0 \exp(\frac{a_1 + b_1 C^*}{RT}) \exp(a_2 C^*) \tag{2.46}$$

where a_1, b_1, and a_2 are empirical parameters. In this model, the activation energy of flow shows a linear dependence on conversion.

Using oscillatory shearing flow measurements, Tung and Dynes [148] reported that during the isothermal cure of epoxy resins the time at which the storage modulus ,G', and loss modulus ,G'', intersected coincided with the gel time. Lee and Han [81] also applied the oscillatory measurements and obtained comparable results with the gel time calculated by plotting of the viscosity ratio, η_0/η , versus cure time.

2.6 NOMENCLATURE

a	parameter
a_1-a_3	parameters
A	frequency factor (s^{-1}, min^{-1})
A_0,A_p	frequency factor of the propagation reactions (s^{-1})
b_1,b_2	parameters
B	a parameter in Eq. 2.16 and a constant in Eq. 2.22
B_0	frequency factor of the termination reactions (s^{-1})
c_1,c_2	parameters of Eq. 2.42
C_1-C_3	parameters of Eq. 2.7
C	constant
C^*	degree of cure
C^*_f	final degree of cure
E,E_a,E_k	activation energy of the cure reactions (kJ/mol)

E_p	activation energy of the propagation reactions (kJ/mol)
E_t	activation energy of the termination reactions (kJ/mol)
$E_\eta, E_{\dot{\gamma}}$	activation energy of flow (kJ/mol)
f	efficiency of the initiator
$f(\alpha)$	diffusion factor in Eq. 2.15
$f(\alpha, T)$	isothermal conversion rate defined by Eq. 2.31 and a function appeared in Eq. 2.44
g	a function of gel point conversion in Eq. 2.45
$g(\alpha)$	a function given by Eq. 2.9
$(\partial h/\partial T)_t$	a temperature dependent quantity in Eq. 2.29
I	initiator concentration at a given time t
I_0	initiator concentration at the beginning of the cure
k_0	frequency factor of the cure reactions (s^{-1})
k, k_1, k_2	reaction rate constants (s^{-1})
k_1^*, k_2^*	reaction rate constants which are functions of filler content (s^{-1})
k_c	rate constant for the chemical reaction (s^{-1})
k_d	rate constant for the diffusion (s^{-1})
k_e	effective rate constant (s^{-1})
k_p	rate constant of the propagation reactions (s^{-1})
k_t	rate constant of the termination reactions (s^{-1})
k_∞	kinetic analog of η_∞
K_2	constant

m,n,p	reaction exponents
n'	power-law index
p	pressure
Q	total isothermal heat of cure generated up to a given time t (J/g)
Q_M	a temperature dependent quantity given by Eq. 2.7 (J/g)
Q_u	ultimate enthalpy of cure (J/g)
R	universal gas constant
t	time (s)
t_g	gel time (s)
T	temperature (°C, °K)
T_0	a theoretical temperature where no cure reaction could occur (°K)
T_{cure}	cure temperature (°K)
T_g	glass transition temperature (°C)
T_m	peak temperature (°K)
T_s	a reference temperature (°C)
α	cumulative conversion at a given time t
α_c	degree of conversion where diffusion becomes controlling
α_f	final isothermal degree of conversion
α_g	gel point conversion
α_p	conversion at peak time
α_u	total ultimate conversion

$\dot{\alpha}$	conversion rate (s^{-1})
$d\alpha/dt$	conversion rate (s^{-1})
β	heating rate (°C/s)
ΔH_u	ultimate enthalpy of cure (J/g)
ΔV^*	volume of the activated complex minus the volume of the reactants
η	viscosity (Pa.s)
η_0	viscosity of the unreacted resin (Pa.s)
η_∞	viscosity at $T = \infty$
η^*	constant
φ	heating rate (s^{-1})
$\dot{\gamma}$	shear rate (s^{-1})

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PRESENTATION OF CHAPTER 3

The cure time for composite manufacturing processes is mainly determined by the resin formulation. Since the thermosetting resins generally contain a variety of additives, a good understanding of the influence of different additives on the kinetics of cure is of great importance in mathematical modeling of composite manufacturing processes. The major goal of the work presented in Chapter 3 is to verify if a promoted polyester resin requires a specific kinetic model accounting for the acceleration of the cure reactions caused by the promoter. Since the effect of a promoter is more pronounced at low temperatures, well below the decomposition temperature of the initiator, an effective kinetic model should be capable of predicting the curing behavior in the entire temperature range even at high cure temperatures. In Chapter 3, the kinetic parameters of an unsaturated polyester resin cured in the presence of a cobalt-based promoter and glass fibers were estimated by a new procedure. In spite of the ordinary estimation procedures which generally ignore the unrecorded part of cure exotherm, during the stabilization period of the calorimeter at high cure temperatures, the procedure developed in Chapter 3 is capable of accounting for the unrecorded extent of cure. It is also shown that the implemented procedure makes the kinetic parameters temperature dependent to account for the complexity of cure reaction in the presence of the promoter. Since the inhibition of cure caused by a particular reinforcement may affect the kinetic parameters of the cure system, the inhibition effect of glass fiber reinforcement is discussed in Chapter 3 regarding the changes in the kinetic parameters. Two sets of kinetic parameters estimated in this chapter are employed in the numerical analysis of the RTM post-filling phase in Chapter 5.

CHAPTER 3

THE EFFECTS OF COBALT PROMOTER AND GLASS FIBERS ON THE CURING BEHAVIOR OF UNSATURATED POLYESTER RESIN

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3.1 ABSTRACT

Thermosetting resins frequently used in engineering applications contain a variety of additives, including promoting agents and fillers. A good understanding of the influence of these additives on the kinetics of the cure is of great importance in mathematical modeling of composite manufacturing processes. In this study, a phenomenological autocatalytic kinetic model was used to describe the cure of a polyester system containing a cobalt-based promoter. The effect of including the promoter in the cure system was discussed regarding the changes in the kinetic parameters. It was found that the cure characteristics of the unsaturated polyester system was affected by the presence of the promoter. This effect resulted in a temperature dependency of the reaction exponents as well as in a significant increase of the Arrhenius frequency factor at low temperatures. The changes in cure characteristics of promoted polyester system caused by incorporation of chopped glass fibers were also investigated. The obtained results indicated that unlike promoter, the presence of glass fibers did not appreciably affect the reaction exponents. However, the presence of glass fibers resulted in some changes in the overall reaction rate of the cure system. The values assigned to the kinetic parameters were found to yield theoretical estimations that were in good agreement with the experimental data obtained from isothermal differential scanning calorimetry (DSC). To take into account the unrecorded extent of reaction at high cure temperatures, a new procedure was implemented. This procedure estimates a correction factor related to the total isothermal heat of cure obtained from DSC experiments at

different isothermal cure temperatures.

3.2 INTRODUCTION

Thermosetting resins play an important role in the material industry because of their flexibility in achieving the desired ultimate properties. A good understanding of the effects of various additives, *e.g.* fillers, promoters, etc., is the most important prerequisite in process optimization of composites.

Various methods have been employed to monitor the progress of the cure reactions. However, only a few of these methods are capable of following the cure reactions from beginning to end. Thermal analysis by differential scanning calorimeter (DSC) in both isothermal and nonisothermal modes is a well-established technique for studying the kinetics of the cure reactions that can be used for time-temperature predictions and optimization of process variables [1].

Many experimental studies have been conducted concerning the kinetics of the cure of thermosetting materials. In most cases, an nth order kinetic model was employed to describe the mechanism of cure [2-5]. It is shown that the following model represents adequately the cure kinetics of both epoxy and unsaturated polyester systems [6-10]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\,\alpha^m)(1-\alpha)^n \tag{3.1}$$

where α is the conversion, k_1 and k_2 are rate constants which follow an Arrhenius temperature dependency and m and n are constants independent of temperature.

In general, thermosetting resins exhibit the vitrification phenomenon which stops the reaction before completion of the cure. In order to satisfy the condition of zero reaction rate at the vitrification conversion, where $\alpha = \alpha_{max}$, some researchers have employed the following expression:

$$\frac{d\alpha}{dt} = (k_1 + k_2\,\alpha^m)(\alpha_{\max} - \alpha)^n \tag{3.2}$$

For industrial formulations, the temperature of chemical decomposition of the initiator is too high, so most industrial formulations are cured at ambient temperature in the presence of promoters which yield a more complex reaction mechanism. To account for the complexity of the cure reactions in the presence of a promoter, some kinetic parameters are considered temperature dependent instead of being constant [11].

There are some works on the effect of additives on curing of thermosetting materials in the literature [12-15]. Using DSC, Salla and Ramis [14] studied the role of tertiary amines as promoter in the kinetics of unsaturated polyester resin. It was reported that the activation energy could vary with regard to the effectiveness of the promoter used. Moreover, they found that the influence of either the type of promoter or the ratio of initiator/promoter was more pronounced at the start of the reaction. Performing Electron Spin Resonance (ESR) spectroscopy on unsaturated polyester resins promoted by various quantities of cobalt naphthenate promoter, Slupkowski and coworkers [16] reported that the concentration of free radicals produced during the cure reactions reached its maximum value more rapidly when the concentration of the promoter was increased. By applying adiabatic temperature rise technique, Rojas and coworkers [17] presented an nth order kinetic model to predict the curing behavior of unsaturated polyester resins promoted by cobalt octoate. The broad range of n values, $2 \leq n \leq 4$, that was reported implies that the overall reaction order for promoted unsaturated polyester resin is temperature dependent. Assuming a 3rd order kinetic model, $n = 3$, they calculated the best values of the Arrhenius frequency factor and activation energy for the promoted system. However, a considerable discrepancy was reported between theoretical and experimental values obtained in a heated mold. This discrepancy was partly attributed to the values assigned to the kinetic parameters.

McGee [3] applied a simple nth order kinetic model to express the cure characteristics of a polyester resin filled by a variety of fillers (*e.g.* glass, calcium carbonate, and aluminum). No attempts were made in his study to verify the possible interaction of fillers with resin formulation that might have resulted in a more complicated kinetic expression. He reported that the gel time of polyester system increases with increasing the glass content [3]. Based on the results obtained by Dutta and Ryan [18], the sum of the kinetic exponents is approximately 2, irrespective of the temperature and type of filler incorporated in the cure system. Moreover, the filler influences the reaction rate by altering the rate constants. Ng and Manas-Zloczower [19] investigated the influence of glass fibers on the curing of a polyester resin. Their observations confirmed that the total heat of reaction per unit mass of resin remains approximately constant and the presence of filler does not affect the peak temperature. However, these observations may not be valid in low temperature cure systems where glass fibers may have an inhibiting effect on room-temperature cures [20].

In this article, the influence of a cobalt-based promoter on the cure characteristics of an unsaturated polyester formulation is discussed. Moreover, the kinetic parameters of the glass-fiber-filled promoted polyester system are compared to those of unfilled system. A new procedure is developed to compensate for the unrecorded extent of cure at high cure temperatures in the isothermal DSC measurements. This procedure is shown to be valid as well for low cure temperatures where the rate of heat generation falls beyond the sensitivity of the calorimeter, and the obtained cure data are not reliable.

3.3 EXPERIMENTAL

The unsaturated polyester resin was obtained from Ashland Co. This resin was promoted by a cobalt-based promoter for room-temperature-cure. The free radical initiator employed was methyl ethyl ketone peroxide supplied by Ashland Co.

The thermal and kinetic data were obtained using a Dupont DSC 910. Since the heat of decomposition of the initiator was found negligible, it was assumed that the measured exothermic heat comes exclusively from the consumption of double bounds in the propagation step of styrene/polyester reaction. The temperature and heat flow calibration of the DSC were performed by using gallium and indium as calibration standards. The effect of heating rate on the melting temperatures of gallium and indium was found negligible.

The initiator (1 wt %) was mixed thoroughly with the polyester resin until a homogeneous solution was obtained. The sample container was kept in the refrigerator at -20°C. Two sets of isothermal experiments were conducted to obtain the kinetic data for both unfilled and filled polyester systems. In the first set of experiments, about 7-13 mg of the sample was transferred to an empty sample pan. In the second set, a droplet of the sample weighing between 20-25 mg was transferred into the sample pan containing chopped glass fibers. The approximate fiber content was about 10-15 wt%. For all experiments, a dry nitrogen supply was employed to purge the existing oxygen and moisture in the sample holder. An empty pan with an equivalent weight of that of the sample pan was used as the reference.

The data acquisition system was started by a computer program and the sample was introduced into the DSC cell. Rate of heat generation, $\dot{Q}$, was recorded as a function of time. The reaction was considered complete when the rate curve leveled off to a base line. Material losses due to monomer volatilization were negligible.

Dynamic DSC scans were performed at heating rates of 5, 10, 15, and 20°C/min using the samples without filler. A second scanning run was conducted on the cured sample to determine the base line (see Appendix A). Looking at the DSC thermograms obtained from dynamic measurements in Fig. 3.1, it is noticed that the initial cure temperature as well as the peak temperature are increasing with increasing heating rate. However, the total heat of reaction estimated from the area under the dynamic exotherm decreases with increasing the heating rate. Several authors have reported ΔH_u to be independent of the heating rate [21,22]. However, it is also reported that complete conversion can be achieved by incorporating a sufficient amount of the initiator into the cure formulation, and conducting the dynamic cure experiments at very low scan speeds [23]. In the present study, the best value of the ultimate heat of reaction for 100% monomer conversion, Q_u, was obtained by extrapolating the dynamic heat of cure to zero scan speed. The value obtained for the heat of reaction was 316 (kJ/kg of resin) which is in good agreement with the findings of other researchers (see Table 3.1). It is worth noting that each data in dynamic measurements was the average value of three experiments. The reproducibility was quite acceptable.

As can be seen in Fig. 3.1, the second peak in dynamic thermograms, representing the thermally induced cure of the promoted resin, becomes sharper with increasing heating rate. This observation implies that at low heating rates, the chemically induced cure reactions are predominant and give rise to less significant thermally initiated cure reactions at high temperatures. Therefore, the second peak almost vanishes at isothermal cure thermograms.

To establish a kinetic model for the cure reactions, isothermal DSC experiments giving the extent of cure as a function of time were performed in the range of 25-75°C. At temperatures higher than 75°C, a significant extent of reaction took place during the stabilization period of the calorimeter, so the results obtained at these temperatures were not considered in the kinetic analysis. To measure the residual activity after an isothermal run, a scanning run with a heating rate of 10°C/min was performed from room temperature to 200°C. A second isothermal run was conducted to determine the isothermal base line. Assuming that the heat of reaction is directly proportional to the extent of cure, the total heat generated during isothermal DSC measurement was related to the extent of cure by:

$$\alpha = \frac{1}{\Delta H_u} \int_0^t \left(\frac{dH}{dt}\right) dt \tag{3.3}$$

where α is the extent of reaction at time t, dH/dt is the rate of heat generation per unit mass of the resin, and ΔH_u is the ultimate heat of reaction when 100% monomer conversion is achieved. It should be noted that to establish the kinetic model from isothermal DSC results, it was assumed that heat capacity of the reactants remained constant during the entire period of reaction. This assumption has been found reasonable for thermosetting resins [24].

To calculate the total isothermal heat of cure, Q_T, and final degree of conversion, α_f, two different methods are suggested in the literature [25]. In the first method, Q_T and α_f are directly evaluated by integration of the isothermal DSC rate profile:

$$\alpha_f = \frac{1}{Q_u} \int_0^{t_f} \left(\frac{dH}{dt}\right) dt = \frac{Q_T}{Q_u} \tag{3.4}$$

where t_f is the time representing the end of reaction, and Q_u is the ultimate heat of cure. This method is relevant when the rate of heat generation is higher than the minimum value detectable by the calorimeter. However, the values of Q_T obtained by this method are not reliable at high temperatures where a significant extent of reaction takes place during the stabilization period of the instrument. The second method becomes important at low rates of heat generation or at low cure temperatures, where the sensitivity of the instrument is too low to detect accurately the produced heat of reaction. By measuring the residual heat of cure, Q_R, the final degree of conversion, α_f is calculated from:

$$\alpha_f = \frac{Q_u - Q_R}{Q_u} = \frac{Q_T}{Q_u} \tag{3.5}$$

For convenience, the experimental heats of cure and final degrees of conversion calculated by these two methods will be refered to as Q_{M1} (α_{M1}) and Q_{M2} (α_{M2}), respectively, throughout this article. In the present study, the values obtained from these two methods will be compared to evaluate the unrecorded extent of cure in isothermal thermograms.

3.4 RESULTS AND DISCUSION

Fig. 3.2 shows the variation of Q_{M1} and Q_{M2} as a function of isothermal cure temperature. A significant discrepancy can be seen between the two curves. At low cure temperatures, the discrepancy is attributed to the low rate of heat generation which is beyond the values detectable by DSC. However, for filler incorporated samples, because of the high conductivity of glass fibers and higher sample weights used in the glass-filled set of experiments, Q_{M1} and Q_{M2} are comparable at low cure temperatures. The values of Q_{M1} are not reliable at high temperatures since the extent of reaction occurring during the transient heating of calorimeter is significant but is not directly measurable. The values of Q_{M2} for both unfilled and filled samples are approximately identical. This implies that glass fibers have no significant influence on the final extent of reaction achieved in the isothermal cure of promoted polyester system.

Sourour [9] recommended a method to calculate the unrecorded extent of reaction during the transient heating period of the calorimeter. This method is based on the presumption that the area under the isothermal thermogram from the beginning of the curve up to the peak,

Q_p , is a constant value independent of the cure temperature. Using this method, experimental values of Q_T at high cure temperature can be corrected by integrating the isothermal thermogram from the peak to the completion of the cure and adding to the results the constant value of Q_p. However, for the promoted polyester resin applied in the present study, the calculated values of Q_p did not yield a constant value due to the presence of the promoter.

Salla and Ramis [14] introduced a method to take into account the unrecorded part of the isothermal DSC thermogram, by defining the following terms:

$$\alpha^c = \alpha \, . (\frac{Q_u - Q_R}{Q_{tot}}) \tag{3.6}$$

$$(\frac{d\alpha}{dt})^c = \frac{d\alpha}{dt} . (\frac{Q_u - Q_R}{Q_{tot}}) \tag{3.7}$$

where :

α^c	corrected conversion
$(d\alpha/dt)^c$	corrected conversion rate
Q_u	ultimate heat of cure obtained by dynamic DSC
Q_R	residual heat of cure obtained by dynamic DSC
Q_{tot}	total isothermal heat of cure obtained by integrating the area under each individual isothermal DSC thermogram

α conversion at a given time t

$(d\alpha/dt)$ conversion rate at a given time t

It should be noted that Q_{tot} and $(Q_u\text{-}Q_R)$ in their work are equivalent to Q_{M1} and Q_{M2}, respectively, in the present study.

At high cure temperatures where the entire part of the unrecorded isothermal thermogram is related to the beginning of the reaction, Eqs. 3.6 and 3.7 would result in an overestimation of the conversion rate for intermediate and high conversions. The same conclusion holds for low cure temperatures. At low temperatures, isothermal DSC data are mostly unreliable at the beginning and end of reaction where the rate of heat generation is too low to be detected by DSC. Consequently, the error introduced by Eqs. 3.6 and 3.7 also becomes important for intermediate extent of cure at low cure temperatures.

In the present work, a new procedures was implemented to correct the unrecorded extent of cure during isothermal DSC measurements. This procedure attempts to estimate the kinetic parameters in a certain way to predict the Q_{M1} (instead of Q_{M2}) in Figs. 3.2-a and 3.2-b. It is also assumed that the first kinetic parameter, α_{max}, increases with cure temperature, passes through a maximum value, then decreases. Consequently, the theoretical values of Q_T predicted by the kinetic parameters would reveal the same variation with temperatures as that of Q_{M1} in Figs. 3.2-a and 3.2-b. This assumption enabled us to correct the predicted isothermal enthalpy of cure and degree of cure in the entire temperature range using the following expressions:

$$Q_T^c = C \cdot Q_{T,cal} \tag{3.8}$$

$$\alpha^c = C \cdot \alpha_{cal} \tag{3.9}$$

where $Q_{T,cal}$ and α_{cal} represent the calculated enthalpy of cure and extent of reaction, respectively, predicted using estimated kinetic parameters, Q_T^c and α^c are their corresponding corrected values, and C is the correction factor defined as:

$$C = \frac{Q_{M2}}{Q_{M1}} \tag{3.10}$$

By implementing this procedure, the degree of cure is corrected after estimation of the kinetic parameters. Moreover, in spite of the method proposed by Salla and Ramis [14], this procedure does not affect the conversion rate data. To demonstrate the ability of the new procedure, the results predicted using this procedure are compared with the predictions of the ordinary estimation procedure, where no attempt is made to correct for the unrecorded part of cure exotherms.

The isothermal data were fitted to Eq. 3.2 by the multiple nonlinear least squares method. Fig. 3.3-a shows the variation of α_{max}, as the first kinetic parameter, with cure temperature without applying the new procedure. Since the estimated values of α_{max} at high cure temperatures exceeded unity, a full conversion, α_{max} = 1, was assumed at temperatures above 60°C. The lack of precision in estimating α_{max} at high temperatures was due to the presence of a broad peak at the end of cure period. This event was attributed to the slight extent of thermally induced reactions at elevated temperatures. For this reason, the estimated values of α_{max} at 60 °C and higher were unrealistic.

Applying the new procedure, the isothermal DSC data were fitted to Eq. 3.2 by the multiple nonlinear least squares method. The initial guess for parameters of Eq. 3.2 at the beginning of the nonlinear regression was provided by the estimation technique proposed by Keenan [26] and by assuming an overall reaction order equal to 2 ($m+n = 2$). At temperatures higher than 55°C, corresponding to the inflection point of Q_{M1} in Figs. 3.2-a and 3.2-b, the following approximation was held:

$$\alpha_{\max} \approx \alpha_f = \frac{Q_{M1}}{Q_u} \tag{3.11}$$

This assumption enabled us to estimate the kinetic parameters yielding $Q_{T,cal}$ values with a similar temperature dependency as that of Q_{M1} in Figs. 3.2-a and 3.2-b. In Fig. 3.3-b, estimated values of α_{max} were correlated with cure temperature using a 3rd order polynomial regression. The resulting expressions are tabulated in Tables 3.2 and 3.3. The rest of kinetic parameters in this work were evaluated based on the estimates of α_{max} illustrated in Fig. 3.3-b.

Fig. 3.4 shows the variation of reaction exponents *versus* cure temperature for both unfilled and filled samples. More realistic results can be obtained if one represents the temperature dependencies of reaction exponents in Fig. 3.4-a in the following forms:

$$m = a_0 + a_1 T^{a_2} (a_3 - T)^{a_4} \tag{3.12}$$

$$n = b_0 + b_1 T^{b_2} (b_3 - T)^{b_4} \tag{3.13}$$

In spite of relatively complex variation of the reaction exponents, these expressions asymptotically approach the reaction exponents for nonpromoted polyester systems (a_0 and b_0). The reaction exponents outside the range of influence of promoter (a_0 and b_0) add up to 1.57 which is a good approximation of the overall reaction order for nonpromoted polyester systems ($n+m = 2$, Sourour, [9]). Fig. 3.4-a also indicates that the promoter is more effective at low temperature (below 60°C) where reaction is mainly induced by chemical reaction of the promoter with the cure system. For glass-fiber-filled samples in Fig. 3.4-b, the variations of reaction exponents with cure temperature correlate with temperature according to the Arrhenius equation in the first part of the temperature range. The kinetic Exponents of the filled samples were therefore assumed to have the following form:

$$\begin{aligned} m &= m_0 \exp\left(-\frac{E_m}{RT}\right) \\ n &= n_0 \exp\left(-\frac{E_n}{RT}\right) \end{aligned} \tag{3.14-3.15}$$

here m_0, and n_0 are constants independent of temperature, E_m and E_n are the activation energies attributed to m and n, R is the universal gas constant, and T is absolute temperature. The temperature dependency of reaction exponents is attributed to the way a promoter affects the cure mechanism. The cure reactions in the presence of the promoter can be chemically (at low temperatures) or thermally (at high temperatures) induced. Therefore, a variable cure mechanism justifies the existence of different kinetic parameters in different temperature ranges. The comparison between Figs. 3.4-a and 3.4-b indicates that the incorporation of glass fibers in the promoted polyester system does not appreciably affect the reaction exponents at low temperatures (below 60°C). This implies that the effect of the promoter on the reaction orders is probably more significant than the potential effect of glass fibers. Due to the limited number of experimental data at temperatures higher than 60°C, the small variations of m and n at these temperatures were ignored by assigning constant values to these parameters. This uncertainty lead to a less accurate estimation of the kinetic parameters at high temperatures for glass-fiber-filled samples.

Fig. 3.5-a shows the Arrhenius plots of reaction rate constants *versus* reciprocal cure temperature. The rate constant data in each temperature range correlate with reciprocal absolute temperature according to the following equation:

$$k = k_0 \exp(-\frac{E_k}{RT}) \qquad (3.16)$$

where k_0 stands for the Arrhenius frequency factor and E_k represents the activation energy of reaction. Having two temperature ranges with different activation energies implies that the effect of the promoter is different at different cure temperatures. The presence of the promoter causes a significant increase in the rate constant at low temperatures (below 60°C) whereas, at higher temperatures a considerable decrease is observed. It is reported that cobalt-based promoters can considerably increase the reaction rate of unsaturated polyester resins cured at low temperatures [17].

By incorporating some fillers, *e.g.* carbon black and silica, Dutta and Ryan [18] reported that the overall reaction order of the epoxy cure system was not significantly affected by the presence of fillers. However, it was reported that the presence of these fillers changed the rate constants of Eq. 3.2. Their results indicated that some fillers influence the kinetic rate constants through the Arrhenius frequency factor whereas, the others may affect kinetic rate constant through the activation energies. Fig. 3.5-a shows a similar trend in the present work. At low temperatures, the value of Arrhenius frequency factor is not comparable with that of unfilled samples. Hence the addition of glass fibers caused some decrease in the overall reaction rate at low temperatures, the decelerating effect was attributed to the inorganic radicals produced in the cure system. According to Plueddemann [20], free radical polymerization is inhibited in the presence of filler due to the termination of growing chains. The inhibiting effect of glass is mainly explained by the termination of the free radicals through the electron transfer and through the production of new inorganic free radicals.

These radicals do not have adequate activity to initiate other radicals at low temperatures. However, the inorganic radicals have adequate activity at higher temperatures [20]. Kinetic parameters obtained in the present work are tabulated in Table 3.2 and 3.3 where a comparison has been made between unfilled and filled promoted polyester systems and a nonpromoted formulation.

To justify the accelerating effect of the promoter at temperatures below 60°C, the Arrhenius plots of rate constants estimated without applying the new procedure are given in Fig. 3.5-b. The same trend observed in this figure for the changes of the reaction rate constants indicates that the results demonstrated in Fig. 3.5-a are reliable, in terms of the effect of additives, regardless of the applied estimation procedure. Based on the obtained results, two observations are worth noting:

1. Below 60°C, where the role of promoter is more pronounced, the promoter acts by increasing the Arrhenius frequency factor of the cure reactions. Moreover, due to the complexity of the cure reactions in the promoted system, reaction exponents become temperature dependent. The addition of glass fibers in the cure system gives rise to some decrease in the cure rate at low cure temperatures. This effect is noticed at 45°C and below.

2. Above 60°C, both the frequency factor, k_0 , and activation energy, E_k , reveal

considerable decreases with cure temperature. The same decreasing trend is observed for the reaction exponents. These results indicate that the effect of the promoter is less significant at temperatures higher than 60°C.

On the basis of experimental results obtained in this study, incorporation of glass fibers in the cure system at low temperatures, up to 60°C, causes a longer induction period than that of the unfilled system. The induction period is defined as the time at the beginning of the cure reactions before the onset of cure. This time lag may be explained by the preventing effect of glass fibers on the cure reactions. The glass fibers act as heat sinks, absorbing the heat of reaction, and yield a lower reaction rate by unfavorably affecting the cure.

Figs. 3.6 and 3.7 give the plots of the isothermal conversion rate and extent of conversion at various temperatures for unfilled and filled systems. It is seen that all experimental conversion rate data are in good agreement with the expected curves obtained from Eq. 3.2 and the estimated kinetic parameters. Good concordance is also observed in the corresponding extent of cure data *versus* cure time. For comparing the experimental conversion data with the predicted values in Fig. 3.7, the experimental data were modified in the following form:

$$\alpha_{\mathbf{exp}}^{c} = C \, . \, \alpha_{\mathbf{exp}} \tag{3.17}$$

where C is the correction factor given by Eq. 3.10, α^{c}_{exp} stands for the corrected experimental degree of conversion at a given time t, and α_{exp} represents the experimental degree of conversion obtained by isothermal DSC runs.

Figs. 3.8-a and 3.8-b give the $Q_{T,cal}$ evaluated using the estimated kinetic parameters. A fairly good agreement exists between the curves representing $Q_{T,cal}$ and experimental results, Q_{M1}. Figs. 3.8-c and 3.8-d compare the curves representing experimental enthalpy of cure, Q_{M2}, with the theoretical predictions corrected using Eqs. 3.8 and 3.10. Since the success of the implemented procedure entirely depends on the precision of the estimated kinetic parameters, weak estimates can have a high impact on the precision of the predicted enthalpies of cure. To reduce the existing discrepancy between the predicted values and experimental results in Figs. 3.8-c and 3.8-d, an alternative correction factor can be used:

$$C = \frac{Q_{M2}}{Q_{T,cal}} \tag{3.18}$$

where C is the alternative correction factor and $Q_{T,cal}$ is the predicted enthalpy of cure. The corrected values resulted by applying Eq. 3.18 are represented by filled circles in Fig. 3.9-a. The magnitude of improvement in prediction of the conversion profile resulted by applying two different correction factors, Eq. 3.10 and Eq. 3.18, are compared in Fig. 3.9-b. This figure indicates that both correction factors yield significant improvement in the prediction of conversion profile. For comparison, the conversion profile predicted without accounting for the unrecorded extent of cure, $\alpha_{incor.}$, is also given in Fig. 3.9-b.

3.5 CONCLUSION

In spite of the fact that nonpromoted polyester resins show constant kinetic parameters, in the case of the promoted polyester resin kinetic parameters were considered temperature dependent to account for the complexity of the cure mechanism in the presence of the promoter. It was found that this complexity was caused by the promoter which chemically induced the cure reactions at low temperatures.

The primary effect of the glass fibers was a decrease in the overall reaction rate at low cure temperatures. Acting as heat sinks, glass fibers absorbed the heat of reaction, and yielded a different cure behavior in the isothermal cure. On the basis of estimated kinetic parameters, two temperature regions with different cure characteristics were observed:

1. At low temperatures, below 60°C, the essential role of the promoter was to increase the overall reaction rate through the Arrhenius frequency factor. It also affected the reaction exponents in the entire temperature range. The role of filler at low temperatures was some decrease in the Arrhenius frequency factor. The inadequate reactivity of inorganic free radicals produced in the presence of glass fibers was found responsible for deceleration of the cure reactions. Unlike promoter, glass fibers did not

appreciably affect the reaction exponents.

2. At high temperatures, above 60°C, a significant decrease was noticed in the reaction rate constant of the promoted resin through the changes in both the Arrhenius frequency factor, k_0, and the activation energy of cure, E_k. The reaction orders, *m* and *n*, asymptotically approached the values reported in the literature for nonpromoted polyester systems. This implies that the overall effect of the promoter at high temperatures was less significant. For glass-fiber-incorporated samples, some increase in the reaction rate constant was observed at 45°C and higher. This event was attributed to the inorganic free radicals produced in the presence of glass fibers which were adequately active at high cure temperatures. The effect of glass fibers on the reaction exponents was a slight alteration of their temperature dependency at low temperatures.

Our results indicated that the sum of reaction exponents was not a constant value due to the changes caused by the promoter in the cure characteristics of the polyester system. Moreover, the total isothermal heat of reaction was almost identical for both filled and unfilled promoted systems. The results obtained in this work will be used for the simulation of RTM process.

3.6 APPENDIX A

A precise procedure was implemented in the present study to find a more accurate base line based on the one established by reheating a fully cured sample. There is a method recommended by Brennan and coworkers [27] which takes into account the effect of changes in the heat capacity of the cure system due to the chemical reaction. Based on this method, the base line beneath the dynamic DSC thermogram is considered a linear function of conversion. To implement the method, the initial and final base lines of the dynamic DSC thermogram are needed. However, for some cure systems, the initial, or final base line, cannot be accurately established to approximate the heat capacities of reactants, or product. In this case, the method introduced by Tajima and Crozier [28] can be applied.

Fig. 3.10-a shows the base line obtained in the present study by reheating the fully cured promoted polyester resin. Taking the first region of the base line as an approximation of the heat capacity of the reactants, one can introduce a considerable error in the estimation of the enthalpy of cure. Based on the method introduced by Tajima and Crozier, the heat capacity contribution of the products to the final base line is determined by the base line obtained in reheating of the fully reacted sample. Consequently, it is assumed that the temperature dependency of the heat capacity of reactants is parallel to that of product. The parallel line in Fig. 3.10-b represents the base line constructed regarding the above presumption. The corrected final base line was constructed as a linear combination of the initial and final base

lines (dotted line).

3.7 NOMENCLATURE

a_0-a_4	adjustable parameters
b_0-b_4	adjustable parameters
C	correction factor given by Eqs. 3.10 and 3.18
E_k	activation energy of the cure reactions (kJ/mol)
E_m	activation energy attributed to m (kJ/mol)
E_n	activation energy attributed to n (kJ/mol)
H	enthalpy of cure (J/g of resin)
k_0	frequency factor of the cure reactions (s^{-1})
k_1, k_2	reaction rate constants (s^{-1})
m, n	reaction exponents
m_0, n_0	frequency factors attributed to m and n
Q_{M1}	total isothermal enthalpy of cure calculated by Eq. 3.4 (J/g of resin)
Q_{M2}	total isothermal enthalpy of cure calculated by Eq. 3.5 (J/g of resin)
Q_R	residual heat of cure (J/g of resin)
Q_T, Q_{tot}	total isothermal enthalpy of cure (J/g of resin)
$Q_{T,cal}$	predicted enthalpy of cure (J/g of resin)
Q_T^c	predicted isothermal enthalpy of cure corrected by Eq. 3.8 (J/g of resin)

Q_u, ΔH_u	ultimate enthalpy of cure (J/g of resin)
R	universal gas constant
t	time (s)
t_f	time representing the end of reaction (s)
T	temperature (°C, °K)
α	cumulative conversion at a given time t
α^c	degree of conversion corrected by Eqs. 3.6 and 3.9
α_{exp}	experimental degree of conversion
α^c_{exp}	experimental degree of conversion corrected by Eq. 3.17
α_f	final isothermal degree of conversion
α_{max}	vitrification conversion
$d\alpha/dt$	conversion rate (s^{-1})
$(d\alpha/dt)^c$	conversion rate corrected by Eq. 3.7 (s^{-1})

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3.9 TABLES AND FIGURES

Table 3.1 Ultimate enthalpy of cure for unsaturated polyester resin obtained by some researchers.

Investigator	**Q_u (J/g)**
Kubota [29]	391
Sourour [9]	297 - 347
Cuadrado [30]	293
Lem and Han [31]	411
Ng and Manas-Zloczower [23]	415
Lucas *et al.* [32]	312 - 546
Present study	316

Table 3.2 Summary of kinetic parameters obtained in the present study for unfilled promoted polyester resin in comparison with the values reported in the literature.

Model	Parameters					
	a_0	a_1	a_2	a_3	a_4	r^2
$Q_{M1} = a_0+a_1T+a_2T^2+a_3T^3$	-65.0	14.0	-0.15	3.5e-04	-	0.986
$Q_{M2} = a_0+a_1T+a_2T^2+a_3T^3$	-48.8	16.1	-0.248	-1.3e-03	-	0.992
$Q_{cal} = a_0+a_1T+a_2T^2+a_3T^3$	-12.3	10.5	-0.101	9.0e-05	-	0.967
$\alpha_{max} = a_0+a_1T+a_2T^2+a_3T^3$	-0.014	0.033	-3.0e-04	6.6e-08	-	0.980
$m = a_0+a_1T^{a2}(a_3-T)^{a4}$	0.373	1.1e-33	10.9	101	8.10	-
$n = a_0+a_1T^{a2}(a_3-T)^{a4}$	1.12	1.7e-33	8.61	133	9.44	-
$k = k_0\exp(-E_k/RT)^{\dagger}$	T ≤ 60°C: T > 60°C:	$K_0 = 2.98e09$ $K_0 = 9.83$		$E_K = 70657$ $E_K = 16544$		$r^2 = 0.996$ $r^2 = 0.987$
non-promoted polyester resin (Ref. [9]) $\dot{\alpha} = k_0\exp(-E_k/RT)\alpha^m(1-\alpha)^n$	$k_0 = 2.87e07$		$E_k = 72732$	$m = 0.33$		$n = 1.67$

† : T is in degrees Kelvin.

Table 3.3 Summary of kinetic parameters obtained in the present study for glass-fiber-filled promoted polyester resin.

Model	Parameters				
	a_0	a_1	a_2	a_3	r^2
$Q_{M1} = a_0+a_1T+a_2T^2+a_3T^3$	92.0	5.03	0.027	-9.2e-04	0.986
$Q_{M2} = a_0+a_1T+a_2T^2+a_3T^3$	70.5	8.44	-0.089	2.6e-04	0.996
$Q_{cal} = a_0+a_1T+a_2T^2+a_3T^3$	19.7	10.4	-0.1	-	0.950
$\alpha_{max} = a_0+a_1T+a_2T^2+a_3T^3$	0.554	7.0e-05	-3.2e-04	1.3e-06	0.909
$m = m_0\exp(-E_m/RT)^{\dagger}$	T ≤ 60 °C: T > 60 °C:	$m_0 = 358$ $m_0 = 0.667$	$E_m = 17479$ $E_m = 0$		$r^2 = 0.988$
$n = n_0\exp(-E_n/RT)^{\dagger}$	T ≤ 60 °C: T > 60 °C:	$n_0 = 6.88e04$ $n_0 = 2.47$	$E_n = 28.5$ $E_n = 0$		$r^2 = 0.996$
$k = k_0\exp(-E_k/RT)^{\dagger}$	T ≤ 46 °C: T > 46 °C:	$k_0 = 2.39e09$ $k_0 = 1.08e12$	$E_k = 71232$ $E_k = 87451$		$r^2 = 0.996$ $r^2 = 0.998$

† : T is in degrees Kelvin.

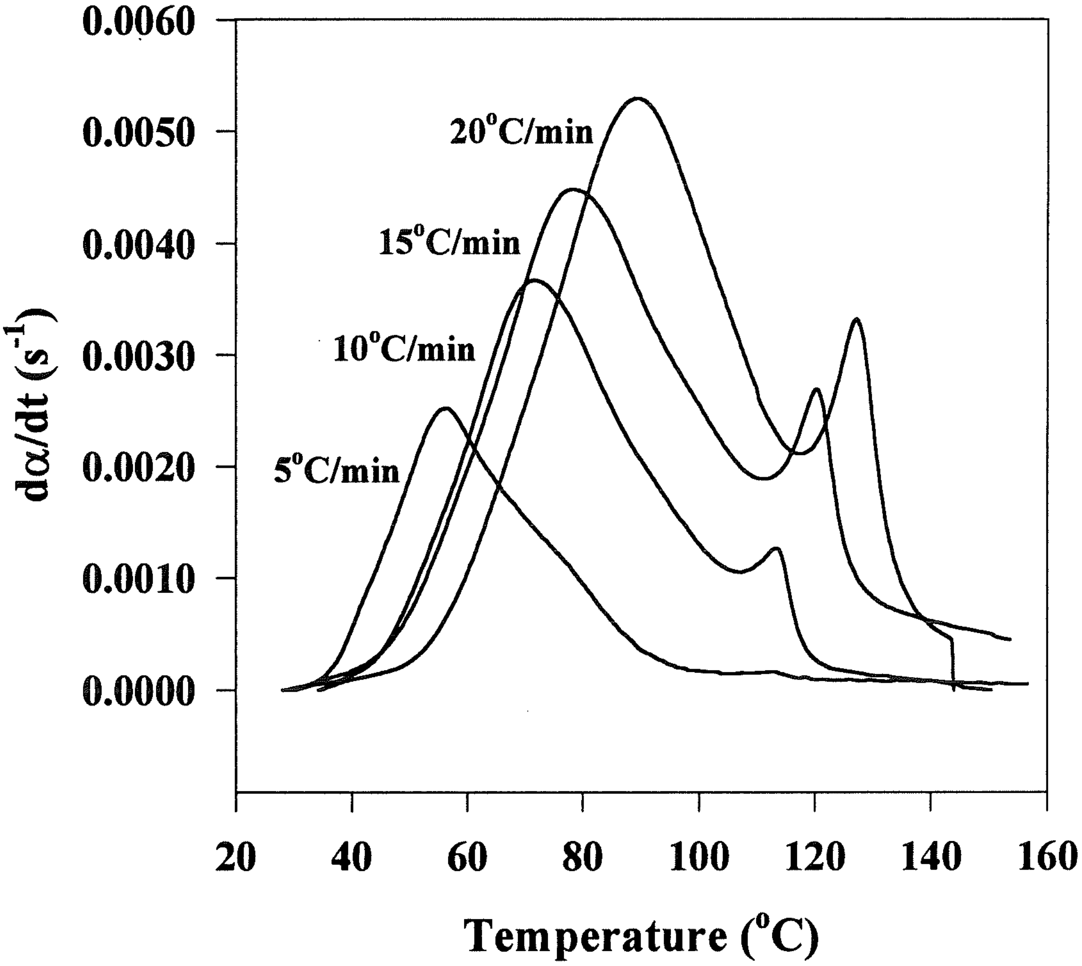

Fig. 3.1 Variation of conversion rate as a function of temperature at different heating rates obtained in dynamic DSC measurements for the promoted polyester resin.

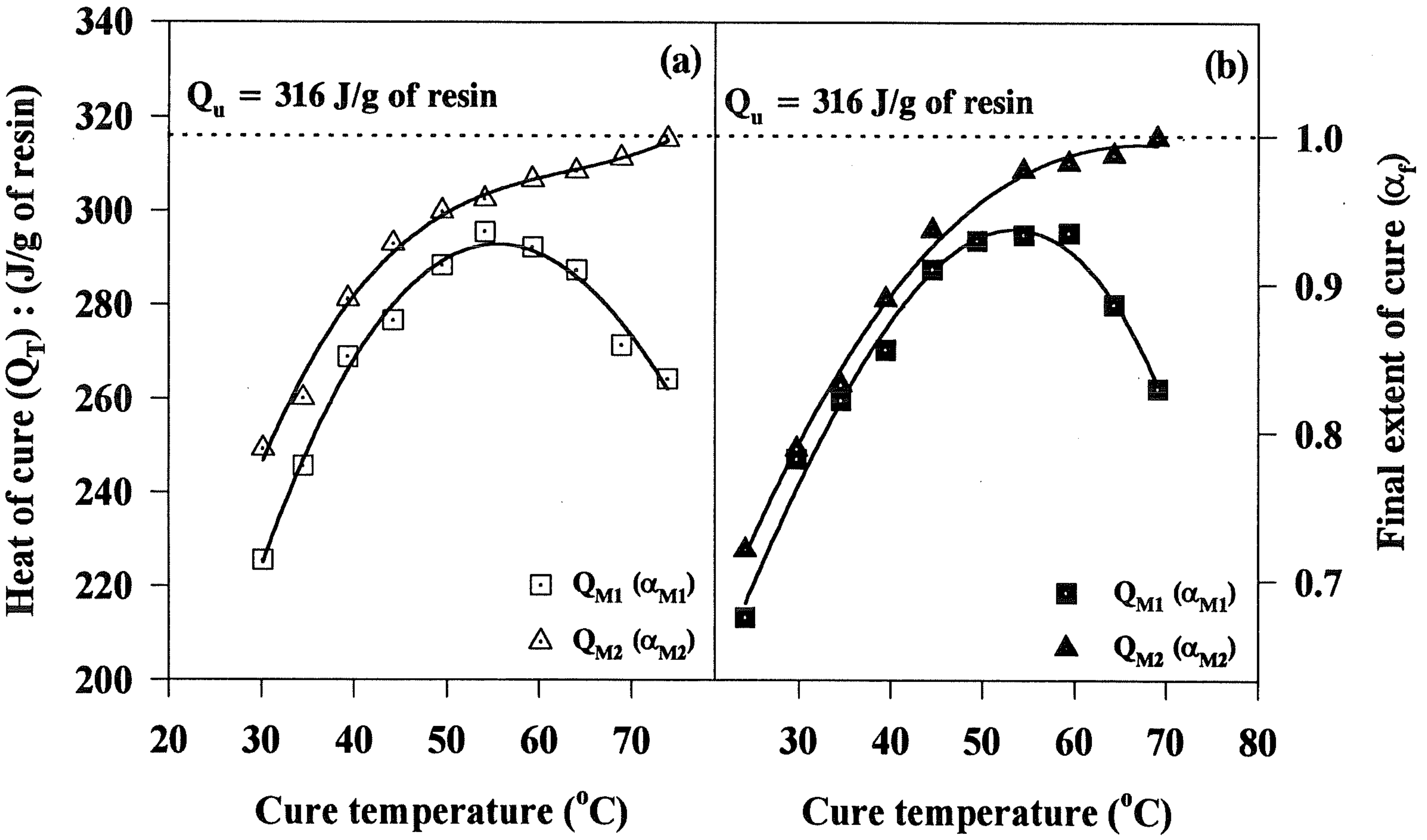

Fig. 3.2 Comparison of isothermal heat of cure and final extent of cure obtained by two different methods as a function of isothermal cure temperature for the promoted samples **(a)** without glass fibers. **(b)** with glass fibers.

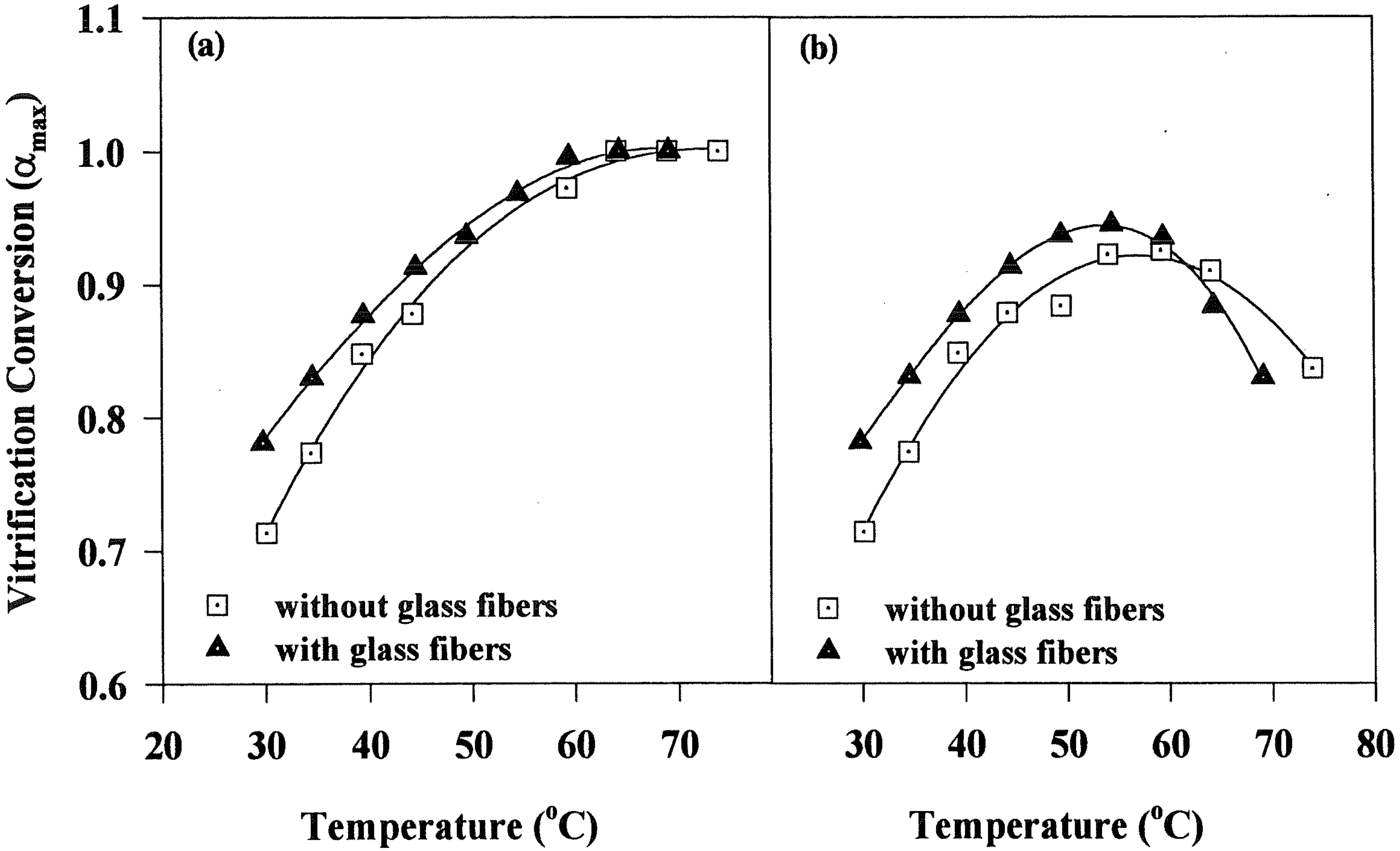

Fig. 3.3 Vitrification conversion, α_{max}, of promoted samples with and without glass fibers as a function of isothermal cure temperature estimated by:
(a) the conventional procedures. **(b)** the new procedure.

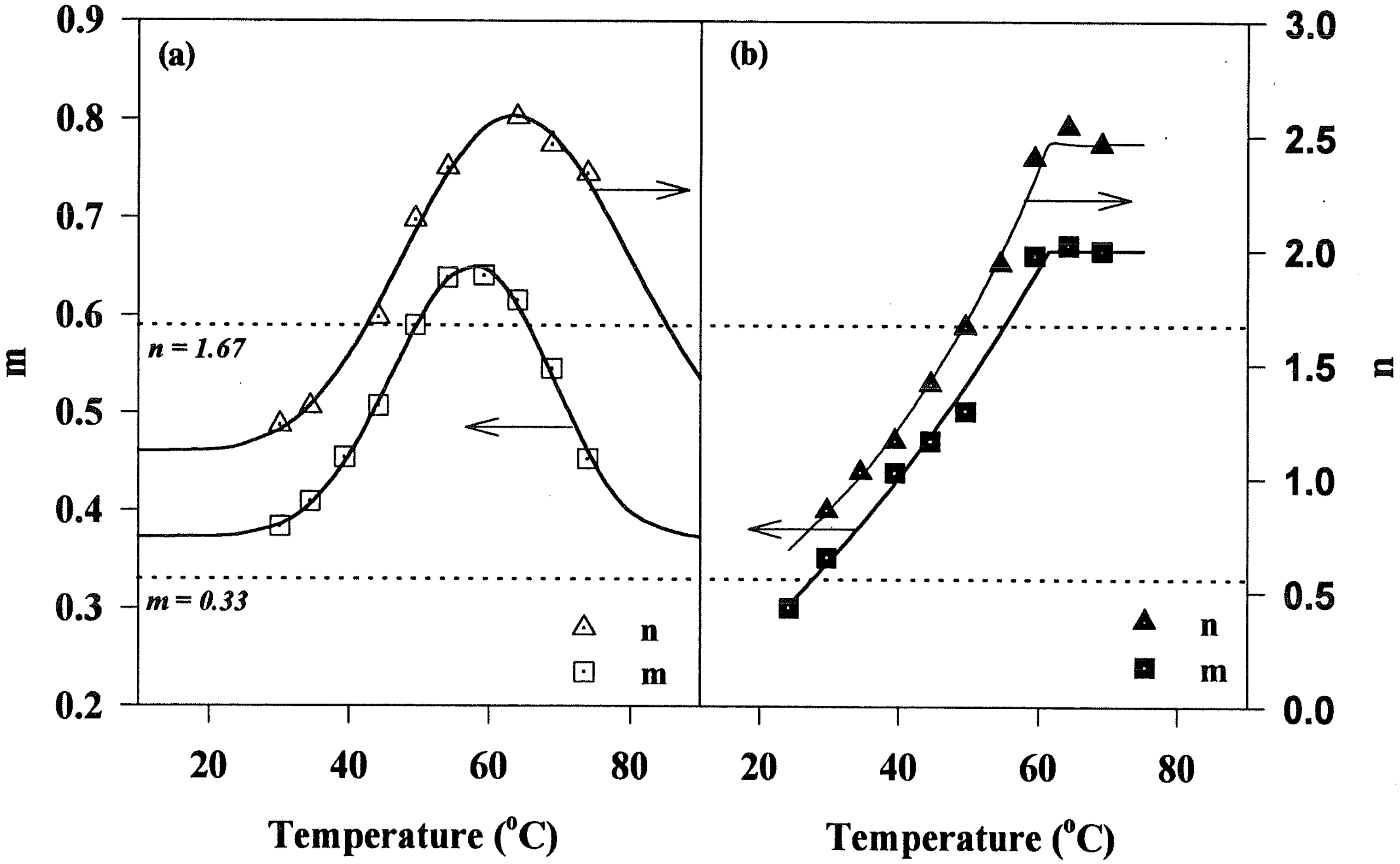

Fig. 3.4 Reaction exponents, m and n, as functions of isothermal cure temperature for the promoted samples. **(a)** without glass fibers. **(b)** with glass fibers. The dotted lines represent the exponents for nonpromoted polyesters (Ref. 9).

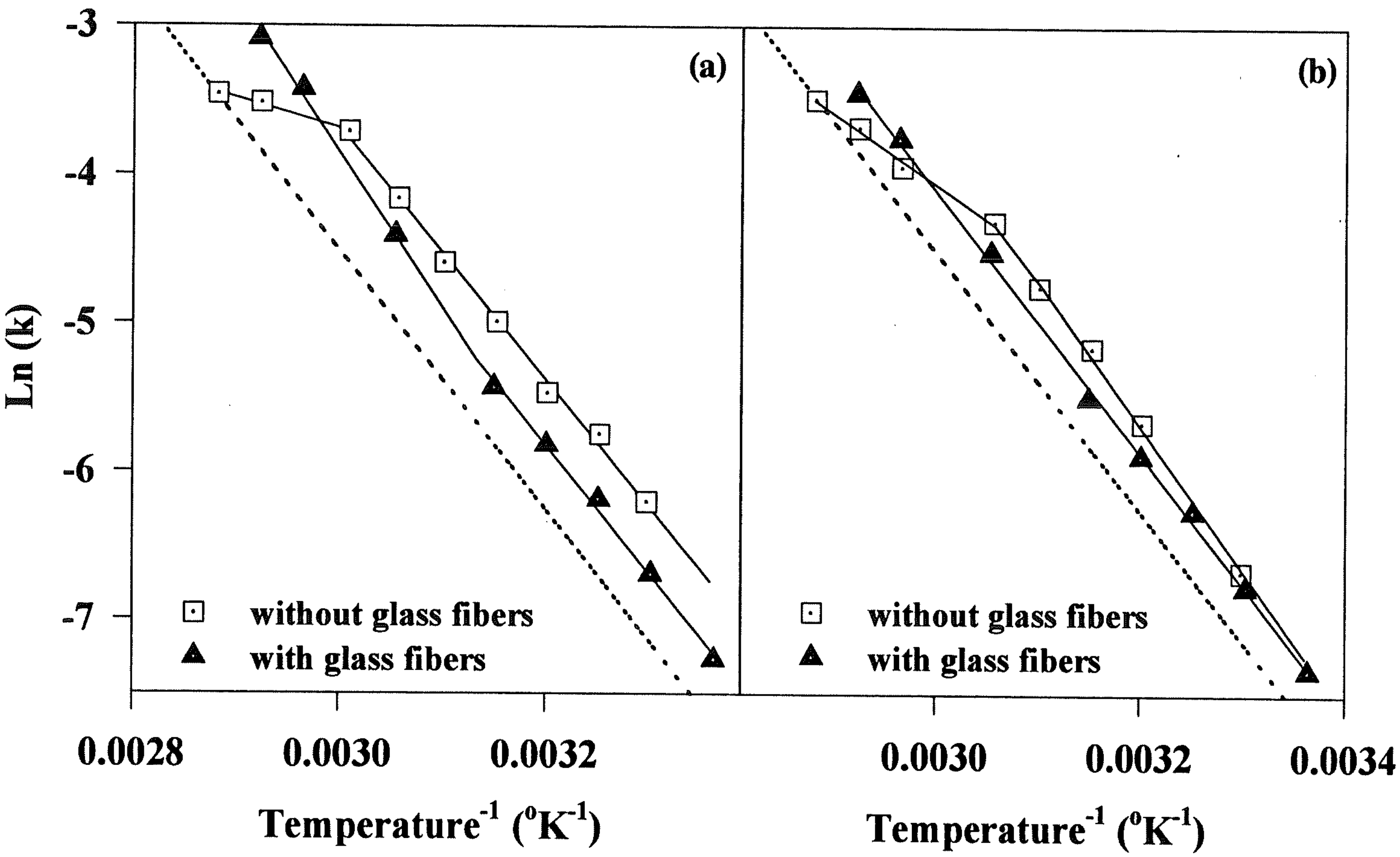

Fig. 3.5 Logarithm of kinetic rate constant, k, as a function of reciprocal absolute temperature for promoted samples without and with glass fibers estimated **(a)** by the new procedure. **(b)** by the conventional procedures.
The dotted line represents the changes of rate constant for nonpromoted polyester (Ref. 9)

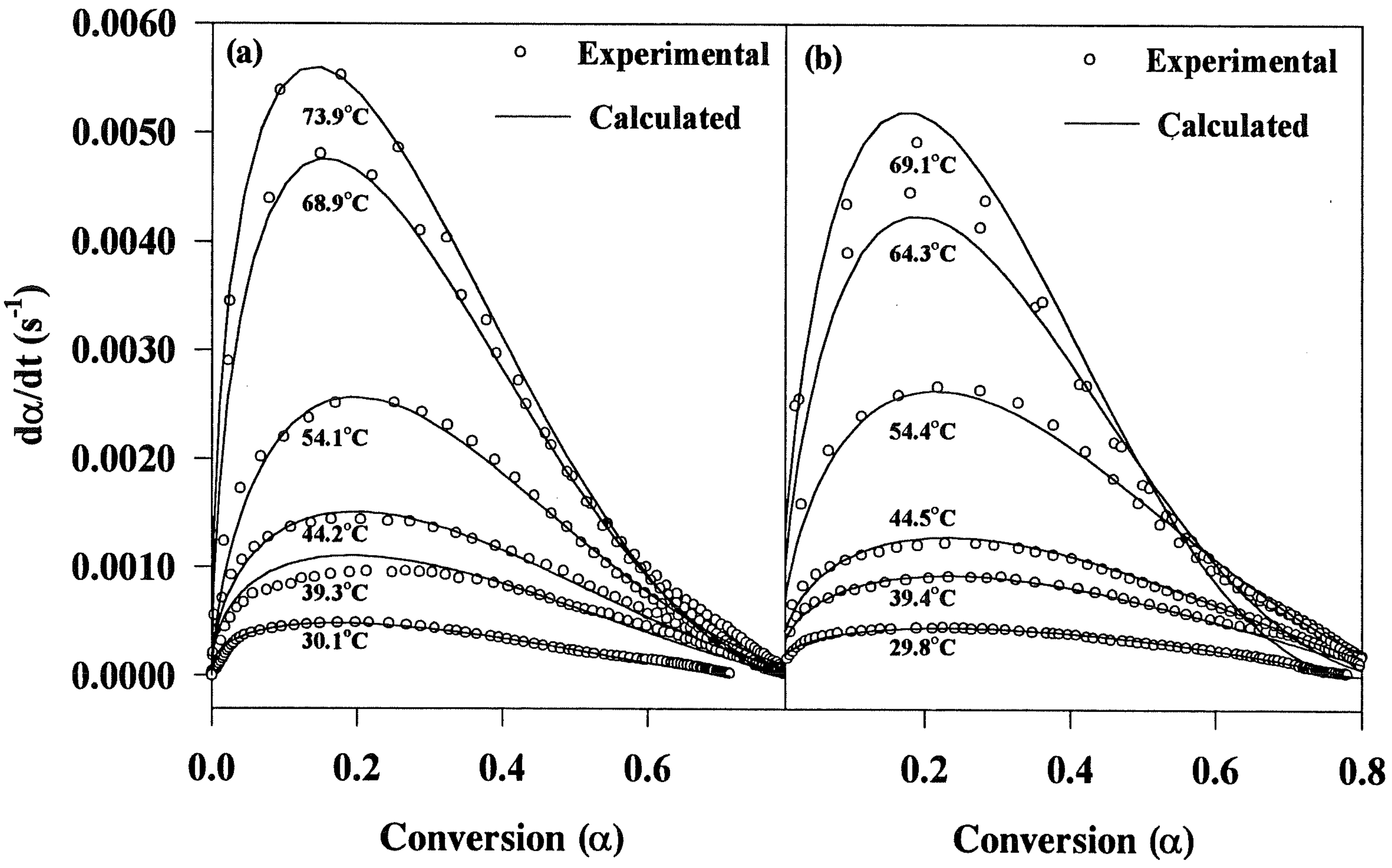

Fig. 3.6 Comparison of experimental and calculated conversion rates as a function of relative conversion for the promoted samples **(a)** without glass fibers. **(b)** with glass fibers.

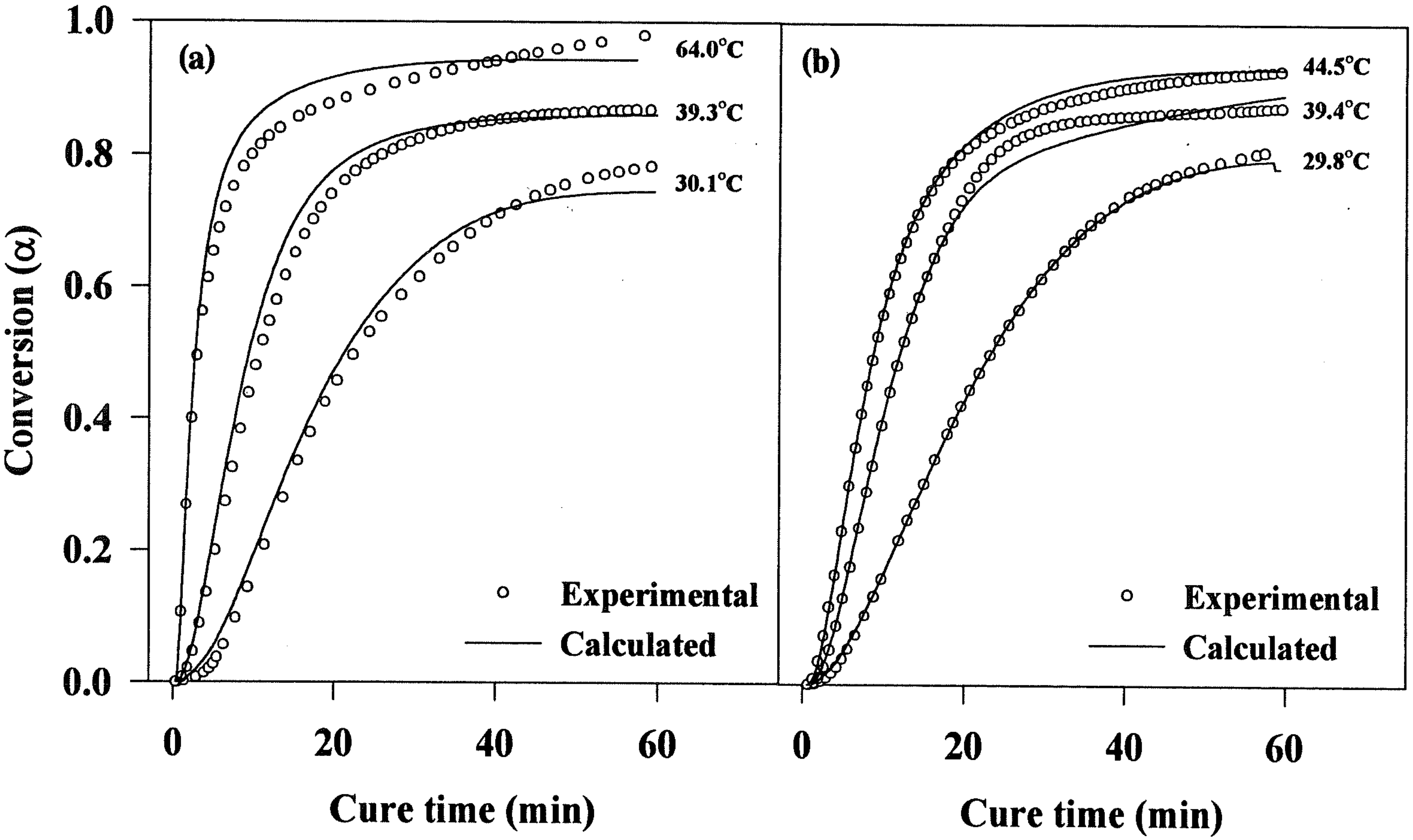

Fig. 3.7 Comparison of experimental and calculated conversions as a function of cure time for the promoted samples **(a)** without glass fibers. **(b)** with glass fibers.

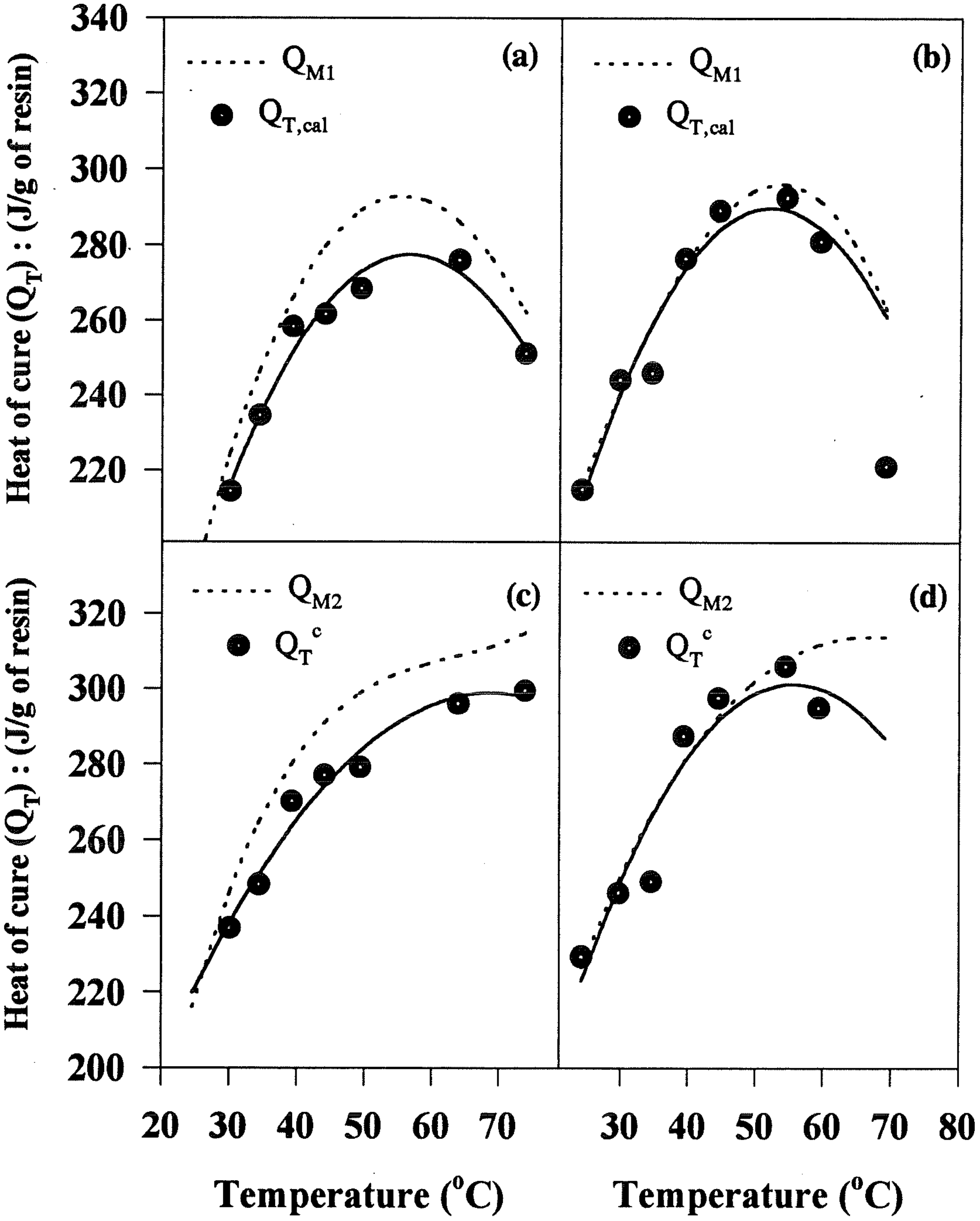

Fig. 3.8 Comparison of calculated and corrected heats of cure, $Q_{T,cal}$ and Q_T^c, with experimental results, Q_{M1} and Q_{M2}, as functions of temperature for the promoted samples;
(a & c) without glass fibers. **(b & d)** with glass fibers.

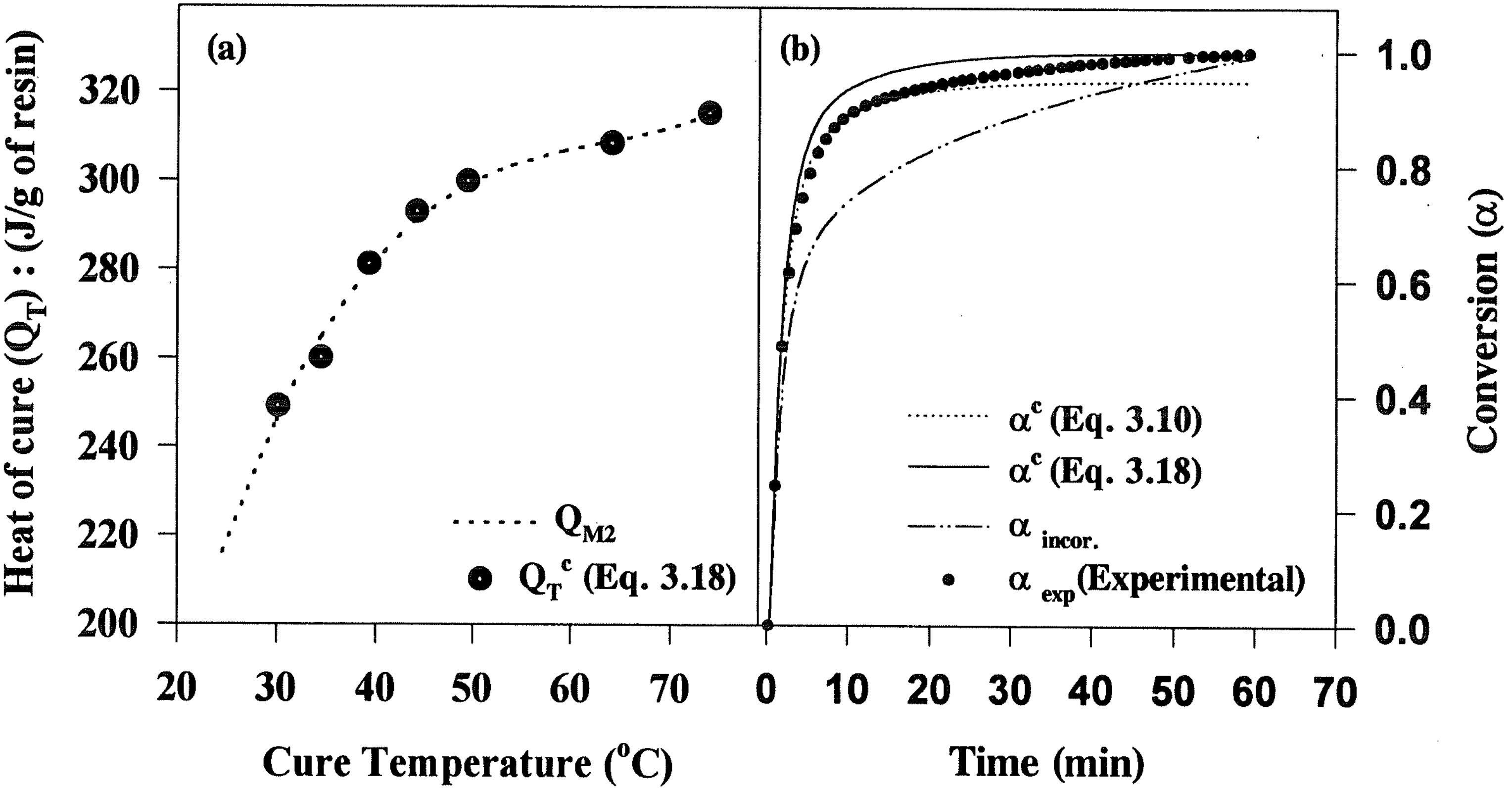

Fig. 3.9a Comparison of heats of cure corrected using Eq. 3.18 (Q_T^c) with experimental results, Q_{M2}, as a function of temperature for promoted samples without glass fibers.

Fig. 3.9b Comparison of theoretical conversions, corrected using two different correction factors, and experimental data as a function of time for a promoted sample cured at 75°C. $\alpha_{\text{incor.}}$ is the estimated conversion calculated by the conventional procedures.

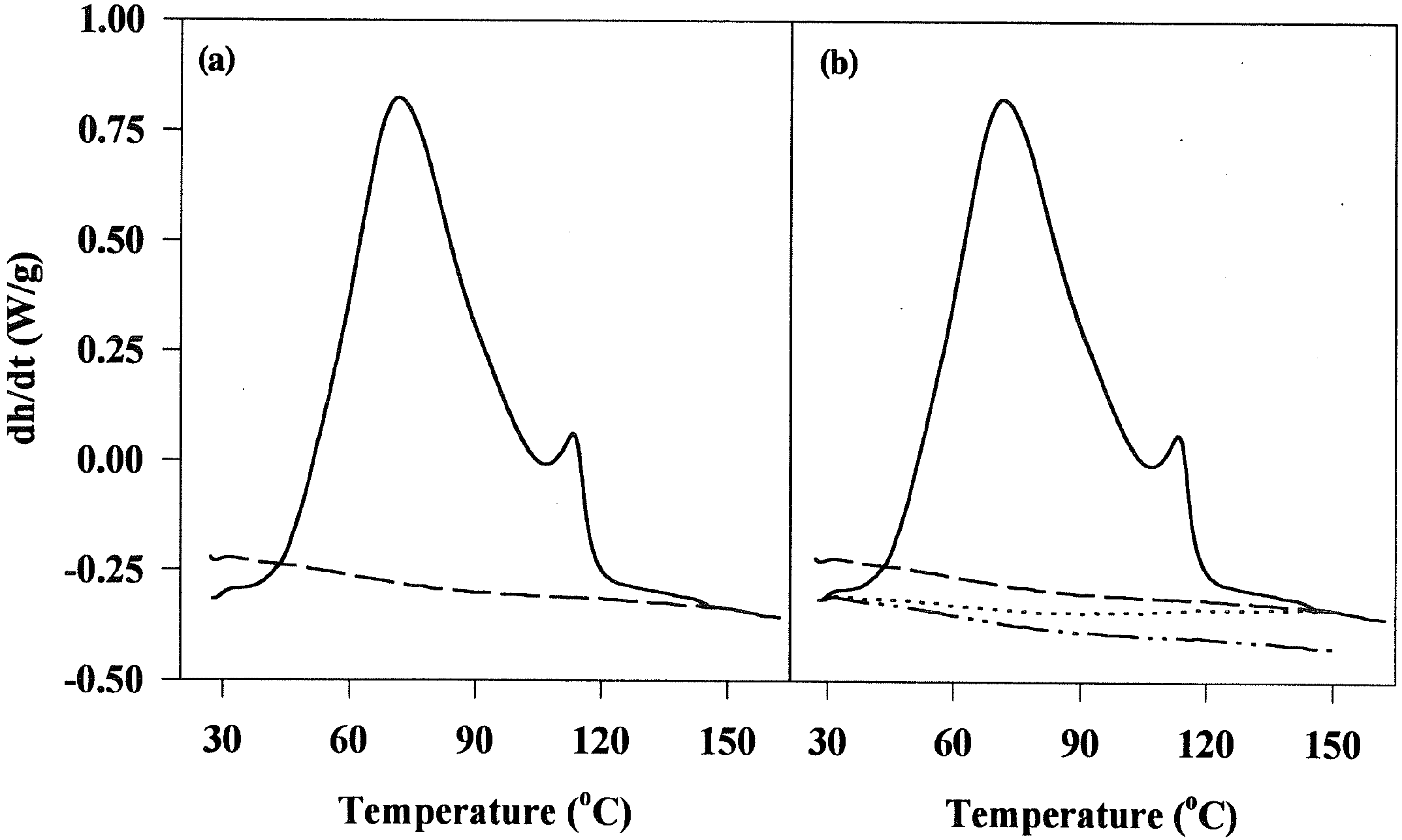

Fig. A1. Comparison of alternative baselines in dynamic DSC measurements discussed in Appendix A:

(a) —— – base line obtained by reheating a fully cured sample.

(b) - - - - - base line costructed based on the procedure recommended in Appendix A.

PRESENTATION OF CHAPTER 4

Vinylester resins are often classified with unsaturated polyesters because of curing and handling similarities. So, processors usually use these two products interchangeably in the same process with little or no process modifications. However, in the case of promoted vinylester resin a quite different curing behavior may be obtained. Chapter 4 verifies the distinctions between the cure characteristics of promoted polyester and vinylester resins with and without glass fiber reinforcement. Thus in Chapter 4, the promoted vinylester resin is treated in the same way as the promoted polyester resin in Chapter 3. That is, the cure characteristics of the vinylester resin is discussed with regard to the changes in the kinetic parameters caused by the promoter and glass fiber reinforcement. Since the modification in the curing behavior of vinylester resin caused by the promoter is too complicated, two different kinetic models are applied to the cure system in order to choose the more reliable rate equation. The results obtained in Chapter 4 indicate that the inhibition of cure caused by the oxide surfaces may yield an unexpected curing behavior in the case of promoted vinylester resin. As a consequence, the requirement of applying a specific kinetic model accounting for the inhibition effect of glass fiber reinforcement is emphasized in Chapter 4. Two sets of kinetic parameters estimated in this chapter are used in the numerical analysis of the RTM post-filling phase in Chapter 5.

CHAPTER 4

CURE ANALYSIS OF VINYLESTER RESIN IN THE PRESENCE OF A COBALT-BASED PROMOTER AND GLASS FIBERS

by

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4.1 ABSTRACT

The effects of promoter and glass fibers on the curing kinetics of vinylester resin at 25-90°C were studied by Differential Scanning Calorimetry (DSC). It was found that in the presence of a cobalt-based promoter, the kinetics of cure is too complicated to be represented by a simple autocatalytic rate equation. The major effect of promoter was a significant deviation of rate exotherms from bell-shaped profile. To take into account this deviation, a modified kinetic model with three reaction exponents was used. By fitting experimental data to the rate equation, the changes in the kinetics of cure caused by promoter was investigated. In the presence of the promoter, the vitrification conversion as well as the reaction exponents revealed temperature dependent characteristics. On the basis of experimental data, it was found that the addition of glass fibers to the cure formulation gave rise to a severe deceleration of the cure reactions. A significant decrease in the final extent of cure and ultimate heat of reaction was detected in glass fiber filled samples. The inhibiting effect of glass fibers was explained with regard to the chemical structure of vinylester resins. Rheological measurements were conducted on the promoted resin to evaluate the variation of viscosity in the course of cure reactions. A modified chemorheological model accounting for the accelerating effect of promoter was introduced.

4.2 INTRODUCTION

Vinylester resins are commercially attractive because of their toughness and chemical resistance which are generally superior to unsaturated polyesters. Vinylesters also possess some advantageous characteristics including excellent reactivity due to terminal vinyl unsaturations, improved elongation, superior acid resistance offered by the epoxy resin backbone, and better wetting and bonding to glass reinforcements [1].

Kamal and coworkers [2-5] have shown that the following rate expression is capable of representing the cure kinetics of some thermosetting resins:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \tag{4.1}$$

where:

$d\alpha/dt$	conversion rate
α	cumulative conversion at a given time t
k_1, k_2	reaction constants with Arrhenius temperature dependency
m,n	reaction exponents

Most of the commercially available resins are pre-promoted with a variety of promoters for room-temperature cure processing. In general, for some promoted cure systems an ordinary autocatalytic model, *e.g.* Eq. 4.1, is not adequate to represent the whole cure process. Composites manufactured by Resin Transfer Molding (RTM) process are often cured at low temperatures that can give rise to partial conversion due to the vitrification phenomenon [6]. On the other hand, the cure exotherm of some promoted systems deviates from bell-shaped profile. To overcome these deficiencies, Eq. 4.1 was modified [6,7]:

$$\frac{d\alpha}{dt} = k\alpha^{m}(\alpha_{\max} - \alpha)^{n}(1 - \alpha)^{p} \tag{4.2}$$

where p is a third reaction exponent and α_{max} is the maximum conversion (or vitrification conversion) at a given isothermal cure temperature. The modified rate expression in Eq. 4.2 accounts for both partial conversion, through α_{max}, and deviation of the cure exotherm from bell-shaped profile by including a third term, $(1-\alpha)^{p}$, in the rate expression.

A variety of fillers are generally used in cure systems to improve the curing shrinkage, hardness, modulus, and to decrease the peak exotherm by acting as heat sinks. Since unreinforced cure formulations offer only moderate physical properties, outstanding physical properties including good toughness and impact quality can be achieved by incorporation of high strength reinforcements. Glass fiber is one of the mostly used reinforcements in polymer composites. Since in certain low temperature cure systems glass fibers may cause a severe inhibition of the cure reactions [8], a good understanding of the cure kinetics is an essential prerequisite in process optimization of composites.

Extensive research has been devoted to the effect of various factors on cure characteristics of unsaturated polyester resins in the literature [9-14]. However, a limited number of researches have discussed the curing behavior of vinylester resins in the presence of additives. It is reported that promoting agents can considerably increase the reaction rate of cure systems [15]. Lee and Lee [16] presented the variation of glass transition temperature *versus* degree of conversion for the cure system of vinylester resin. The inflection point observed in the glass transition temperature was considered as the gel point of the cure system. Consequently, two sets of kinetic parameters corresponding to the cure mechanism before and after gelation were estimated. It was also indicated that the glass transition temperature of the fully cured samples is identical regardless of the isothermal cure condition. According to Salla and Ramis [17], the effect of promoter is more pronounced at the start of cure. In spite of the fact that a unique value is generally assigned to the activation energy of cure at a constant cure temperature, Salla and Ramis [17] estimated different activation energies for the entire cure period. The lower activation energy estimated at the start of cure was attributed to the effectiveness of promoter in increasing the rate of reaction. Lem and Han [18] estimated the kinetic parameters of pure polyester and vinylester resins and their promoted formulations by assuming an overall reaction exponent equal to 2. They applied the estimation technique proposed by Ryan and Dutta [19] for rapid evaluation of kinetic parameters from isothermal cure exotherms. A rate expression proposed in the literature [20] was used in their work to theoretically predict the cure rate for the non-isothermal cure process [18]. The discrepancy between theoretical and experimental rate data was significant in the case of promoted vinylester system. Huang and Lee [21] investigated the effects of temperature, initiator and promoter on the curing kinetics of unsaturated polyester resins. On the basis of a microgel kinetic model, it was reported that increasing the promoter concentration caused a higher conversion of polyester vinylene over styrene conversion from the beginning of the cure reaction up to a point beyond the start of diffusion-controlled step. It was also indicated that an increase in the promoter concentration yielded a sharper cure exotherm profile, and a slight increase in the final extent of cure. Mohand and Grentzer [6] applied Eq. 4.2 to the cure system of promoted vinylester resin and estimated the kinetic parameters of the rate equation using nonlinear least squares regression. The reaction exponent, m, and vitrification conversion, α_{max}, were made temperature dependent to account for the complexity of cure reactions. Lucas and coworkers [22] reported a decrease in the induction period of the styrene/polyester system cured in the presence of $CaCO_3$ as a filler. This event was attributed to the preferential adsorption of inhibitors, including dissolved oxygen, in the filler-rich phase. Yousefi and coworkers [23] studied the individual effects of a cobalt-based promoter and glass fibers on the curing behavior of an unsaturated polyester resin. A significant increase in the reaction rate constant was reported due to the presence of the promoter. It was also demonstrated that the incorporation of glass fibers in the cure system of promoted polyester resins gave rise to a slight deceleration of reaction rate at low temperatures (below

45°C).

Viscosity is one of the most essential properties of a polymer considering its importance in polymer processing. For a fast curing resin, Gonzalez [24] applied an empirical model to express the dependency of viscosity on degree of cure:

$$\frac{\eta}{\eta_0} = (1-g)^{-f_\eta(g)} \qquad (where: \quad g = \frac{\alpha}{\alpha_g}) \tag{4.3}$$

where η_m is the monomer viscosity, α is the conversion at a given time t, α_g is the gel point conversion, and $f_\eta(g)$ is a linear function of g.

Kim and Kim [25] represented the variation of viscosity during the polymerization of unsaturated polyester resin in the following form:

$$\eta = \eta_0 \exp(\frac{a_1 + b_1 \alpha}{RT}) \exp(a_2 \alpha) \tag{4.4}$$

where a_1, b_1, and a_2 are empirical constants, and α is degree of conversion. In this model, the activation energy of flow shows a linear dependence on conversion.

This paper discusses the influence of a cobalt-based promoter and glass fibers on the curing behavior of a vinylester resin. A modified autocatalytic rate equation, Eq. 4.2, is used in the present work to account for both the partial cure at low temperatures and unusual rate profile obtained in the cure process of promoted vinylester resin. The estimation procedure developed in our previous work [23], compensating for the unrecorded part of the cure exotherm at high temperatures, is implemented to evaluate the kinetic parameters of the cure reactions. The effects of both promoter and glass fibers on the cure kinetics of vinylester resin is discussed with regard to the changes of the kinetic parameters. In the rheological study of the cure system, a modified form of Eq. 4.4 was employed to represent the variation of viscosity during the polymerization of promoted resin.

4.3 EXPERIMENTAL

A commercial vinylester resin, RCI ATLAC 31632-00 IVE, obtained from Reichold Co. was used in this study. This resin was promoted with 2 wt% of RCI 46566-00 promoter for room-temperature-cure. The reaction was initiated by 1.5% by weight of tert-butyl perbenzoate (TBPB) supplied by Aldrich Co. All the materials were employed as received without further purification.

The thermal and kinetic data were obtained using a Dupont DSC 910. The temperature and heat flow calibration of the DSC were performed by using gallium and indium as calibration standards. The effect of heating rate on the melting temperatures of gallium and indium was found negligible. It was assumed that the measured exothermic heat during the cure process comes exclusively from the consumption of double bounds in the propagation step of cure reaction. To establish the kinetic model from isothermal DSC results, it was also assumed that heat capacity of the reactants remained constant during the entire period of reaction. This assumption has been found reasonable for thermosetting resins [26].

The initiator was mixed thoroughly with the promoted vinylester resin until a homogeneous solution was obtained. The sample container was kept in a refrigerator at -20°C. Two sets of isothermal experiments were conducted to obtain the kinetic data for unfilled and filled samples. In the first set of experiments, about 5-8 mg of the sample was transferred to an empty sample pan. In the second set, chopped glass fiber was transferred to a pre-weighed sample pan containing 5-8 mg of vinylester resin. The approximate fiber content was about 10-15 wt%. For all experiments, a dry nitrogen supply was used to purge the existing oxygen and moisture in the sample holder. An empty pan with an equivalent weight of that of the sample pan was used as the reference. The data acquisition system was started, and the sample was introduced into the DSC cell. Rate of heat generation, $\dot{Q}$, was recorded as a function of time. The reaction was considered complete when the rate curve levelled off to a base line. Material losses due to monomer volatilization were negligible.

Dynamic DSC measurements were conducted at heating rates of 5, 10, 15, and 20°C/min on all promoted samples including those containing glass fibers. A second scanning run was conducted on the cured sample to determine the base line. The procedure implemented to build a precise baseline from the one obtained in the second scanning run is discussed elsewhere [22,27]. As it can be seen from dynamic rate profiles in Fig. 4.1, the peak height is increasing with increasing the heating rate. However, Fig. 4.2 shows that the total heat of reaction obtained from integration of dynamic cure exotherms decreases with increasing the heating rate. It should be mentioned that each data point in Fig. 4.2 is the average of two measurements. In this series of experiments the reproducibility was quite satisfactory.

A major difference is observed in Fig. 4.2 between the values of dynamic heat of cure obtained at different heating rates for unfilled and filled samples. This behavior is mostly attributed to the chemical structure of vinylester resin. Polyester resins filled with glass fibers generally reveal comparable heat of cure with their unfilled formulations [23]. As a consequence, in the case of polyester resins the degree of conversion is not significantly affected by addition of glass fibers. A quite different trend observed for vinylester resin reveals a significant difference between the structure and characteristics of the two aforementioned resins. In general, vinylester resins have superior reactivity over unsaturated polyesters due to terminal vinyl unsaturations. On the other hand, a better wetting and bonding to glass reinforcements due to secondary hydroxyls on the vinylester resin molecules provides a higher concentration of inorganic radicals produced in the presence of glass fibers. As pointed out by Plueddemann [8], inorganic radicals are not adequately active to start the cure reaction particularly at low temperatures. Since oxide surfaces inhibit free radical polymerization by terminating growing chains, proper surface treatments can overcome the inhibition of cure caused by electron-donor proprties of the glass fibers. It should be noted that commercial coupling agents and sizes are generally formulated for a particular cure system, and they may not be as effective for another cure formulation. We believe that the significant inhibition of cure in the case of vinylester resin is partly attributed to the sizing agent of utilized reinforcement which is formulated for polyester resins.

In Fig. 4.2, the value of the ultimate heat of reaction for 100% monomer conversion, Q_u, was obtained by extrapolating the dynamic heat of cure to zero scan speed. The values obtained for pure promoted vinylester resin and glass fibers filled promoted resin were 423 (kJ/kg of resin) and 361 (kJ/kg of resin) respectively.

To establish a kinetic model for the cure reactions, isothermal DSC experiments were performed in the range of 25-90°C. To measure the residual activity after each isothermal run, a scanning run with a heating rate of 10°C/min was performed from room temperature to 230°C. A second isothermal run was conducted to determine the isothermal baseline. The cumulative conversion was calculated as:

$$\alpha = \frac{Q}{Q_u} \tag{4.5}$$

where α is the degree of conversion at a given time t, Q is the isothermal heat generated per unit mass of the resin obtained from integration of the rate exotherm up to time t, and Q_u is the ultimate heat of reaction when 100% monomer conversion is achieved.

In the present work, two different methods were used to evaluate the total isothermal heat of cure and final degree of conversion [28]. In the first method, the following expression was used:

$$\alpha_f = \frac{Q_T}{Q_u} = \frac{Q_{M1}}{Q_u} \tag{4.6}$$

where Q_T denotes the total isothermal heat of cure obtained from direct integration of the cure exotherm, and subscript *M1* represents the first method. The second method is generally used at low cure temperatures where the rate of heat evolution is too low to be accurately detected by the calorimeter. In this method, the total isothermal heat of cure, Q_{M2} is evaluated by the following expression:

$$\alpha_f = \frac{Q_u - Q_R}{Q_u} = \frac{Q_{M2}}{Q_u} \tag{4.7}$$

here Q_u and Q_R are the ultimate heat of cure and residual heat of cure, respectively, and subscript *M2* represents the second method. For convenience, the experimental values of isothermal heat of cure (and final degree of conversion, α_f) calculated by these two methods will be referred to as Q_{M1} (α_{M1}) and Q_{M2} (α_{M2}), respectively, throughout this article. The values obtained from these methods will be compared throughout this article to evaluate the unrecorded extent of cure in the course of isothermal DSC measurements.

4.4 RESULTS AND DISCUSSION

Fig. 4.3 shows the variations of Q_{M1} and Q_{M2} as a functions of isothermal cure temperature. A significant discrepancy can be seen between the two curves obtained by different methods. At low cure temperatures, the discrepancy is attributed to the low rate of heat generation which is beyond the values detectable by DSC. At high temperatures, the values of Q_{M1} are not reliable since the extent of reaction occurring during the stabilization period of the calorimeter is significant but is not directly measurable. As it was expected (see Fig. 4.2), the values of Q_{M1} and Q_{M2} for pure promoted resin are considerably different from those obtained for glass-filled samples. The inhibition effect of glass fibers is evident in the entire temperature range of isothermal cure.

In the present work, the procedure introduced in our previous work [23] was used to estimate the kinetic parameters. The first kinetic parameter, α_{max}, was estimated by the non-linear least squares method. The resulted extimated values are given in Fig. 4.4. It can be seen that the temperature dependency of α_{max} for both unfilled and filled systems show similar trends with that of Q_{M1} in Figs. 4.3-a and 4.3-b. This similarity enables us to implement the procedure introduced in our previous work. By applying this procedure, the theoretical values of Q_T predicted by the estimated kinetic parameters would reveal the same variation with temperatures as that of Q_{M1} in Figs. 4.3-a and 4.3-b. As a consequence, the calculated isothermal enthalpy of cure and the extent of reaction may be corrected in the entire temperature range using the following expressions:

$$Q_T^c = C.Q_{T,cal} \tag{4.8}$$

$$\alpha^c = C.\alpha_{cal} \tag{4.9}$$

where, $Q_{T,cal}$ and α_{cal} represent the calculated enthalpy of cure and degree of conversion, respectively, $Q_T{}^c$ and α^c are their corresponding corrected values, and C is a correction factor. By implementing this procedure, the extent of reaction can be corrected after the estimation of the kinetic parameters without altering the original cure data.

Fig.4.4 gives the experimental cure data obtained at 80°C for promoted vinylester resin as well as the prediction of the rate profile obtained from fitting Eq. 4.1 to the cure data (dotted line). It can be seen that a significant discrepancy exists between the experimental data and the expected bell-shaped rate profile predicted by Eq. 4.1. On the basis of isothermal DSC data obtained from isothermal runs, it was found that the magnitude of this deviation strongly depends on the cure temperature. This behavior suggests that an additional kinetic parameter accounting for the deviation of cure exotherm from bell-shaped rate profile should be introduced in Eq. 4.1. Consequently, Eq. 4.2. was used in this work to predict the cure behavior of vinyl ester resin in the presence of the promoter.

The isothermal DSC data were fitted to Eq. 4.2 by the multiple nonlinear least squares method. An initial guess of zero was assigned to the third reaction exponent ($p = 0$), and the summation of two other exponents was assumed to be equal to 2 ($m+n = 2$) at the beginning of the non-linear regression. The initial guess for other parameters of Eq. 4.2 was provided by the estimation technique proposed by Keenan [29].

In Fig. 4.4, the theoretical rate profile predicted by Eq. 4.2 is compared with the experimental data (solid line). It is evident that a significant improvement in the prediction of the rate profile is attained using Eq. 4.2. However, it is worth mentioning that some difficulties arise from using Eq. 4.2 in terms of the magnitude of the estimated kinetic parameters. The limits of the reaction exponents, n and p, with cure temperature is wider than what is usually expected ($2 < n < 33$, and $-39 < p < -4$). As a consequence, the major shortcoming of this behavior is that one can not easily interpret the changes in the kinetic parameters caused by addition of additives.

In Fig. 4.5 the estimated values of α_{max} as a function of temperature are fitted to 3rd order polynomials for both unfilled and filled promoted samples. The resulting expressions are tabulated in Tables 4.1 and 4.2. Fig. 4.5 shows that the estimated values of α_{max} for pure promoted samples are significantly higher than those obtained for the glass fiber filled resin. Since this parameter approximates the conversion at vitrification, the significant difference between two curves in Fig. 4.5 implies that the cure system of vinylester resin vitrifies at low conversions in the presence of glass fibers.

Fig. 4.6 depicts the variation of the first reaction exponent, *m*, *versus* cure temperature for both unfilled and filled samples. The temperature dependency of the reaction exponent can be represented with the following equations:

$$m = a_0 + a_1 T^{a_2} (a_3 - T)^{a_4} \tag{4.10}$$

where a_0, a_1, a_2, a_3, and a_4 are adjustable parameters. In spite of the relatively complex form assigned to the reaction exponent, at elevated temperatures this expression asymptotically approaches the reaction exponent of non-promoted vinylester systems ($m = a_0 = 1.01$, see Table 4.1). Fig. 4.6 also shows that the reaction exponent, *m*, is a constant value independent of cure temperature ($m_{ave} = 0.551$) for glass fiber filled samples. This difference between unfilled and filled systems can be mainly attributed to counterbalancing of the acceleration effect caused by the promoter and the deceleration effect of glass fibers.

Figs. 4.7 and 4.8 give the changes in the reaction exponent, *n* and *p*, with cure temperature. Expressions similar to that of Eq. 4.10 can be used to fit the estimated values of the reaction exponents:

$$n = b_0 + b_1 T^{b_2} (b_3 - T)^{b_4} \tag{4.11}$$

$$p = (c_0 + c_1 T^{c_2})(c_3 - T)^{c_4} \tag{4.12}$$

where b_0 to b_4, and c_0 to c_4 are adjustable parameters. At elevated temperatures, Eqs. 4.11 and 4.12 asymptotically yield the reaction exponents of non-promoted vinylester systems ($n = b_0 = 1.86$, and $p = 0$). In Figs. 4.7 and 4.8, n and p for the filled samples shows linear dependency with cure temperature up to 60°C. However, at higher temperatures these two parameters become temperature independent.

To discuss the overall effects of the promoter and glass fibers, the summation of n and p, representing the pseudo-reaction order of the non-autocatalytic cure reactions, is illustrated in Fig. 4.9. The role of promoter in accelerating the cure rate is mostly manifested in the severe changes of $n+p$ at temperatures below 60°C. The moderate change in $n+p$ with cure temperature for glass fiber filled samples is attributed to the inhibiting effect of glass fibers which counterbalances the accelerating influence of the promoter.

Temperature dependency of reaction exponents is explained by the way a promoter affects the cure mechanism. The cure reactions in the presence of a promoter can be chemically (at low temperatures) or thermally (at high temperatures) induced. Therefore, a variable cure mechanism justifies the existence of variable kinetic parameters in different temperature ranges. It is also inferred that in the case of promoted polyester resin, kinetic parameters including reaction exponents might be considered temperature dependent to account for the complexity of the cure mechanism in the presence of a promoting agent [6].

Fig. 4.10 shows the Arrhenius plots of the reaction rate constants *versus* the reciprocal cure temperature. The rate constants in each temperature range correlate with reciprocal absolute temperature according to the following equation:

$$k = k_0 \exp(-\frac{E_k}{RT}) \tag{4.13}$$

where k_0 stands for the Arrhenius frequency factor and E_k represents the activation energy of reaction. Three temperature ranges with different activation energies can be seen in Fig. 4.10 for both filled and unfilled promoted resin. At low temperatures (below 60°C) unfilled samples show higher reaction rate constants. The complex variation of rate constant with temperature is mostly due to the complexity of cure mechanism. All kinetic parameters obtained in the present work are tabulated in Tables 4.1 and 4.2.

Fig. 4.11 gives the plots of the isothermal conversion rate *versus* extent of conversion at various temperatures for unfilled and filled systems. It can be seen that almost all experimental conversion rate data are in good agreement with the expected curves obtained from Eq. 4.2 and the estimated kinetic parameters. Good concordance is also observed in Fig. 4.12 between the corresponding extent of cure data and predicted theoretical values.

It should be noted that to verify the capability of the applied procedure in correcting the unrecorded extent of cure, it was necessary to modify the experimental data based on the isothermal entalpy values given by Eq. 4.7. So, to compare the theoretical and experimental conversions, the experimental data in Fig. 4.12 were modified in the following form:

$$\alpha^{c}_{\exp} = \frac{Q_{M2}}{Q_{M1}}.\alpha_{\exp} \tag{4.14}$$

where $\alpha^{c}_{\exp}$ stands for the corrected experimental degree of conversion at a given time *t,* and $\alpha_{\exp}$ represents the experimental degree of conversion obtained by isothermal DSC runs. The theoretical conversions were corrected using Eq. 4.9 with the following correction factor:

$$C = \frac{Q_{M2}}{Q_{M1}} \tag{4.15}$$

Figs. 4.13-a and 4.13-b give the $Q_{T,cal}$ evaluated using the estimated kinetic parameters. A fairly good agreement exists between the curves representing $Q_{T,cal}$ and experimental results, Q_{M1}. Figs. 4.13-c and 4.13-d compare the curves representing experimental enthalpy of cure, $Q_{M2,}$ with the theoretical predictions corrected using Eqs. 4.8 and 4.15. Since the success of the implemented procedure entirely depends on the precision of the estimated kinetic parameters, weak estimates can have a high impact on the precision of the predicted enthalpies of cure. As a consequence, if the agreement between the calculated and experimental values of Q_T is not satisfactory (*e.g.* at 90°C, Fig. 4.13-b), an alternative correction factor can be used to reduce the existing error:

$$C' = \frac{Q_{M2}}{Q_{T,cal}} \tag{4.16}$$

where C' is the alternative correction factor.

4.5 RHEOLOGICAL CHANGES

The rheological measurements were made with a Bohlin concentric cylinders and a Bohlin parallel plates viscometer. In the first set of experiments, the viscosity of the promoted resin without initiator was measured under isothermal conditions at different temperatures (25, 30, 35, 45°C). A set of concentric cylinders (C25-Bohlin) was used featuring a rotating cylinder (ϕ : 25 mm) located in a fixed outer cylinder (ϕ : 27.5 mm) with the sample contained in the annular gap between them. Steady shear measurements were conducted at shear rates of 0.58-58 S^{-1}. In the second set of experiments, 1.5 wt% of initiator was mixed thoroughly with the promoted vinyl ester resin to measure the variation of viscosity during the cure process. The reactive sample was injected into the gap between a rotating upper plate (ϕ : 25 mm) and a fixed lower plate (ϕ : 40 mm) equipped with side-wall to minimize the unwanted effects of cure shrinkage. Assuming that the partially cured thermoset resins exhibit Newtonian viscosity at low shear rates [27], the upper plate was rotated to give a constant shear rate of 1.16 S^{-1}.

Fig. 4.14 shows plots of viscosity *versus* shear rate at various temperatures for promoted vinylester resin without initiator. It can be seen that the mixture of vinyl ester resin and promoting agent follows a Newtonian behavior in the range of shear rates applied in these experiments. The activation energy of flow, E_η, was determined using the Arrhenius equation:

$$\eta_0(T)=k_\eta \exp\left(\frac{E_\eta}{RT}\right) \tag{4.17}$$

where η_0 is the zero shear viscosity, k_η is the frequency factor, R is the universal gas constant, and T is the absolute temperature. The estimated parameters of Eq. 4.17 are tabulated in Table 4.1.

Considering that the conversion at gel point, α_g, is a parameter independent of isothermal cure temperature [16], the value of α_g was calculated by constructing the plot of η_0/η *versus* degree of conversion. The results are shown in Fig. 4.15 for a promoted resin cured at 30°C on a parallel plates viscometer. The obtained value ($\alpha_g = 0.21$) is in a good agreement with the values reported in the literature for a non-promoted vinylester cure system ($\alpha_g = 0.15$, [16]).

Viscosity measurements on vinylester resin cured at 30°C are shown in Fig. 4.16-a. A reasonably good reproducibility can be observed between consecutive runs conducted at this cure temperature. In Fig. 4.16-b a comparison is made between the experimental viscosities and the values predicted by Eqs. 4.3 and 4.4. It can be seen that, the rate of increase in viscosity is somewhat higher than those predicted by these equations. Since it is reported that a promoter has a higher accelerating effect at the start of reaction [17], a chemorheological model featuring a single activation energy of flow within the entire range of reaction period is not adequate to represent the chemoviscosity of a promoted reactive system. In Fig. 4.16-b, the high rate of increase in viscosity of the promoted sample may be explained by the way a promoter takes part in the cure system. In general, a promoters acts by forming intermediate chemical complexes which in turn can alter the viscosity of the cure medium. So, a proper chemorheological model accounting for the effect of the promoter must be used.

Taking the approach introduced by Salla and Ramis [17], different activation energies of flow were considered throughout the entire cure period. As a consequence, Eq. 4.4 was modified in the following form to account for the effect of promoter at the start of cure:

$$\eta_r = \frac{\eta}{\eta_0} = \exp\left[\frac{(d_0 + d_1 \alpha^{d_2})}{RT}\right].\exp(d_3 x_g) \qquad (4.18)$$

$$where: \; x_g = \left(\frac{\alpha_g}{\alpha_g - \alpha}\right) \qquad (4.19)$$

here d_0 to d_3 are empirical constants, α is conversion, α_g is the conversion at gel point, η_r

is the relative viscosity, and η_0 is the viscosity of promoted resin before onset of reaction given by Eq. 4.17. In Eq. 4.18, the activation energy of flow is considered as being a conversion dependent parameter. Two sets of parameters obtained for two different regions of the cure ($\alpha < 0.07$ and $\alpha > 0.07$) are tabulated in Table 4.1. The model predictions are compared to the experimental viscosity rise in Fig. 4.17.

4.6 CONCLUSION

It was shown that for promoted vinylester resin, the mechanism of cure is too complicated to be represented by an ordinary autocatalytic kinetic model. To take into account the deviation of cure exotherm from bell-shaped profile caused by the addition of promoting agent, a modified kinetic model was used. The latter model introduced an additional rate exponent, *p*, accounting for the complexity of cure reactions. On the other hand, it was demonstrated that in spite of the good estimation of the rate profile resulted from the modified kinetic model, this model had the shortcoming of yielding unusual kinetic parameters in terms of magnitudes which are usually expected.

The estimated kinetic parameters for the cure system of promoted vinylester resin had a temperature dependent characteristic within the temperature range studied in this work (25-90°C). This characteristic was attributed to the different cure mechanisms governing in different temperature ranges. The effect of promoter was found to be more pronounced at low cure temperatures where the cure reactions are chemically induced.

By adding glass reinforcements to the cure formulation, a severe inhibiting influence on the cure of promoted vinylester resin was detected. This inhibition was mainly attributed to the superior wetting and bonding of vinylester resin molecules to glass reinforcements due to the secondary hydroxyls on the vinylester resin molecules. As a consequence, a high population of inorganic radicals produced in the reaction medium was found responsible for the lower extent of cure obtained in the presence of glass fibers. Generally, these radicals are not so active to initiate other free radicals particularly at low temperatures. It was also pointed out that a proper selection of surface treating agent can overcome the cure inhibition caused by oxide surfaces in the case of glass fiber reinforced composites. Consequently, the inhibition was also attributed to the sizing agent of the reinforcement which was formulated for polyester resins.

A modified chemorheological model accounting for the effect of promoters was introduced because a simple chemorheological model featuring a single activation energy of flow was not capable of representing the rheological behavior of promoted vinylester cure systems. Two sets of values were assigned to the rheological parameters from the onset of reaction up to the gel point. It was inferred that a chemorheological model with conversion dependent activation energy was able to represent adequately the chemoviscosity of a promoted system.

4.7 NOMENCLATURE

a_0-a_4	adjustable parameters
b_0-b_4	adjustable parameters
b_0-b_4	adjustable parameters
b_0-b_3	adjustable parameters
C, C'	a correction factors given by Eqs. 4.15 and 4.16
E_k	activation energy of the cure reactions (kJ/mol)
E_m	activation energy attributed to m (kJ/mol)
E_n	activation energy attributed to n (kJ/mol)
E_η	activation energy of flow (kJ/mol)
H	enthalpy of cure (J/g of resin)
k_0	frequency factor of the cure reactions (s^{-1})
k_1, k_2	reaction rate constants (s^{-1})
m, n	reaction exponents
m_0, n_0	frequency factors attributed to m and n
Q_{M1}	total isothermal enthalpy of cure calculated by Eq. 4.4 (J/g of resin)
Q_{M2}	total isothermal enthalpy of cure calculated by Eq. 4.5 (J/g of resin)
Q_R	residual heat of cure (J/g of resin)
Q_T, Q_{tot}	total isothermal enthalpy of cure (J/g of resin)
$Q_{T,cal}$	predicted enthalpy of cure (J/g of resin)

Q_T^c	predicted isothermal enthalpy of cure corrected by Eq. 4.8 (J/g of resin)
$Q_u, \Delta H_u$	ultimate enthalpy of cure (J/g of resin)
R	universal gas constant
t	time (s)
t_f	time representing the end of reaction (s)
T	temperature (°C, °K)
α	cumulative conversion at a given time t
α^c	degree of conversion corrected by Eqs.4.6 and 4.9
α_{exp}	experimental degree of conversion
α_{exp}^c	experimental degree of conversion corrected by Eq. 4.17
α_f	final isothermal degree of conversion
α_f	final isothermal degree of conversion
α_g	conversion at gel point
$d\alpha/dt$	conversion rate (s^{-1})
$(d\alpha/dt)^c$	conversion rate corrected by Eq. 4.7 (s^{-1})
η	viscosity of reacted resin (Pa.s)
η_0	viscosity of promoted resin before onset of reaction (Pa.s)
η_r	relative viscosity

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4.9 TABLES AND FIGURES

Table 4.1 Summary of kinetic parameters and viscometry results obtained in the present study for unfilled promoted vinylester resin in comparison with the values reported in literature.

Model	Parameters					
	a_0	a_1	a_2	a_3	a_4	r^2
$Q_{M1} = a_0+a_1T+a_2T^2+a_3T^3$	-37.9	14.2	-0.16	5.5e-04	-	0.993
$Q_{M2} = a_0+a_1T+a_2T^2+a_3T^3$	170	5.11	-0.021	-6.5e-05	-	0.999
$Q_{cal} = a_0+a_1T+a_2T^2+a_3T^3$	76.5	7.12	-0.051	-	-	0.907
$\alpha_{max} = a_0+a_1T+a_2T^2+a_3T^3$	-0.12	0.038	-4.3e-04	1.4e-06	-	0.998
$m = a_0+a_1T^{a2}(a_3-T)^{a4}$	1.01	-2.0e-33	4.15	255	11.0	-
$n = a_0+a_1T^{a2}(a_3-T)^{a4}$	1.86	3.4e-32	7.65	147	9.98	-
$p = (a_0+a_1T^{a2})(a_3-T)^{a4}$	-1.2e-14	-1.6e-23	6.30	136	7.00	-
$\eta_0 = k_\eta Exp(-E_\eta/RT)^\dagger$	25°C≤ T ≤ 45°C: K_η=1.8e-14 E_η= 80166 r^2 = 0.998					
η_r=exp($a_0+a_1\alpha^{a2}$)/RTexp(a_3x_g)† For : $\alpha < 0.07$	5750	6563	0.165	-0.054	-	-
η_r=exp($a_0+a_1\alpha^{a2}$)/RTexp(a_3x_g)† For : $\alpha > 0.07$	9572	4.7e+05	3.02	9.7e-03	-	-
$k = k_0 exp(-E_k/RT)^\dagger$	T ≤ 40°C: K_0 = 1.6e17 E_K = 109858 r^2 = 1.000 40°C < T < 53°C: K_0 = 2.0e11 E_K = 74424 r^2 = 0.998 T ≥ 53°C: K_0 = 36.5 E_K = 13673 r^2 = 0.973					
non-promoted vinylester resin (16) $\dot{\alpha} = k_0 exp(-E_k/RT)\alpha^m(\alpha_{max}-\alpha)^n$	$\alpha \le \alpha_g$: k_0 = 7.6e8 E_k = 79967 m = 0.654 n = 1.346 $\alpha > \alpha_g$: k_0 = 1.6e9 E_k = 79967 m = 0.806 n = 1.194					

† : T is in degrees Kelvin.

Table 4.2 Summary of kinetic parameters and viscometry results obtained in the present study for filled promoted vinylester resin.

Model	Parameters				
	a_0	a_1	a_2	a_3	r^2
$Q_{M1} = a_0+a_1T+a_2T^2+a_3T^3$	-20.0	11.2	-0.13	5.7e-04	0.996
$Q_{M2} = a_0+a_1T+a_2T^2+a_3T^3$	154	2.50	0.024	-3.0e-04	0.997
$Q_{cal} = a_0+a_1T+a_2T^2+a_3T^3$	191	3.92	-0.026	-	0.888
$\alpha_{max} = a_0+a_1T+a_2T^2+a_3T^3$	-5.3e-03	0.027	-3.2e-04	1.3e-06	0.909
m = Constant	$m = 0.551$ S.D = 0.015				
$n = a + b\,T$	$T \le 60°C$: $a = -3.18$ $b = 0.241$ $r^2 = 0.998$ $T > 60°C$: $a = 11.1$ $b = 0$ S.D = 0.112				
$p = a + b\,T$	$T \le 58°C$: $a = 1.46$ $b = -0.301$ $r^2 = 0.998$ $T > 58°C$: $a = -15.8$ $b = 0$ S.D = 0.129				
$k = k_0\exp(-E_k/RT)^{\dagger}$	$T \le 38°C$: $K_0 = 5.3e16$ $E_K = 107838$ $r^2 = 0.998$ $38°C < T < 60°C$: $K_0 = 3.2e8$ $E_K = 58948$ $r^2 = 1.000$ $T \ge 60°C$: $K_0 = 17654$ $E_K = 31740$ $r^2 = 0.998$				

† : T is in degrees Kelvin.

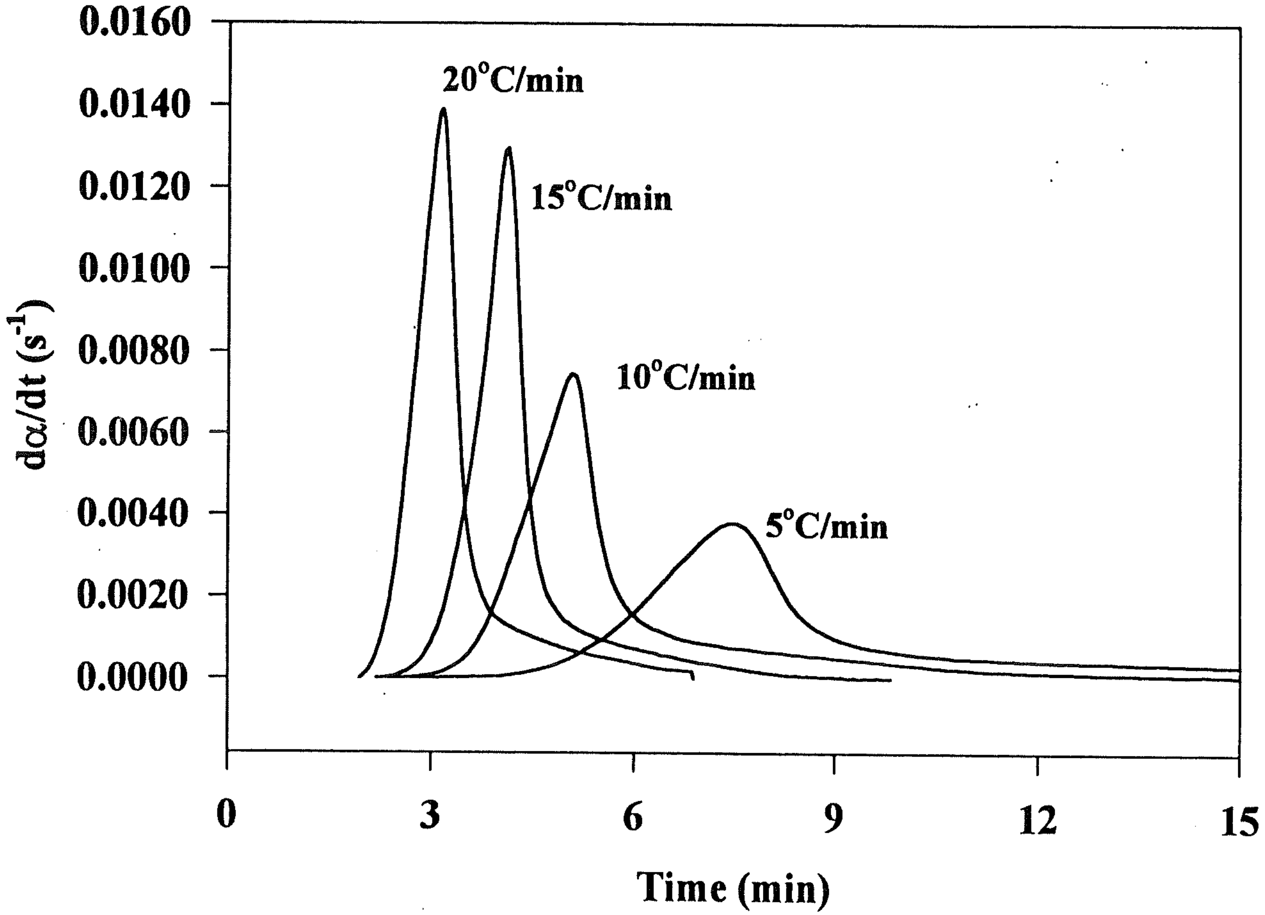

Fig. 4.1 Variation of conversion rate as a function of cure time at different heating rates obtained in dynamic DSC measurements for the promoted resin containing glass fibers.

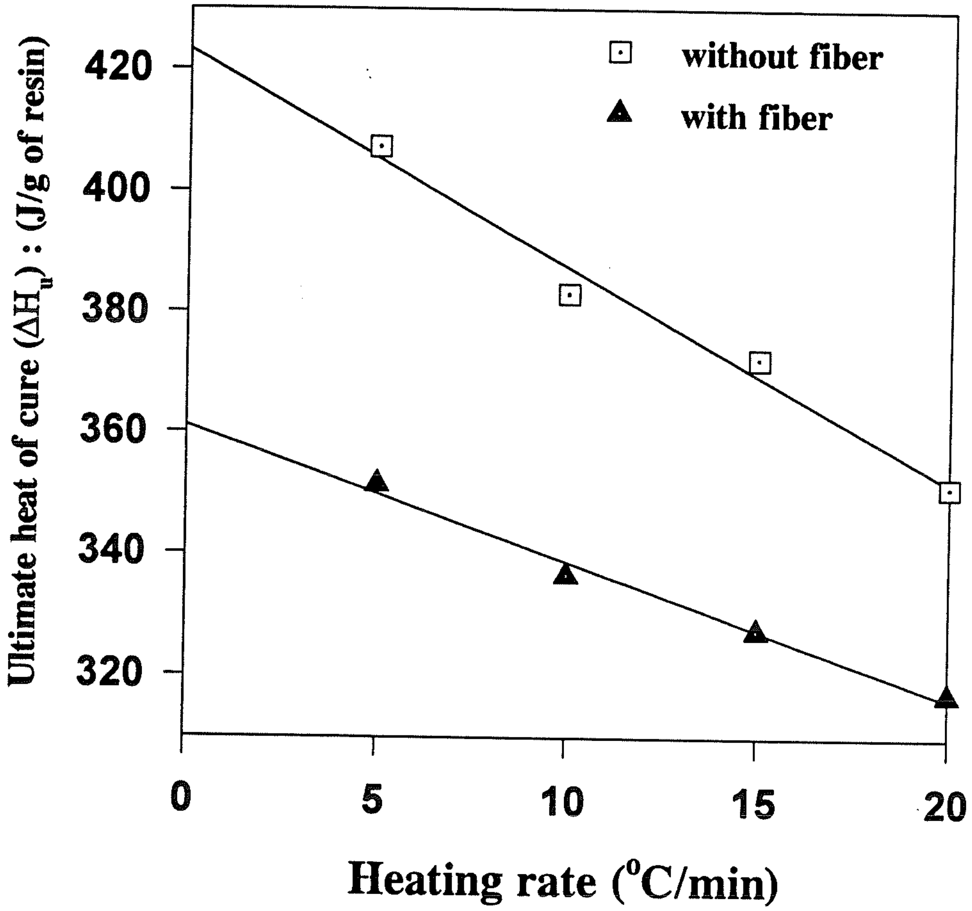

Fig. 4.2 The effect of heating rate on ultimate heat of cure for the unfilled and filled promoted vinylester resin.

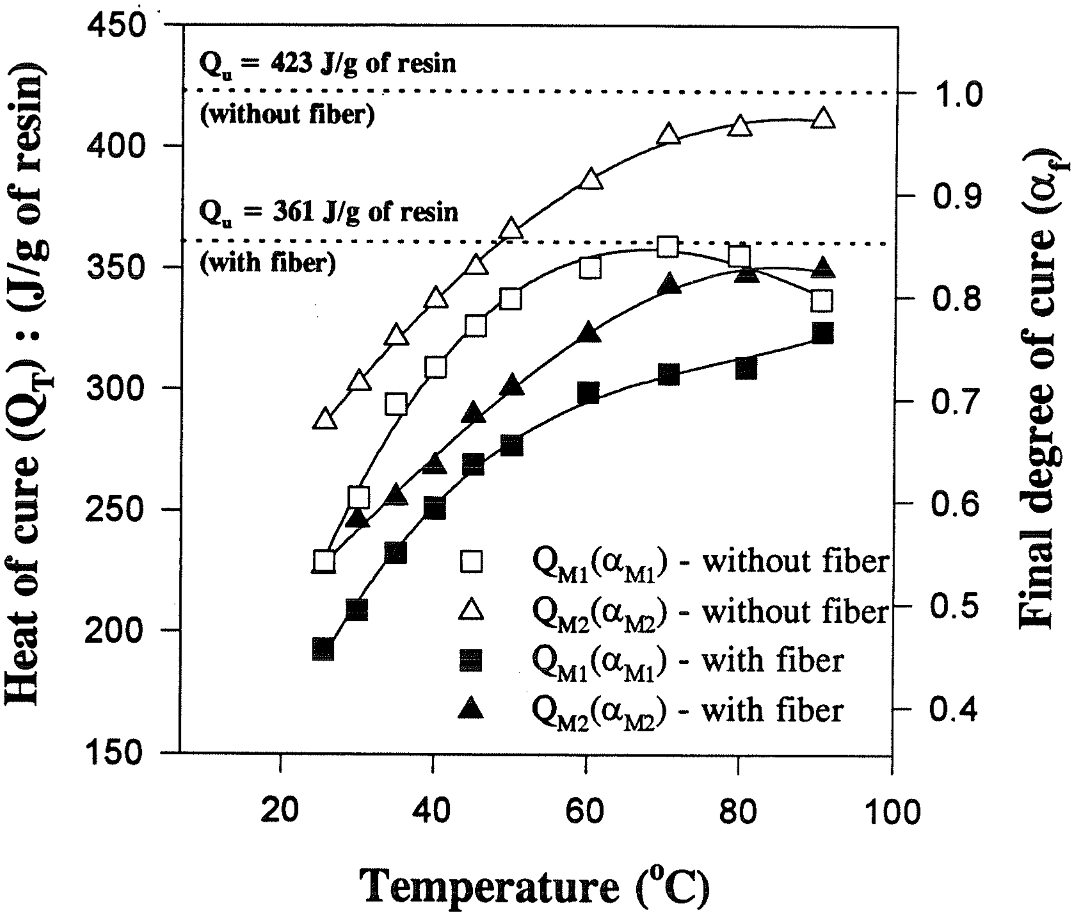

Fig. 4.3 Values of isothermal heat of cure and final degree of conversion obtained by Method 1 (Q_{M1}, α_{M1}) and Method 2 (Q_{M2}, α_{M2}) for the unfilled and filled promoted vinylester resin.

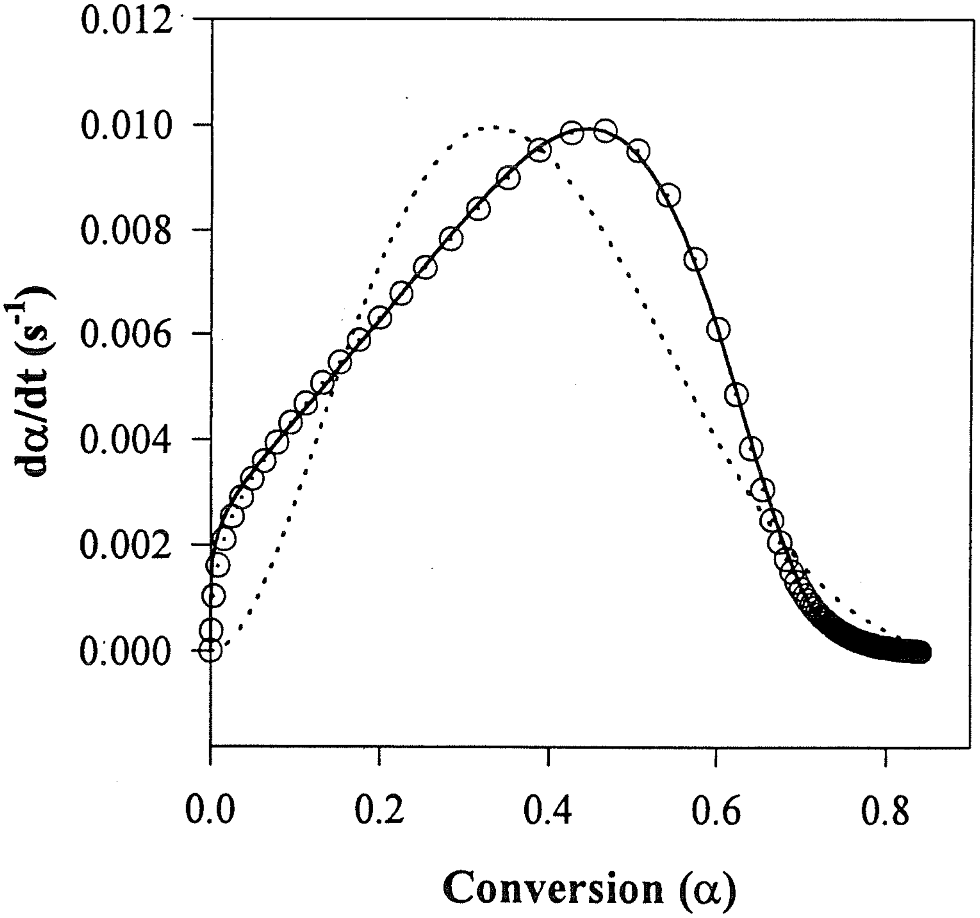

Fig. 4.4 Comparison of kinetic models with 4 and 5 kinetic parameters :

⊙ Experimental data

—— calculated by : $d\alpha/dt = k\alpha^m(\alpha_{max}-\alpha)^n(1-\alpha)^p$

····· calculated by : $d\alpha/dt = k\alpha^m(\alpha_{max}-\alpha)^n$

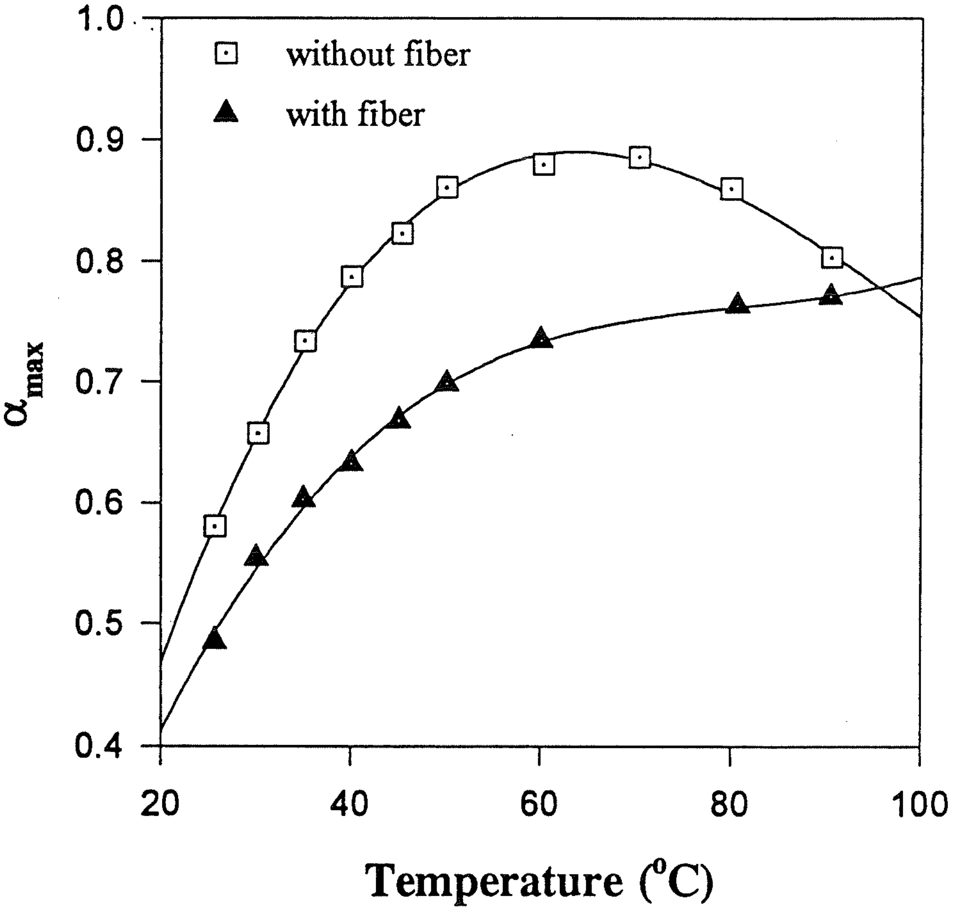

Fig. 4.5 Variation of the first kinetic patameter, α_{max}, as a function of cure temperature for the unfilled and filled promoted vinylester resin.

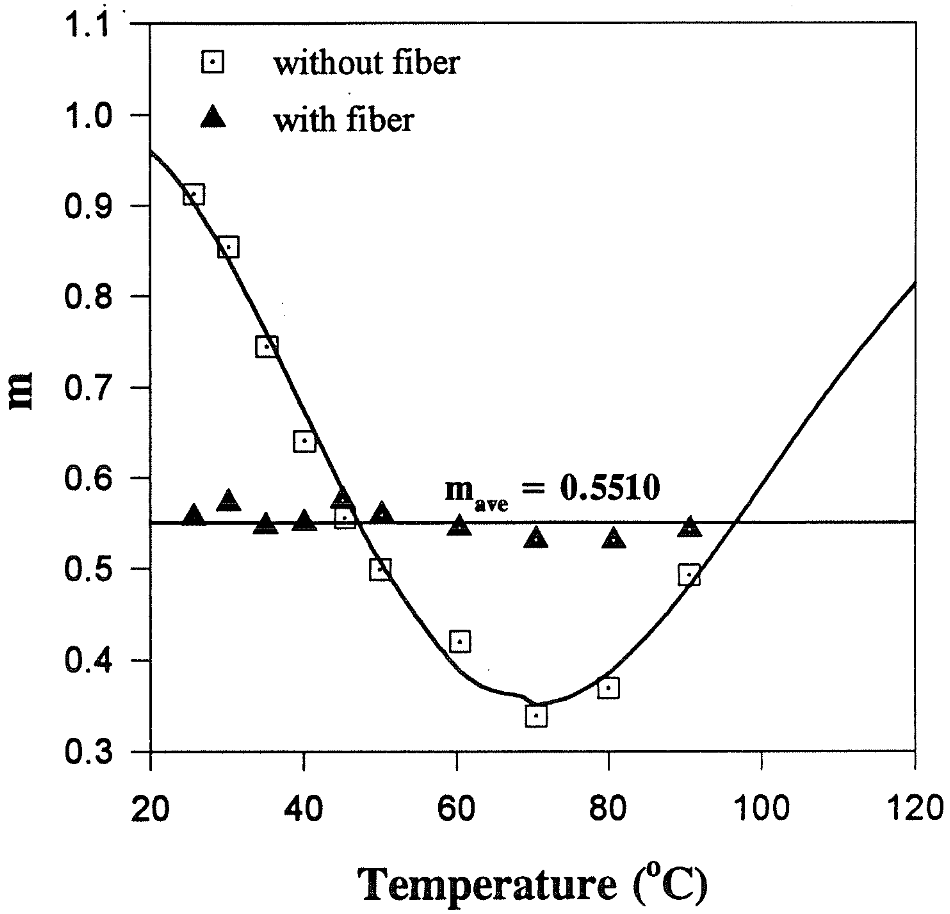

Fig. 4.6 Variation of the first reaction exponent, m, as a function of cure temperature for the unfilled and filled promoted vinylester resin.

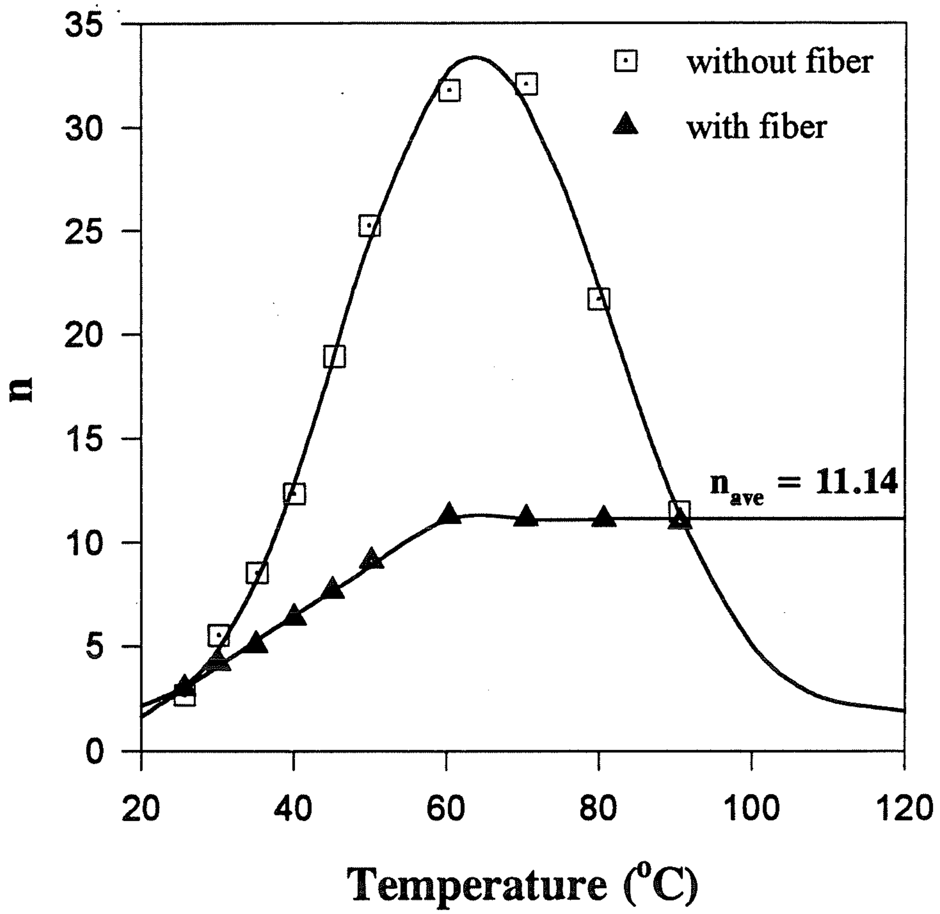

Fig. 4.7 Variation of the second reaction exponent, n, as a function of cure temperature for unfilled and filled promoted vinylester resin.

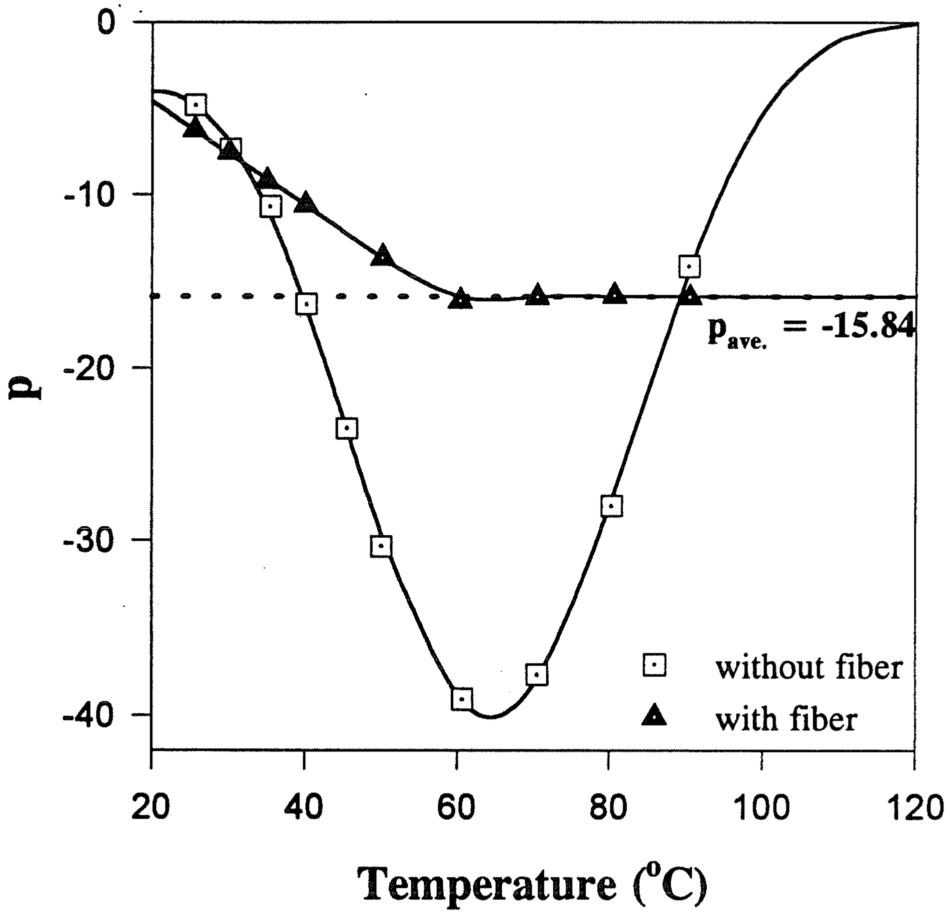

Fig. 4.8 Variation of the third reaction exponent, p, as a function of cure temperature for the unfilled and filled promoted vinylester resin.

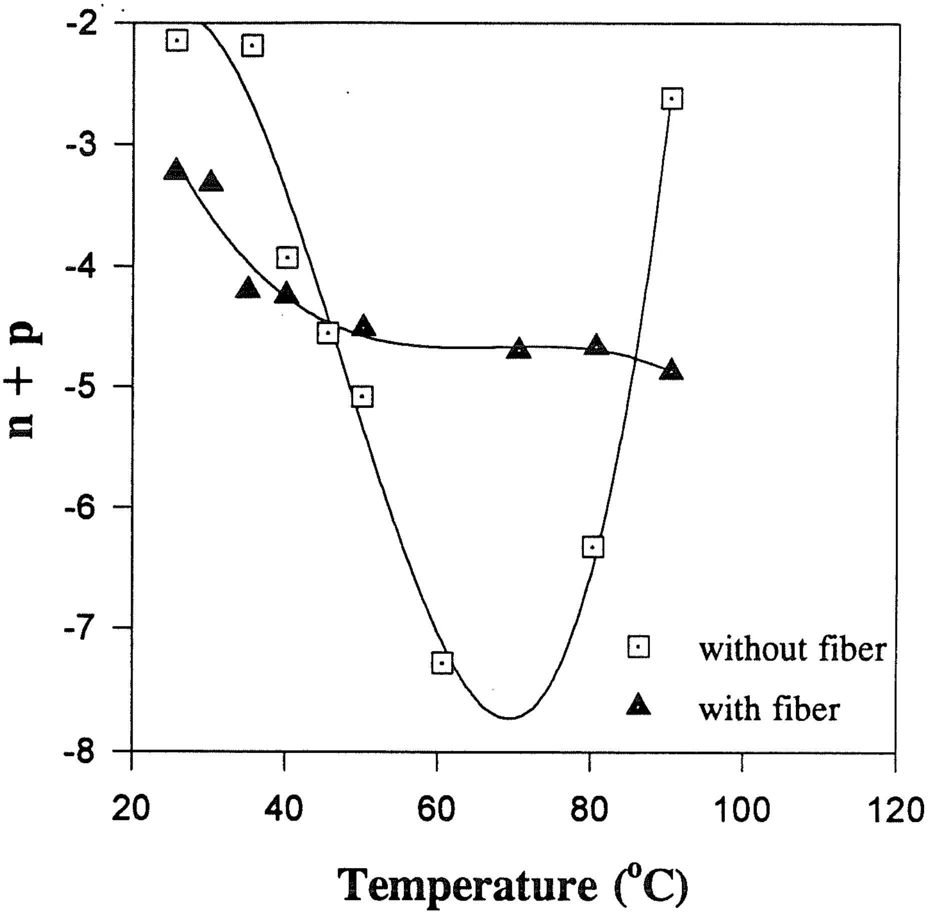

Fig. 4.9 Variation of psedo-reaction order of non-autocatalytic reactions, n+p, as a function of cure temperature for the unfilled and filled promoted vinylester resin.

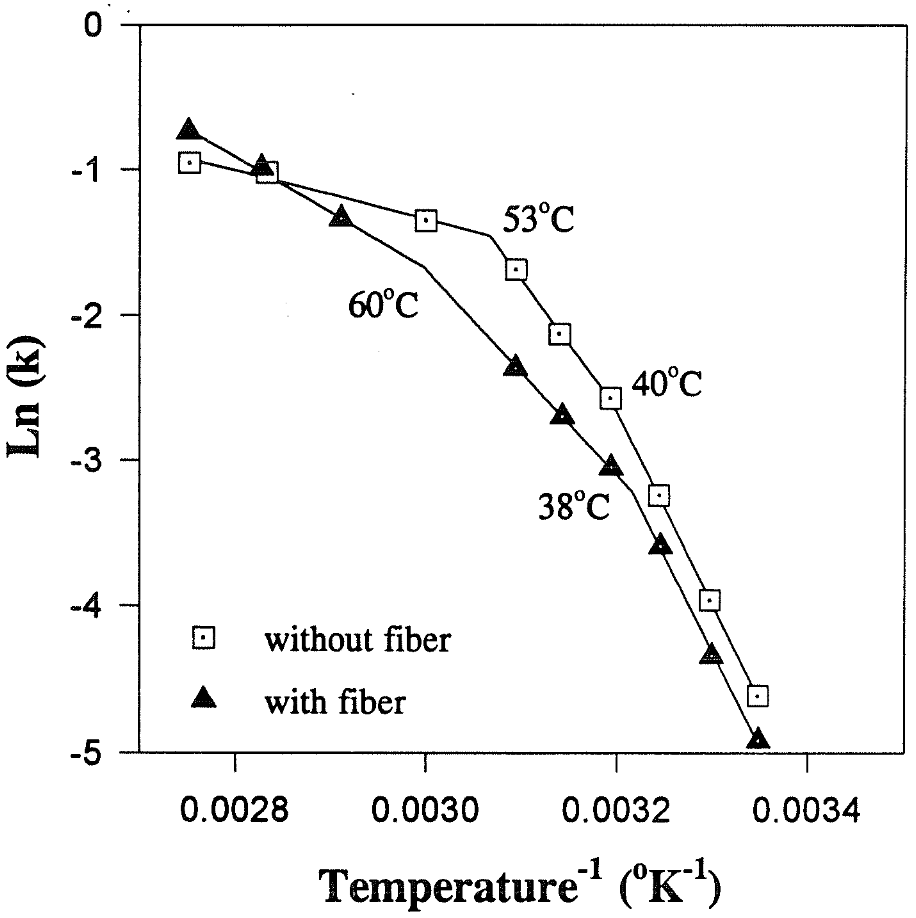

Fig. 4.10 Arrhenius plot of reaction rate constant, k, as a function of reciprocal absolute temperature for the unfilled and filled promoted vinylester resin.

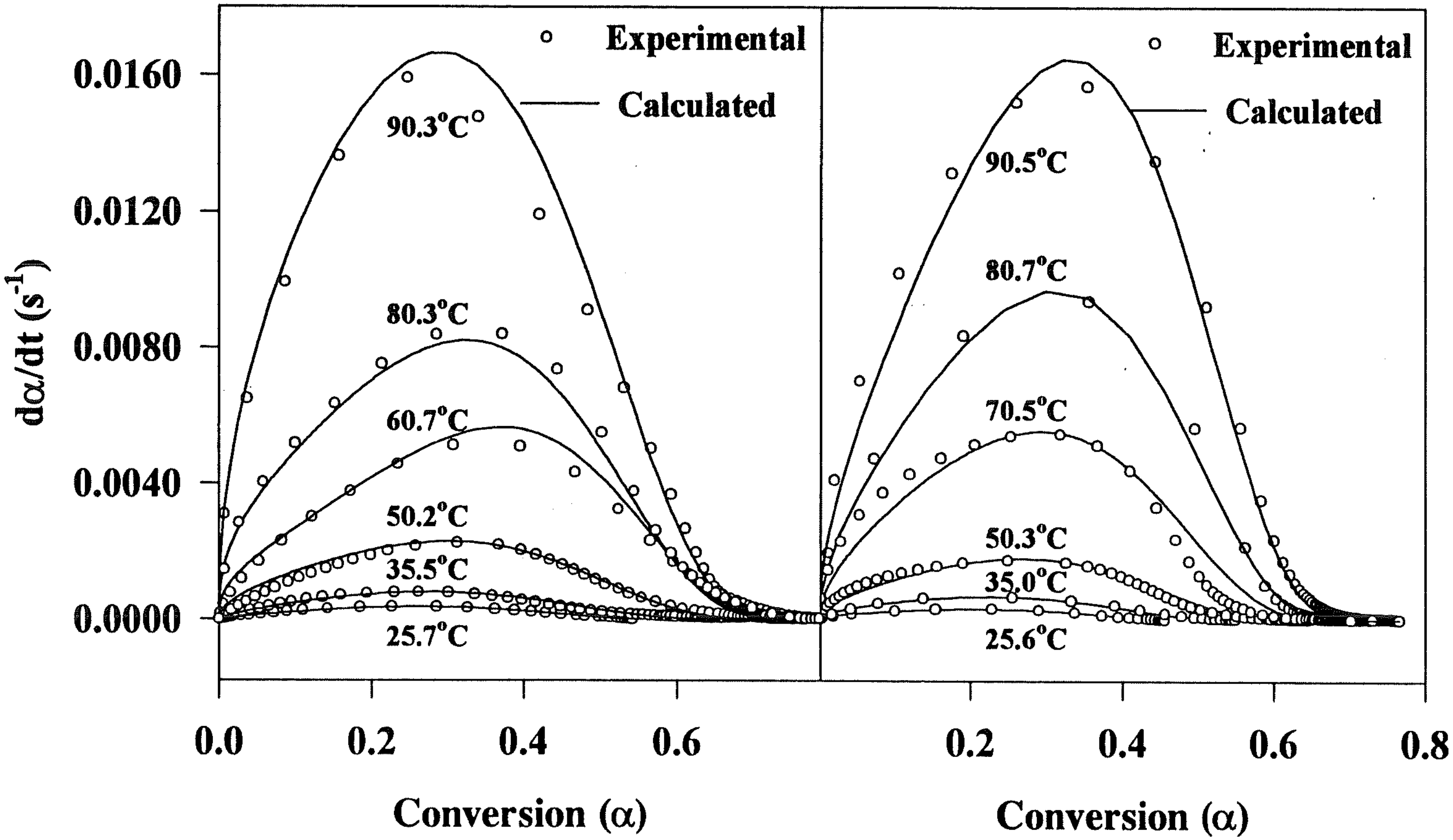

Fig. 4.11 Comparison of experimental and calculated conversion rates as a function of relative conversion for the promoted vinylester resin cured at different isothermal cure temperatures **(a)** without filler. **(b)** with filler.

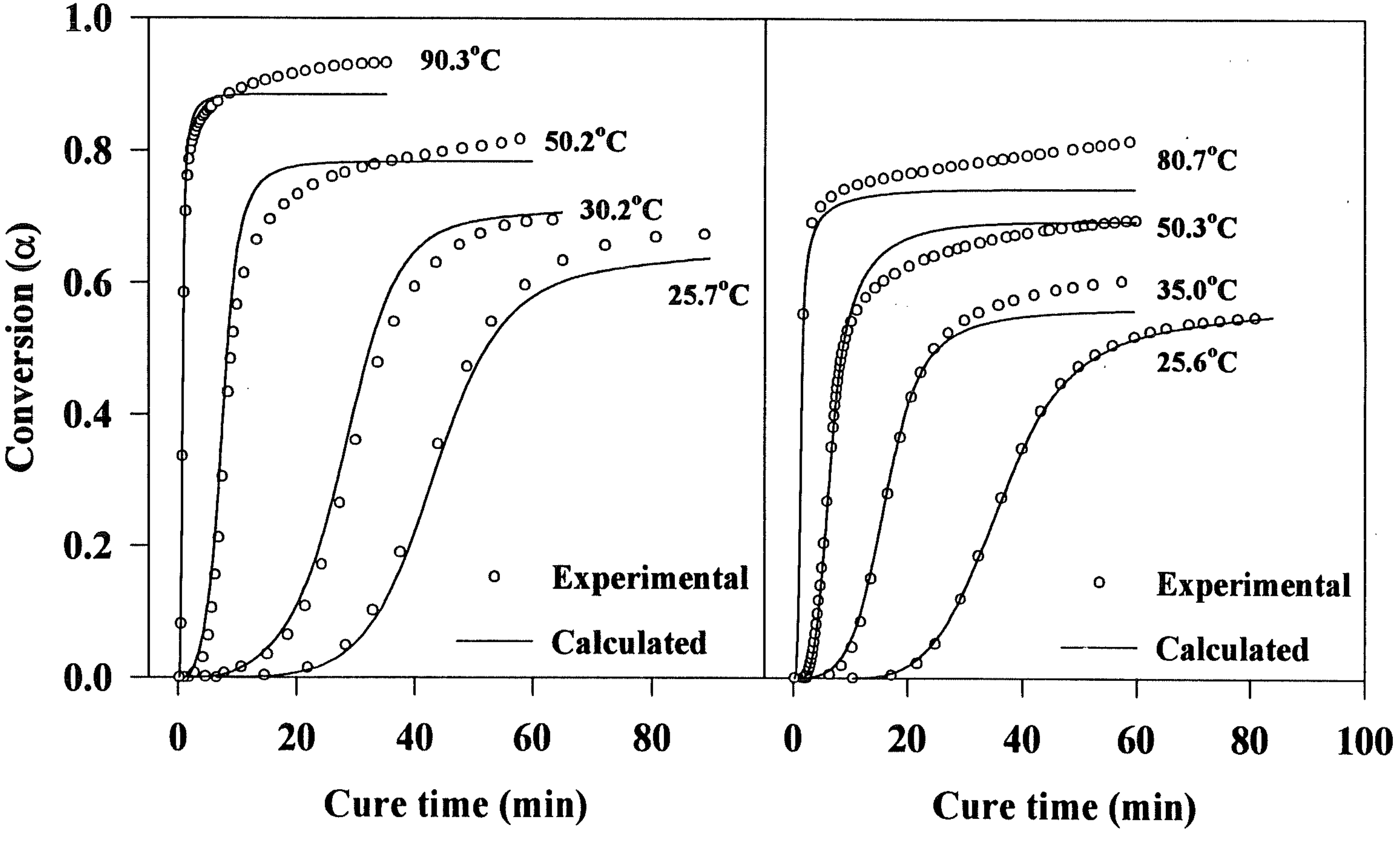

Fig. 4.12 Comparison of experimental and calculated conversions as a function of cure time for the promoted samples cured at different isothermal cure temperatures **(a)** without filler. **(b)** with filler.

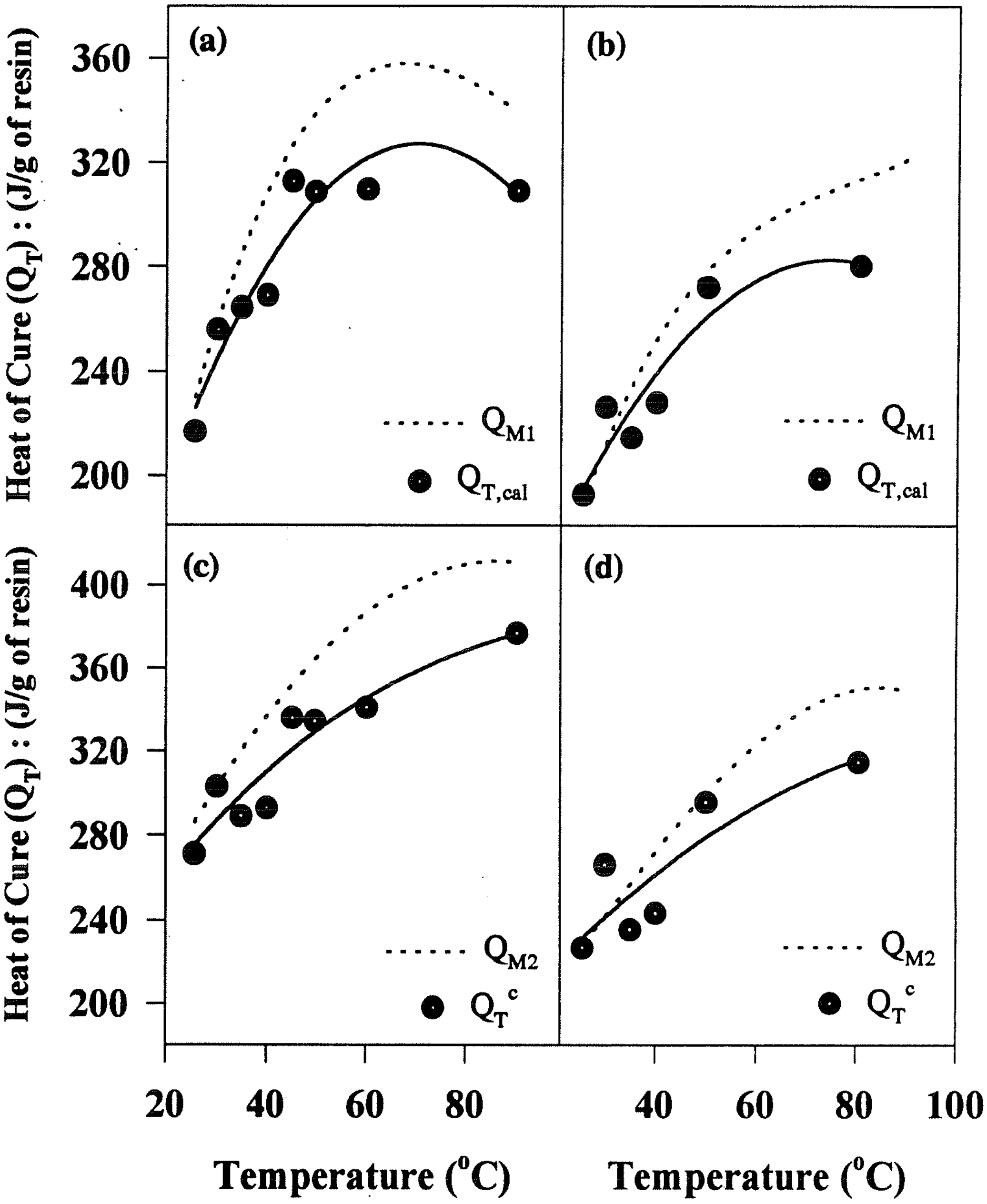

Fig. 4.13 Comparison of calculated and corrected heats of cure, $Q_{T,cal}$ and Q_T^c, with experimental results, Q_{M1} and Q_{M2}, as a function of temperature for the promoted samples **(a & c)** without filler. **(b & d)** with filler.

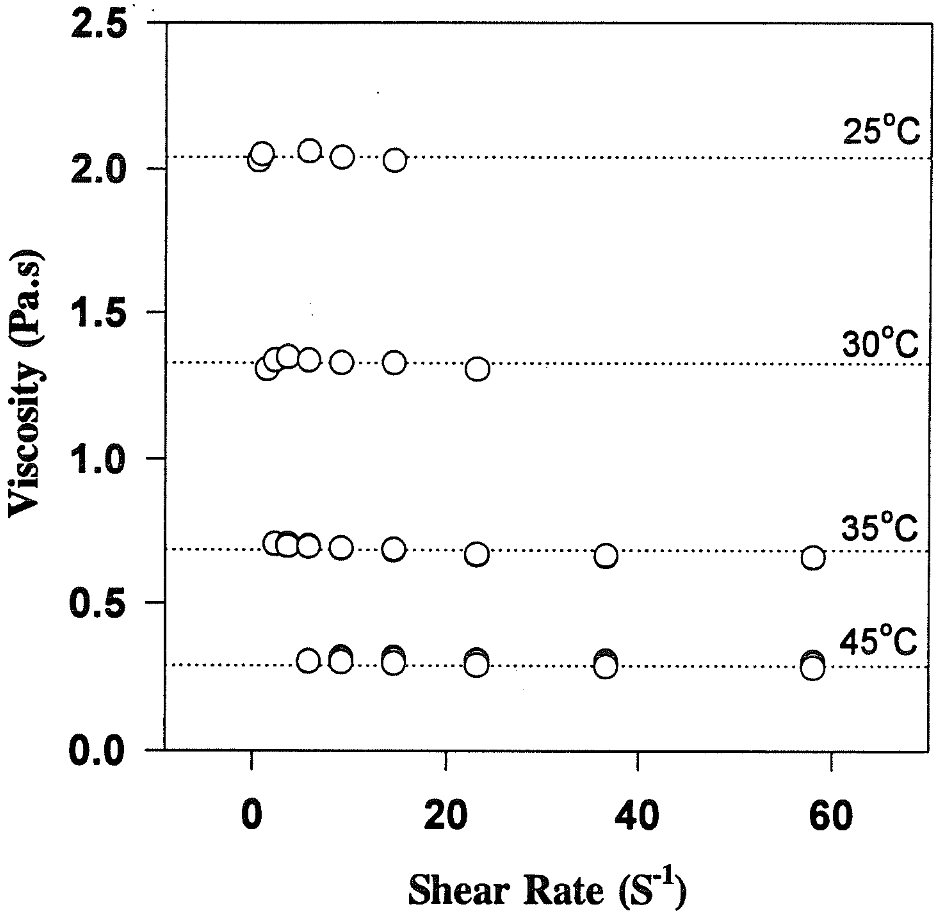

Fig. 4.14 Viscosity of the promoted vinylester resin as a function of shear rate at various temperatures obtained on a set of concentric cylinders.

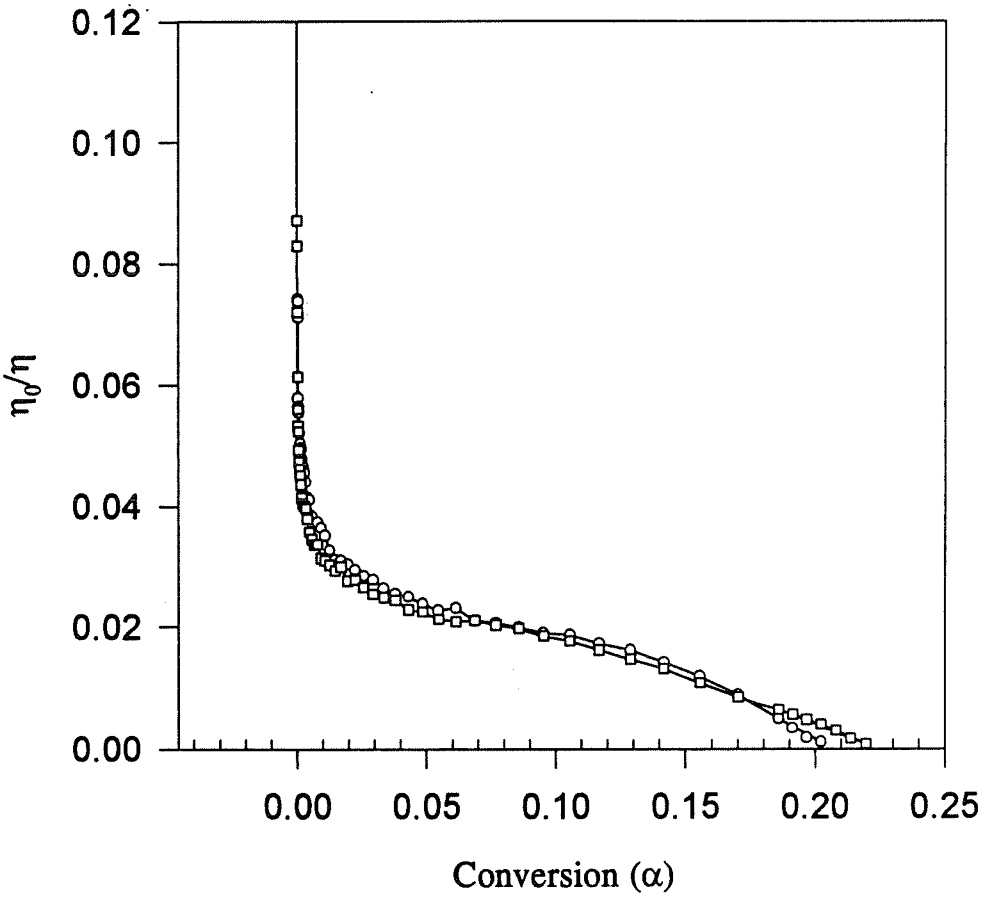

Fig. 4.15 Variation of viscosity ratio as a function of conversion for the promoted samples cured at 30°C on a parallel plates viscometer ($\alpha_{gel} = 0.21$).

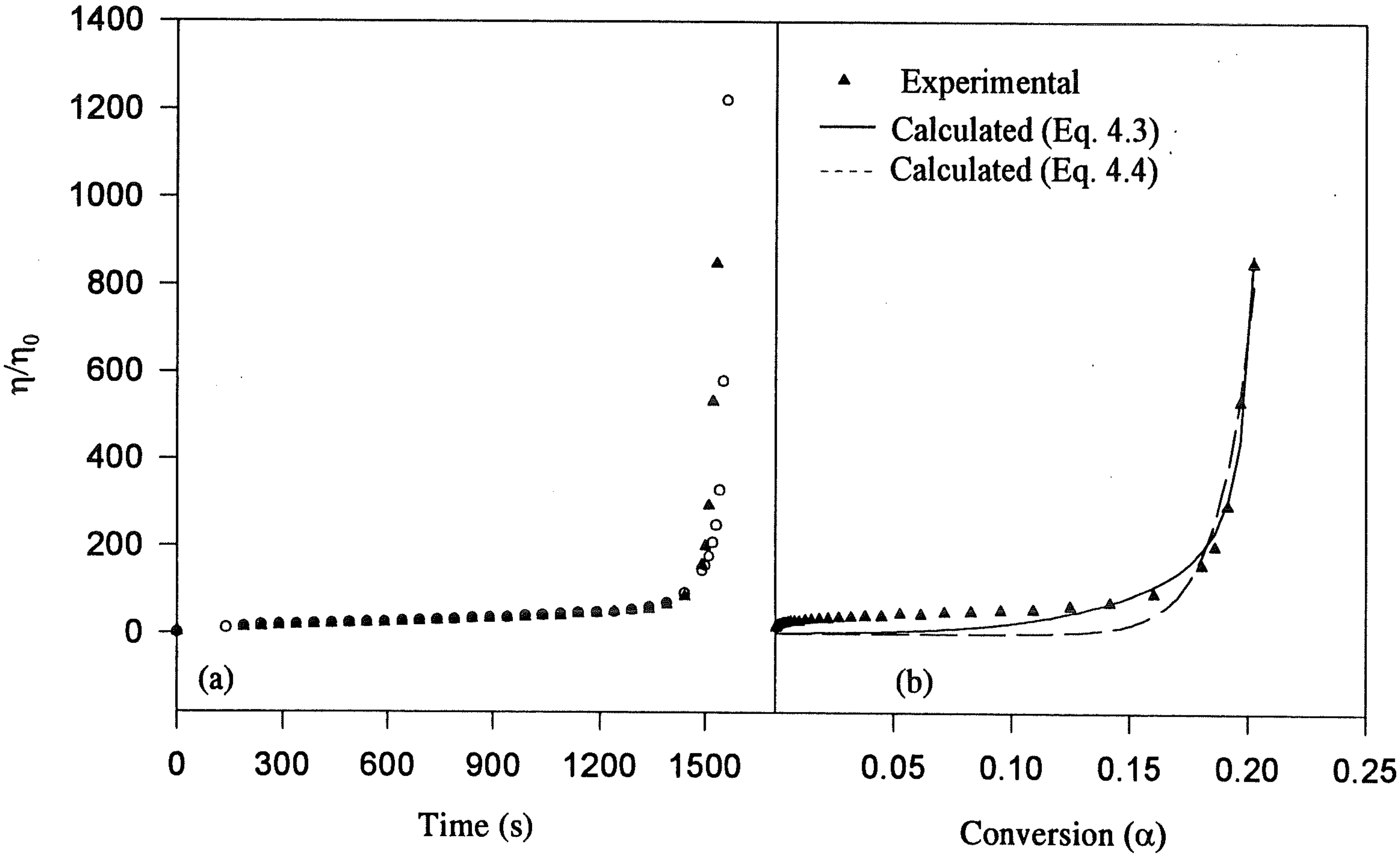

Fig. 4.16 Variation of viscosity for the promoted vinylester resin cured at 30°C on a parallel plates viscometer **(a)** experimental data as a function of time **(b)** experimental data and the calculated values (Eqs.4.3 & 4.4)

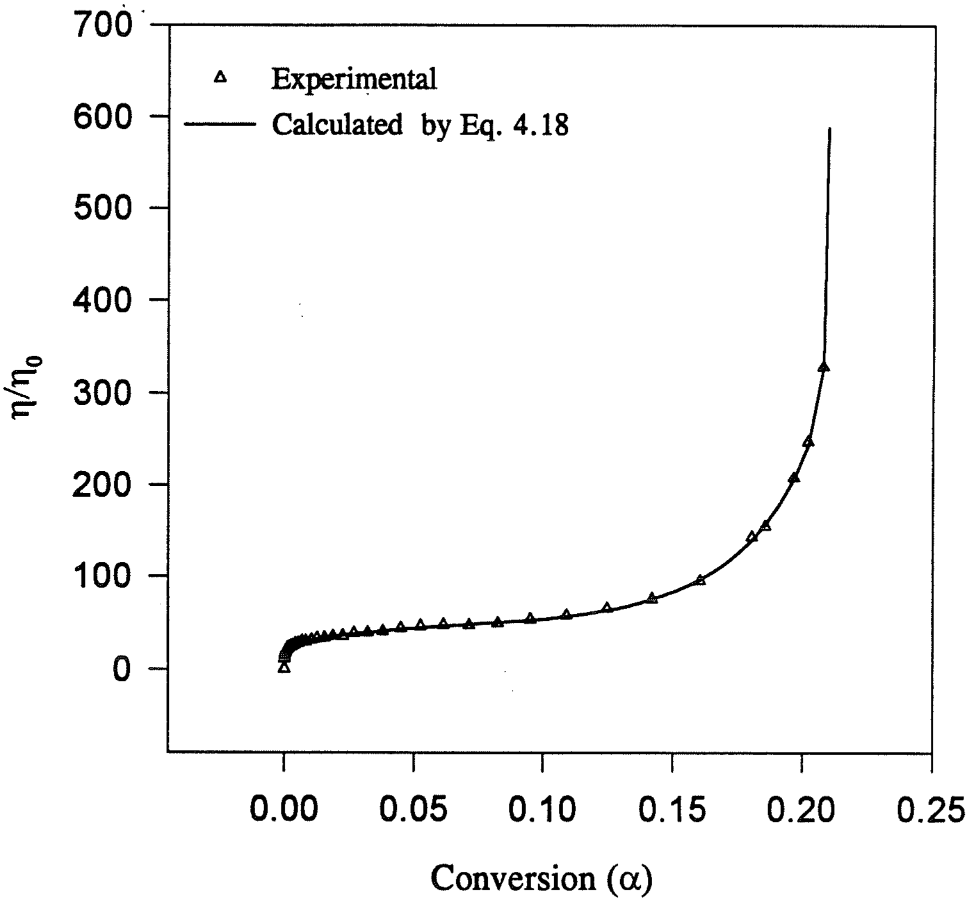

Fig. 4.17 Comparison of experimental and calculated viscosity ratios for the promoted vinylester resin cured at 30°C on a parallel plates viscometer.

PRESENTATION OF CHAPTER 5

The optimization of process variables for composite manufacturing processes is more economic and less time consuming through mathematical modeling. The process modeling by numerical analysis offers the manufacturer the opportunity to reduce the significant amount of experimental work associated with developing new formulations. Having estimated the kinetic parameters of the promoted polyester and vinylester cure systems, see results of Chapters 3 and 4, the post-filling period of the RTM process is analyzed in Chapter 5 by the finite element method. The process variables including gel time and demold time are estimated, and the influence of process conditions, e.g. mold temperature and part thickness, on the temperature and cure profiles are discussed. The main features of the developed mathematical model are: 1) incorporating the effects of a promoter and glass fiber reinforcement through the specifically developed kinetic models; 2) changing thermal conductivity during cure period; and 3) temperature dependent specific heat. On the basis of obtained numerical results, it is explained that in the case of reinforced promoted vinylester systems, the set of kinetic parameters accounting for the inhibiting effect of the sizing agent on the glass fibers should be used in the numerical analysis. Before comparing the estimated temperature profiles to experimental values, it is necessary to examine the sensitivity of temperature and cure predictions to model input parameters. In the following chapter, the effect of variation in isothermal heat of cure on the estimation of temperature and degree of conversion is examined. To verify the developed kinetic and process models, the temperature predictions inside a reinforced polyester composite are compared to experimental measurements at the end of Chapter 5.

CHAPTER 5

NUMERICAL ANALYSIS OF PROMOTED POLYESTER AND VINYLESTER REINFORCED COMPOSITES IN RTM MOLDS

by

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5.1 ABSTRACT

This article presents a one-dimensional simulation of post-filling period in Resin Transfer Molding (RTM) process. In the program developed in this work, transient heat conduction and kinetic of cure equations were solved simultaneously. The Galerkin finite element method was applied to solve the problem. The kinetic models employed in this study were developed with regard to the effects of additives frequently used in the formulation of composite parts (*e.g.* promoting agents and reinforcements). These specialized kinetic models enabled us to predict the influence of incorporated reinforcement on the process variables, e.g. gel time and demold time, and on the distributions of temperature and extent of cure in through-the-thickness direction of the polyester-based and vinylester-based composites. It was shown that in the case of vinylester, the incorporation of glass fibers gave rise to a severe inhibition of the cure reactions at high conversions due to the presence of inorganic radicals generated in the cure system. We believe that this inhibition is mostly due to the surface treating agent which is formulated for a polyester resin. The inhibiting effect of glass fibers in polyester-based formulation was found less significant, and the delay in the exotherm temperature peak was mainly attributed to the thermal effects induced in the presence of glass fibers. The latter effects become important when a considerable difference exists in the thermal conductivities of the reacting resin and reinforcements. As a consequence, glass fibers acts as heat sinks and cause some modifications in the temperature profile inside the molded part. In the present work, the results obtained from the numerical

analysis were compared with experimental data for a reinforced polyester part cured in a heated mold.

5.2 INTRODUCTION

Fiber reinforced polymer composites manufactured by Resin Transfer Molding (RTM) process have gained a great importance because of their good mechanical properties, lower densities and relatively low production costs.

There are numerous investigations in the literature on the modeling of reactive processes. Progelhof [1] applied the autocatalytic kinetic model introduced by Kamal and Sourour [2] to analyze the one-dimensional transient heat conduction in unfilled polyesters and epoxies. Based on the numerical simulation, no exotherm peak was observed at low temperatures up to 65°C; however, an enormous local overheating was reported for the polyester resin when the mold temperature exceeded 90°C. Lee and Macosko [3] included heat transfer through the walls and to the cooling water in their analysis. They reported that in a RIM process, the temperature near the mold center was not affected considerably at short times by the boundary conditions; however, near the mold wall, temperature profiles were significantly altered. To reduce temperature gradients in the part, it was suggested to use a heated mold. On the basis of numerical analysis it was found that if a mold temperature higher than the entering temperature of reactants was used, a significant reduction in the difference between centerline and wall conversion would result.

In the case of thick composite parts, Hojjati and Hoa [4] presented the distribution of temperature and extent of cure through-the-thickness by taking into account the consolidation of the molded part. Rojas and coworkers [5] studied the curing of unsaturated polyester resins in the presence of a promoter. Their results did not show a satisfactory prediction of the temperature profile due to the over-simplifies 3rd order kinetic model applied in the simulation. To predict the temperature variation at the mold wall caused by the reaction exotherm, the theoretical prediction of temperature at 0.9 mm from the wall was assumed to represent the wall temperature in a mold of 30 mm thick. McGee [6] presented an analysis based on the effects of particulate fillers on the curing behavior, heat transfer during the cure process, and maximum mold temperature. His study was based on a simple nth order reaction mechanism for both filled and unfilled polyester systems.

According to Viola and Schmeal [7], the fibrous preform can affect the material and energy balances in two ways: 1) on a per volume basis, less heat is generated in the mold, and 2) acting as a heat sink, the preform decreases the maximum temperature rise in the mold and extends the gel time of incoming resin. Consequently, it was suggested to use the preform configuration to extend the gel time of incoming resin in locations away from the mold wall. Day [8] characterized the cure in polyester sheet molding compound (SMC) using dielectric sensors mounted at various locations through the thickness of the part. A nonuniformity in cure behavior through the thickness was reported for the parts thicker than 5 mm. The model simulation of SMC also showed that in thick parts, a cure wave develops starting at the SMC/mold interface, and proceeds toward the center of the mold. As a consequence, in the middle of the SMC part, a long induction period occurred followed by an extremely fast cure.

The molding time of a composite part is mainly determined by the resin formulation. Since the temperature of chemical decomposition of the polymerization initiators are generally too high, most of the commercially available resins are pre-promoted for room-temperature cure manufacturing processes. A promoter is capable of increasing the cure rate by chemically initiating the cure process. Moreover, it is reported that the addition of promoter to the cure system forces the reaction to start at lower temperatures avoiding thermal degradation at the core which frequently occurs during the molding at elevated temperatures [5]. The main difficulty associated with the promoted cure systems is the complexity of the cure mechanism. It is reported that for epoxy and polyester resins, the following autocatalytic model represents adequately the kinetics of the cure reactions [2,9,10]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\,\alpha^m)(\alpha_{\max} - \alpha)^n \tag{5.1}$$

where:

$d\alpha/dt$ rate of conversion

α	cumulative conversion at a given time t
k_1, k_2	reaction constants with an Arrhenius temperature dependency
α_{max}	maximum conversion (or vitrification conversion) at a given isothermal cure temperature
m, n	reaction exponents

however, it is shown that Eq. 5.1 is not capable of representing the whole cure process for a promoted vinylester resin. To take into account the complexity of the cure mechanism in the case of promoted vinylester resin, the following rate equation is introduced in the literature [11,12]:

$$\frac{d\alpha}{dt} = k_2 \alpha^m (\alpha_{\max} - \alpha)^n (1 - \alpha)^p \tag{5.2}$$

where p is the third reaction exponent.

Unreinforced thermosets generally have moderate physical properties. Outstanding physico-mechanical properties including good impact resistance and high modulus can be achieved by addition of reinforcements [13]. On the other hand, in the processing of thermosetting resins a severe temperature increase may occur at mid-part thickness during the exothermic cure reactions. Due to the low thermal conductivity of the thermosetting resins, it takes a long time for the evolved heat to reach the mold walls by thermal conduction. As a consequence, in the case of fast cure reactions a severe damage to mechanical properties can result. The incorporation of conductive reinforcements, including glass fibers, decreases the temperature at the center of the part by acting as heat sinks. Since the presence of inorganic reinforcements may lead to a more complex cure mechanism, a good understanding of the cure kinetics is an essential prerequisite of the process simulation. According to Plueddemann [14], the addition of glass fibers to the cure system of some thermosetting resins can cause an inhibiting effect particularly at low temperatures.

To establish kinetic models for the cure reactions of promoted polyester and vinylester resins, isothermal differential scanning calorimetry (DSC) measurements were performed [15,16]. To compensate for the unrecorded part of the cure exotherm at high temperatures, a correction factor was employed as follows:

$$C(T) = \frac{Q_T(T)}{Q_{T,cal}(T)} \tag{5.3}$$

here $Q_{T,cal}$ is the theoretical enthalpy of cure predicted by the parameter estimation procedure, and Q_T is the experimental enthalpy of cure obtained from the following expression:

$$Q_T = Q_u - Q_R \tag{5.4}$$

where Q_u and Q_R are the ultimate heat of cure and residual heat of cure, respectively, obtained from dynamic DSC measurements [17]. Consequently, the degree of conversion, α, evaluated in the numerical analysis using Eqs. 5.1 and 5.2 can be corrected in each time step, Δt, in the following form:

$$\alpha^c_{t+\Delta t} = \alpha^c_t + C(T)(\alpha_{t+\Delta t} - \alpha_t) \tag{5.5}$$

here α^c denotes the corrected degree of conversion and C is the temperature dependent correction factor given by Eq. 5.3.

Tables 1 and 3 give the parameters of Eqs. 5.1 and 5.2 estimated in our previous works for polyester and vinylester resins cured in the presence of cobalt-based promoters [15,16]. The estimated kinetic parameters for the two cure systems in the presence of glass fibers are tabulated in tables 2 and 4.

This article attempts to demonstrate the influence of incorporating a promoting agent and glass fibers on different process parameters in a one-dimensional heat transfer analysis. This analysis is valid for composite molding processes where the part thickness is small compared with the width so that heat conduction is essentially one-dimensional. In the present study, a finite element solution using Galerkin method is used to predict the temperature profile and chemical reaction inside the mold. Results are presented for promoted polyester and promoted vinylester resins with varying reinforcement content. This analysis is used to verify the effect of glass fibers on some important aspects of post-filling period, that is time-temperature profiles, extent of cure, gel time and demold time.

5.3 ANALYSIS

Based on the following assumptions, the governing equations may be written as follows :

1. Thin slab geometry implying one-dimensional heat conduction
2. Constant density and thermal conductivity
3. Negligible molecular diffusion
4. Isothermal wall
5. No flow

Energy balance:

$$\rho_c C_{p,c} \frac{\partial T}{\partial t} = k_c \frac{\partial^2 T}{\partial x^2} + v_r \dot{Q}(t,x) \tag{5.6}$$

Mass balance:

$$\frac{\dot{Q}}{\rho_r Q_u} = \frac{d\alpha}{dt} = k_2 \alpha^m (\alpha_{\max} - \alpha)^n \tag{5.7}$$

$$\frac{\dot{Q}}{\rho_r Q_u} = \frac{d\alpha}{dt} = k_2 \alpha^m (\alpha_{\max} - \alpha)^n (1 - \alpha)^p \tag{5.8}$$

where Eqs. 5.7 and 5.8 represent the rate of conversion for polyester and vinylester resins. In these equations, ρ, C_p, and k are the density, specific heat, and thermal conductivity, respectively, $\dot{Q}$ is the heat generation term, Q_u is the ultimate enthalpy of cure obtained for 100% monomer conversion, and subscripts "c", and "r" indicate the physical properties of the composite and polymer matrix, respectively.

The initial and boundary conditions used in this study, were:

$$T(x,0) = T_0 \quad , \quad \alpha(x,0) = 0 \tag{5.9-5.10}$$

$$\frac{\partial T(L,t)}{\partial x} = 0 \quad , \quad T(0,t) = T_w \tag{5.11-5.12}$$

Eq. 5.11 reflects the symmetry around the centerline, and Eq. 5.12 is the boundary condition corresponding to constant wall temperature.

In the development of the dimensionless governing equations, the following dimensionless variables were defined:

$$t' = \frac{k_c t}{\rho_c C_{p,c} L^2} \quad , \quad x' = \frac{x}{L} \tag{5.13-5.14}$$

$$T' = \frac{T - T_0}{T_{ad} - T_0} \quad , \quad \dot{Q}' = \frac{v_r \dot{Q} L^2}{k_c (T_{ad} - T_0)} \tag{5.15-5.16}$$

where L is the half thickness of the part, T_0 is the initial temperature, and T_{ad} is the adiabatic temperature estimated as:

$$T_{ad} = T_w + \frac{Q_u}{C_{p,c}} \tag{5.17}$$

In general, T_{ad} represents the maximum temperature which may occur inside a composite.

To obtain the discretized equations, the Galerkin method was used. The procedure yielding the set of matrix equations for the transient heat conduction in a reactive system is explained elsewhere [18]. The globally convergent Newton-Raphson procedure was adopted to solve the system of nonlinear equations [19].

5.4 PHYSICAL PROPERTIES OF THE COMPOSITE

The addition of glass fibers to the cure formulation changes the physical properties of the reactive system. The thermal conductivity of the polymeric matrix as well as the glass fiber reinforced composite were determined based on ASTM C177-85 by imposing a constant temperature gradient between two sides of the disk shaped samples and by measuring the heat flux passing through the samples. Using the measured conductivities of fully cured composites having 0, 10, and 15 % by weight of random mat glass fibers, the thermal conductivity of the composites having other glass fiber contents was estimated by a variety of theoretical models available in the literature. Table 5 compares the theoretical estimates with the values reported in the literature for the conductivity of glass fibers. As it can be seen, the spherical inclusion model yields a good estimation for the conductivity of glass fibers. This model is generally used to represent the properties of solid particulate composites [20]. Base on this model, the thermal conductivity of a composite can be expressed in the following form:

$$k_c = k_r \left(1 + \frac{3v_f(k_f - k_r)}{v_r(k_f - k_r) + 3k_r} \right) \tag{5.18}$$

where k_c, k_r, and k_f represent the thermal conductivities of composite, resin, and fiber, respectively, v_r is the volume fraction of resin and v_f is the volume fraction of filler. The thermal conductivity of resin in Eq. 5.18, k_r, was calculated by the following form in the numerical analysis:

$$k_r = k_{r,0} + (k_{r,100} - k_{r,0})\,\alpha^c \tag{5.19}$$

here $k_{r,0}$ and $k_{r,100}$ are the thermal conductivities of uncured and fully cured resin, and α^c is the corrected extent of cure given by Eq. 5.5. As already explained, the thermal conductivities of fully cured resins were measured in the present work. The thermal conductivities of uncured resins were taken from the literature (see Table 6). Since it is reported that vinylester resins generally have many properties characteristic of epoxies but the processability of a polyester [21], the thermal conductivity of the uncured vinylester resin was considered to be equal to that of uncured epoxies.

The specific heat of the two promoted resin used in the present work was determined by Differential Scanning Calorimetry (DSC) based on ASTM E1269 using sapphire as the standard [22-24]. Due to the considerable variation of specific heats with temperature, the experimental specific heat data were fitted using the linear least squares method. The specific heat of the composite was estimated using the rule of mixture in the following form [25] :

$$C_{p,c} = (1 - m_f)\,C_{p,r} + m_f C_{p,f} \tag{5.20}$$

where m_f is the weight fraction of filler, and $C_{p,c}$, $C_{p,r}$, and $C_{p,f}$ represent the heat capacities of composite, resin, and filler, respectively.

The density of cured promoted resins was measured based on ASTM D792-91 using distilled water as the liquid phase. The measured values are shown in Table 5.6. The density of composites was approximated using the rule of mixture as follows [20]:

$$\rho_c = v_r \rho_r + v_f \rho_f \tag{5.21}$$

where ρ_c, ρ_r, and ρ_f represent the thermal conductivities of composite, resin, and fiber respectively.

5.5 RESULTS AND DISCUSSION

Figs. 5.1 and 5.2 give the plots of estimated rate of conversion and extent of cure for polyester and vinylester systems obtained from Eqs. 5.1 and 5.2, respectively. It can be seen that the inhibition effect of glass fibers on the cure system of promoted polyester resin is not significant (see Fig. 5.1-c); however, a severe inhibition of cure is observed in the case of promoted vinylester system at high extent of cure (*e.g.* $\alpha > 0.5$ in Fig. 5.2-c). Considering that the conversion at the gel point for the vinylester system is about 0.20, the inhibition region is well beyond the gelation point. However, it is worth mentioning that for both cure systems, higher induction periods, t_{ind}, were noticed in the presence of glass fibers at low isothermal cure temperatures up to 60°C (see Tables 5.1 to 5.4).

The centerline temperature profiles for polyester and vinylester parts containing 15% by volume of glass fiber reinforcement are shown in Fig. 5.3-a and 3-b. The corresponding values of conversion for the two figures are given in Figs. 5.3-c and 5.3-d. In these figures an attempt was made to compare the temperature and cure profiles obtained by the two different sets of kinetic parameters estimated for unreinforced and reinforced cure systems. Comparing the temperature profiles obtained for polyester composites using the two different sets of parameter indicates that a kinetic model without accounting for the effect of glass fibers can introduce a negligible extent of error and it may be used to represent the cure process of a reinforced composite. However, in the case of vinylester resin, the set of parameters estimated for unreinforced cure system, Table 5.3, significantly overestimate the heat evolution in the center of the composite part. Fig. 5.3-d also indicates that at the end of the molding process, the cure reactions are not complete in the glass fiber reinforced vinylester parts. As a consequence, applying a specific kinetic model accounting for the inhibition effect of glass fibers is necessary in the modeling of composite manufacturing processes where a vinylester resin is involved. Comparison of cure exotherms for unreinforced and glass fiber reinforced vinylesters in Fig. 5.2 also indicates the inhibition of cure caused by the presence of glass fibers. The significant difference between the two predicted curves in the case of promoted vinylester system is attributed to the production of inorganic free radicals which lack adequate reactivity to initiate other radicals at low temperatures. Since oxide surfaces inhibit free radical polymerization by terminating growing chains, proper surface treatments can overcome the inhibition of cure caused by electron-donor properties of glass fibers. It should be noted that commercial coupling agents and sizes are generally formulated for a particular cure system, and they may not be as effective for another cure formulation. We believe that the significant inhibition of cure in the case of vinylester resin is mainly attributed to the surface treating agent of the reinforcement which was formulated for a polyester resin.

It is reported that a very good agreement exists between the relative electron-donor properties of oxides and the lowering of cure exotherm by the same oxide [14]. The electron donor activity of the most common glass-forming oxides is as follows:

$$MgO > ZnO > Al_2O_3 > TiO_2 > SiO_2$$

E glass, which is mostly used in general purpose reinforced plastics applications, is also capable of lowering the cure exotherm of polyester resin if a proper surface treating agent is not used in the formulation of the reinforcement [14]. It is also reported that E glass has a particularly poor resistance to attack by acid [26]. So, it is evident that accounting for the inhibition effect of glass fibers in the numerical analysis is a serious requisite for the prediction of temperature and cure profiles particularly in the absence of proper sizing agents.

The transient temperature profiles across the reactive parts are shown in Fig. 5.4. These curves represent temperature profiles up to the peak time of Figs. 5.3-a and 5.3-b. The temperature profiles in these figures are chosen in a certain manner to represent the transient temperatures through the part thickness at 1/3, 2/3, and 3/3 of peak time, t_p. At the beginning, the conversion rate is low and the centerline temperature is well below the mold surface temperature. With the progress of cure, the centerline temperature rapidly increases due to the heat evolution. However, after the peak time, heat is being conducted out of the part. Consequently, a decreasing trend in the temperature profiles would result. The temperature profiles after the peak time are not given in figures 4-a and 4-b in order to keep these figures easy to compare. The corresponding conversion profiles are plotted in Figs. 5.5-a and 5.5-b, where the existing differences between the two cure systems are compared with regard to the progress of cure within the part. For the reinforced vinylester part in Fig. 5.5-b, the conversion achieved at the peak time is about 1/2 of the one obtained in the unreinforced vinylester part.

Figs. 5.6-a and 5.6-b show the centerline temperature rise and cure profiles during the cure process for the two promoted resins containing varying quantities of reinforcement. As expected, the peak temperature decreases due to the presence of glass fibers, and it is delayed because the thermal conductivity of the polymer is smaller than that of glass fibers.

In spite of predominant chemical effects in glass fiber reinforced vinylester parts, which give rise to higher cure rates at the beginning of the cure, the extent of cure is higher for unreinforced vinylester parts at the end of the process.

The influence of the part thickness on the temperature evolution at the centerline of the reinforced parts is shown in Figs. 5.7-a and 5.7-b. The thicker the part, the higher the peak temperature in the centerline. It is reported in the literature [27] that after a critical thickness, the centerline temperature will decrease with increasing the part thickness due to the condition imposed by conduction heat transport. Since the results plotted in Figs. 5.7-a and 5.7-b are obtained for a wall temperature of 25°C and limited thicknesses, the centerline temperatures are increasing steadily. The corresponding cure profiles, Figs. 5.8-a and 5.8-b, show the same trend.

The influence of mold wall temperature on the centerline temperature and cure profiles is shown in Figs. 5.9 and 5.10. The higher the mold wall temperature is, the higher is the peak temperature at the centerline. Furthermore, the centerline peak temperature occurs in a shorter time with increasing the mold temperatures. This leads to higher cure rates and, as a consequence, to high conversions as can be seen in Figs. 5.10-a and 5.10-b.

Figs. 5.11-a to 5.11-c show the effects of part thickness and mold wall temperature on the gelling time of promoted vinylester parts reinforced with varying amount of glass fibers. As expected, the gel time rises with increasing the fiber content and reduces with increasing the mold wall temperature and part thickness. It can be seen in Figs. 5.11-a and 5.11-b that the gel time of unreinforced vinylester part is exceptionally higher particularly at the vicinity of the mold wall due to the lower rates of cure at the beginning of the cure (see Fig. 5.2-a). Comparison of Figs. 5.11-a and 5.11-b indicates that excluding the locations close to the mold wall, for thicker parts the gel time is almost constant. The sudden jump of the gel time at the mold wall in Fig. 5.11-a, particularly for composites with lower loads of reinforcement, is due to the low thermal conductivity of the polymeric matrix. Increasing the mold wall temperature in Fig. 5.11-c causes a considerable decrease in the gel time.

In Figs. 5.12-a to 5.12-c, the effects of part thickness and mold wall temperature on the demold time of polyester parts reinforced with varying amount of glass fibers are illustrated. In these figures, demold time was assumed to be the time needed to attain a conversion of 70% throughout the part. For the thicker parts in Fig. 5.12-a, the demold time is almost constant near the centerline and increases sharply toward the mold wall. This is due to the accumulation of generated heat around the centerline, and is caused by the low thermal conductivity of polymeric matrix. Moreover, it can be shown that increasing the part thickness or reducing the amount of reinforcement yields a rather complex and nonuniform cure. That is, a midplane between the mold wall and centerline can be found where an excessive extent of cure, and as a consequence, the shortest demold time would occur. This reflects the fact that the location of the maximum transient heat evolution in the molding process of thick composites is governed by various factors including the quantity of the reinforcement incorporated in the molded part. The effect of mold wall temperature on the demold time of polyester parts is given in Fig. 5.12-c. The decrease in the demold time is significant for all reinforced parts but is more pronounced for the unreinforced one.

A sensitivity analysis on the basis of isothermal heat of cure was performed in the present work. For example, a variation of ε on the total heat of cure, Q_T, in the following form:

$$Q = Q_T \pm \varepsilon \tag{5.22}$$

will have an influence on the estimation of the peak temperature, ε_T, and extent of cure at peak time, ε_α. The definitions of ε_T and ε_α are graphically illustrated in Fig. 5.13 for a polyester composite containing 15% by volume of reinforcement. It can be seen that an arbitrary error of 20%, ε = 10%, may cause a considerable error in the estimation of temperature and extent of cure particularly at the peak time. Taking this approach, the magnitude of resulted errors in temperature and extent of cure at the peak were estimated using the developed program through the thickness of polyester and vinylester parts. The resulting error profiles are shown in Figs. 5.14-a to 5.14-d for two different values of induced error and varying amount of reinforcement. The results indicate the importance of precision and accuracy in evaluation of isothermal heat of cure. A similar approach can be used to evaluate the estimation errors caused by inaccuracy in the thermo-physical properties of a composite.

5.6 EXPERIMENTS CONDUCTED IN A HEATED MOLD

In order to verify the versatility of the applied kinetic models throughout this work, the changes in temperature evolution during the curing of the promoted polyester resin containing 15% by volume of promoter were measured by conducting some molding experiments in a RTM mold. The reinforcement used for the molding test was Owens Corning OCF8610, a continuous filament random mat having a surface density of 450 gr/m^2. The promoted polyester resin was FRP A-600-10RT provided by Ashland Chemicals. The instrument set up and procedure is reported elsewhere [28,29]. The temperatures recorded at the end of mold filling through the gapwise direction of molded part were utilized as the initial conditions for the numerical analysis. Fig. 5.15 compares the theoretical results and experimental data obtained at a mold temperature of 42°C for a part of 9 mm thick. The agreement between the model predictions and experimental results is reasonably good. However, more satisfactory results could be obtained if better kinetic information was available for the reinforced polyester system at temperatures higher than 55°C. It should also be kept in mind that the precision of thermocouples at high temperatures is limited regarding their delay time in recording sudden temperature changes. The attempts to obtain experimental data in a heated mold for the promoted vinylester system were not successful due to the nonuniformity of the mixture obtained using a static mixer designed for the molding equipment. This nonuniformity was mainly due to the higher viscosity of the vinylester resin used in this work comparing with that of the polyester resin.

The possible sources of error in estimation of the kinetic data and in analyzing the cure process for the two cure systems can be summarized as follows: 1) Fewer number of cure data at temperatures above 55°C in the case of reinforced polyester resin. 2) Sometimes trace amount of thermally induced cure reactions appeared as a small shoulder at the end of polyester cure exotherm particularly for the samples cured at relatively high temperatures. 3) Assuming constant physical properties throughout the entire cure period.

5.7 CONCLUSION

A one-dimensional numerical analysis for the post-filling period of RTM processes was presented. The kinetic model employed in this study was developed with regard to the effects of additives, e.g. promoting agents and reinforcement. The influence of these additives on the process variables such as cure time and demold time, and on the distributions of temperature and extent of cure was studied in through-the-thickness direction. It was shown that in the case of vinylester resin, the presence of glass fibers gave rise to a severe inhibition of the cure reactions at high conversions. It was also pointed out that a proper selection of surface treating agent can overcome the cure inhibition caused by oxide surfaces in the case of glass fiber reinforced composites. Consequently, the inhibition was mainly attributed to the specific sizing agent of the reinforcement which was formulated for a polyester resin. The delayed exotherm peak in reinforced polyester parts was mainly attributed to the thermal effects induced in the presence of glass fibers.

A comparison was made between numerical results and experimental data for a reinforced polyester part cured in a heated mold. The discrepancy between the theoretical and experimental results was attributed to some uncertainties associated with the estimation of kinetic parameters at high cure temperatures, as well as to the delay time of thermocouples in response to sudden temperature changes. It was inferred that in the case of reinforced promoted vinylester systems, the set of kinetic parameters accounting for the inhibiting effect of glass fibers should be used in the numerical analysis of composite manufacturing processes.

The parameter estimation procedure applied in the present work was found to be reliable for the evaluation of kinetic parameters. Considering the complexities involved in the cure process of the promoted thermosetting resins, including the different governing cure mechanism in different temperature regions, it is recommended to express the temperature dependency of kinetic parameters in a precautious manner. Moreover, the temperature dependent expression used should yield reasonable values outside the temperature range in which the cure data were acquired. Therefore, the expressions such as the one used to express the temperature dependency of reaction exponents for unreinforced vinylester resin (see Table 5.3) are mostly recommended.

5.8 NOMENCLATURE

a, a_0-a_4	adjustable parameters
b, b_0-b_4	adjustable parameters
C	correction factor given by Eq. 5.3
C_p	specific heat (J/g.°K)
E_k	activation energy of the cure reactions (kJ/mol)
E_m	activation energy attributed to m (kJ/mol)
E_n	activation energy attributed to n (kJ/mol)
k	thermal conductivity (J/m.s.°K)
k_0	frequency factor of the cure reactions (s^{-1})
k_1, k_2	reaction rate constants (s^{-1})
$k_{r,0}$	thermal conductivity of the uncured resin (J/m.s.°K)
$k_{r,100}$	thermal conductivity of the fully cured resin (J/m.s.°K)
L	half thickness of the mold (m)
m, n, p	reaction exponents
m_0, n_0	frequency factors attributed to m and n
Q	heat of cure (kJ/kg of resin)
Q_R	residual heat of cure (kJ/kg of resin)

Q_T	total isothermal enthalpy of cure (kJ/kg of resin)
$Q_{T,cal}$	predicted total isothermal enthalpy of cure (kJ/kg of resin)
Q_u	ultimate enthalpy of cure (kJ/kg of resin)
$\dot{Q}$	rate of heat generation (kJ/m^3.s)
R	universal gas constant
t	time (s)
t'	dimensionless time
t_{ind}	induction period of cure (s)
T	temperature (°C, °K)
T'	dimensionless temperature
T_0	initial temperature (°C)
T_{ad}	adiabatic temperature (°C)
v_f	fiber volume content
v_r	resin volume content
α	cumulative conversion at a given time t
α^c	corrected degree of conversion given by Eq. 5.5
α_{max}	vitrification conversion
$d\alpha/dt$	conversion rate (s^{-1})
Δt	time step in the numerical analysis (s)
ε	intentionally induced error in evaluation of heat of cure
ε_T	propagated error in estimation of peak temperature

ε_α	propagated error in estimation of peak conversion
ρ	density (Kg/m^3)

Subscripts

c	related to the composite
f	related to the fibers
r	related to the resin

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5.10 TABLES AND FIGURES

Table 5.1 Summary of the kinetic parameters used for the unfilled promoted polyester resin throughout this work [Ref. 15].

Model	Parameters					
	a_0	a_1	a_2	a_3	a_4	r^2
$Q_T = a_0+a_1T+a_2T^2+a_3T^3$	-48.8	16.1	-0.248	-1.3e-03	-	0.992
$Q_{cal} = a_0+a_1T+a_2T^2+a_3T^3$	-12.3	10.5	-0.101	9.0e-05	-	0.967
$\alpha_{max} = a_0+a_1T+a_2T^2+a_3T^3$	-0.014	0.033	-3.0e-04	6.6e-08	-	0.980
$m = a_0+a_1T^{a2}(a_3-T)^{a4}$	0.373	1.1e-33	10.9	101	8.10	-
$n = a_0+a_1T^{a2}(a_3-T)^{a4}$	1.12	1.7e-33	8.61	133	9.44	-
$k = k_0\exp(-E_k/RT)^{\dagger}$	$T \leq 60°C$: $T > 60°C$:	$K_0 = 2.98e09$ $K_0 = 9.83$		$E_K = 70657$ $E_K = 16544$		$r^2 = 0.996$ $r^2 = 0.987$
$t_{ind} = 1/(a_0+a_1T)$	$a_0 = -1.83$	$a_1 = 0.089$				$r^2 = 0.998$

† : T is in degrees Kelvin.

Table 5.2 Summary of the kinetic parameters used for the glass fiber filled promoted polyester resin throughout this work [Ref. 15].

Model	Parameters				
	a_0	a_1	a_2	a_3	r^2
$Q_T = a_0+a_1T+a_2T^2+a_3T^3$	70.5	8.44	-0.089	2.6e-04	0.996
$Q_{cal} = a_0+a_1T+a_2T^2+a_3T^3$	19.7	10.4	-0.1	-	0.950
$\alpha_{max} = a_0+a_1T+a_2T^2+a_3T^3$	0.554	7.0e-05	-3.2e-04	1.3e-06	0.909
$m = m_0\exp(-E_m/RT)^\dagger$	$T \le 60$ °C: $T > 60$ °C:	$m_0 = 358$ $m_0 = 0.667$	$E_m = 17479$ $E_m = 0$		$r^2 = 0.988$
$n = n_0\exp(-E_n/RT)^\dagger$	$T \le 60$ °C: $T > 60$ °C:	$n_0 = 6.88e04$ $n_0 = 2.47$	$E_n = 28.5$ $E_n = 0$		$r^2 = 0.996$
$k = k_0\exp(-E_k/RT)^\dagger$	$T \le 46$ °C: $T > 46$ °C:	$k_0 = 2.39e09$ $k_0 = 1.08e12$	$E_k = 71232$ $E_k = 87451$		$r^2 = 0.996$ $r^2 = 0.998$
$t_{ind} = \exp(a_0+a_1/T)$	$a_0 = -2.30$	$a_1 = 83.5$			$r^2 = 0.998$

† : T is in degrees Kelvin.

Table 5.3 Summary of the kinetic parameters used for the unfilled promoted vinylester resin throughout this work [Ref. 16].

Model	Parameters					
	a_0	a_1	a_2	a_3	a_4	r^2
$Q_{M1} = a_0+a_1T+a_2T^2+a_3T^3$	-37.9	14.2	-0.16	5.5e-04	-	0.993
$Q_{M2} = a_0+a_1T+a_2T^2+a_3T^3$	170	5.11	-0.021	-6.5e-05	-	0.999
$Q_{cal} = a_0+a_1T+a_2T^2+a_3T^3$	-55.4	15.7	-0.218	9.8e-04	-	0.927
$\alpha_{max} = a_0+a_1T+a_2T^2+a_3T^3$	-0.12	0.038	-4.3e-04	1.4e-06	-	0.998
$m = a_0+a_1T^{a2}(a_3-T)^{a4}$	1.01	-2.0e-33	4.15	255	11.0	-
$n = a_0+a_1T^{a2}(a_3-T)^{a4}$	1.86	3.4e-32	7.65	147	9.98	-
$p = (a_0+a_1T^{a2})(a_3-T)^{a4}$	-1.2e-14	-1.6e-23	6.30	136	7.00	-
$k = k_0\exp(-E_k/RT)^{\dagger}$	$T \leq 40°C$: $40°C < T < 53°C$: $T \geq 53°C$:	$K_0 = 1.6e17$ $K_0 = 2.0e11$ $K_0 = 36.5$		$E_K = 109858$ $E_K = 74424$ $E_K = 13673$		$r^2 = 1.000$ $r^2 = 0.998$ $r^2 = 0.973$
$t_{ind} = 1/(a_0+a_1T)$	$a_0 = -1.18$	$a_1 = 0.052$				$r^2 = 0.995$

† : T is in degrees Kelvin.

Table 5.4 Summary of the kinetic parameters used for the glass fiber filled promoted vinylester resin throughout this work [Ref. 16].

Model	Parameters				
	a_0	a_1	a_2	a_3	r^2
$Q_{M1} = a_0+a_1T+a_2T^2+a_3T^3$	-20.0	11.2	-0.13	5.7e-04	0.996
$Q_{M2} = a_0+a_1T+a_2T^2+a_3T^3$	154	2.50	0.024	-3.0e-04	0.997
$Q_{cal} = a_0+a_1T+a_2T^2+a_3T^3$	156	0.234	-0.072	-6.9e-04	0.97
$\alpha_{max} = a_0+a_1T+a_2T^2+a_3T^3$	-5.3e-03	0.027	-3.2e-04	1.3e-06	0.909
m = Constant	m = 0.551				S.D = 0.015
$n = a + b\,T$	$T \leq 60$°C: $T > 60$°C:	a = -3.18 a = 11.1	b = 0.241 b = 0		$r^2 = 0.998$ S.D = 0.112
$p = a + b\,T$	$T \leq 58$°C: $T > 58$°C:	a = 1.46 a = -15.8	b = -0.301 b = 0		$r^2 = 0.998$ S.D = 0.129
$k = k_0\exp(-E_k/RT)^†$	$T \leq 38$°C: 38°C < T < 60°C: $T \geq 60$°C:	$K_0 = 5.3e16$ $K_0 = 3.2e8$ $K_0 = 17654$	$E_K = 107838$ $E_K = 58948$ $E_K = 31740$		$r^2 = 0.998$ $r^2 = 1.000$ $r^2 = 0.998$
$t_{ind} = 1/(a_0+a_1T^2)$	$a_0 = -0.290$	$a_1 = 5.9e-4$			$r^2 = 0.994$

† : T is in degrees Kelvin.

Table 5.5 Thermal conductivity of glass fibers calculated by some theoretical approaches.

Approach or Researcher	**k (J/m.s.°K)**
Serial rule of mixture [Ref. 30]	> 1000
Parallel rule of mixture [Ref. 30]	0.60
Springer - square filament [Ref. 31]	> 1000
Springer - cylindrical filament [Ref. 31]	> 1000
Spherical inclusion model [Ref. 20]	1.18
Handbook [Ref. 32]	0.94 - 1.04

Table 5.6 Physical properties of the promoted polyester, promoted vinylester, and glass fibers used throughout this work.

Physical Property	**Polyester**	**Vinylester**	**Glass fibers**
Density $(\rho)^{\dagger}$: (kg/m^3)	1180	1120	2420
Thermal Conductivity (k) : (J/m.s.°K)	-	-	1.18
Uncured resin $(k_{r,0})$: [Refs. 1,33]	0.289	0.160	-
Fully cured resin $(k_{r,100})^{\dagger}$:	0.194	0.179	-
Partially cured resin† : $k_r = k_{r,0}+(k_{r,100} - k_{r,0}).\alpha^c$	-	-	-
Specific heat† : $C_p = a + b\,T$ (kJ/kg.°K)	a = 666 b = 9.19	a = 915 b = 3.02	1000 -

† measured in the present work.

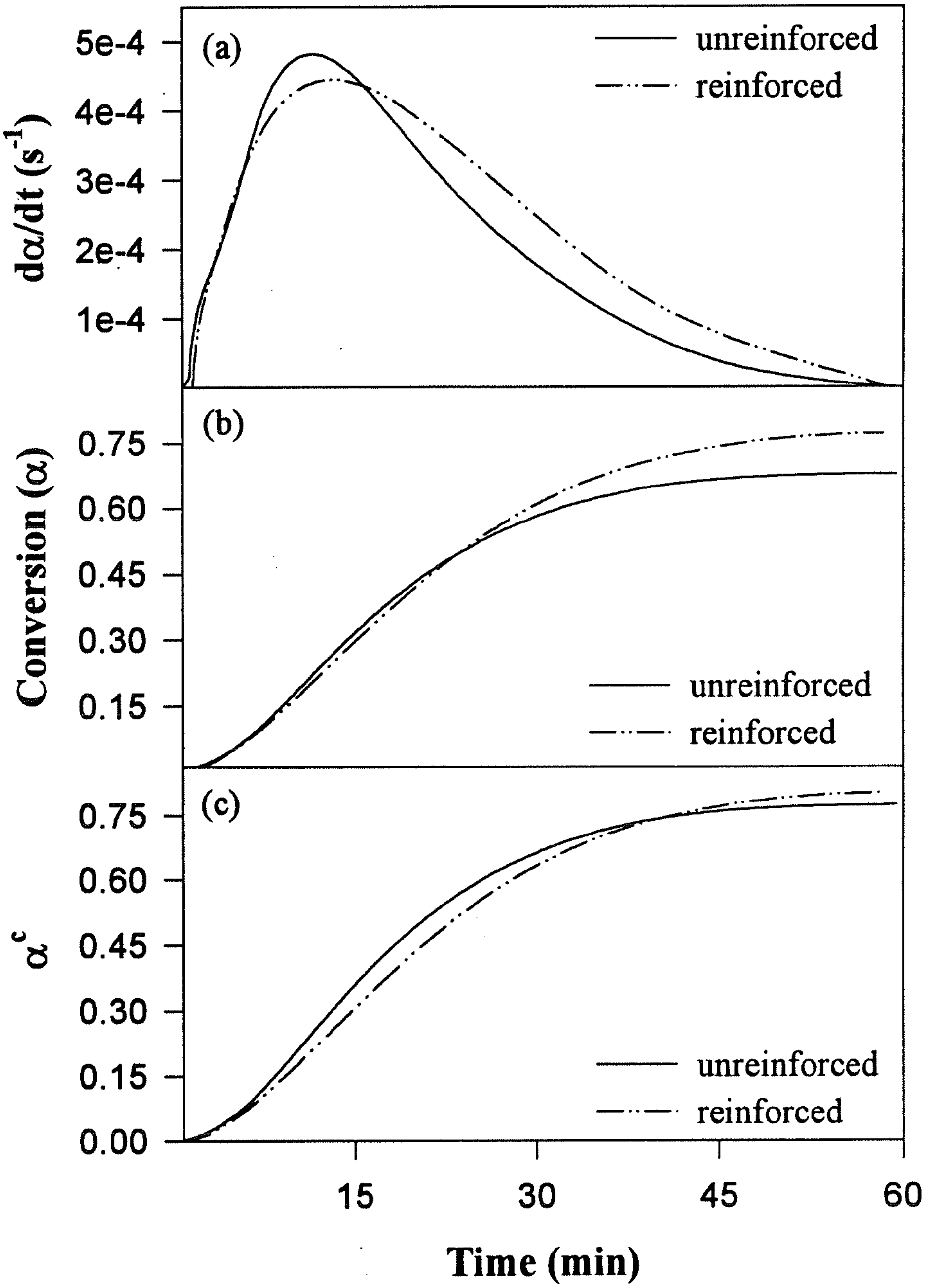

Fig. 5.1 Profiles of **(a)** cure rate and **(b&c)** degree of conversion for unreinforced and glass fiber reinforced (fiber content = 15 wt%) promoted polyester resins obtained at 30°C by isothermal DSC. α^c represents degree of conversion corrected by Eq. 5.5.

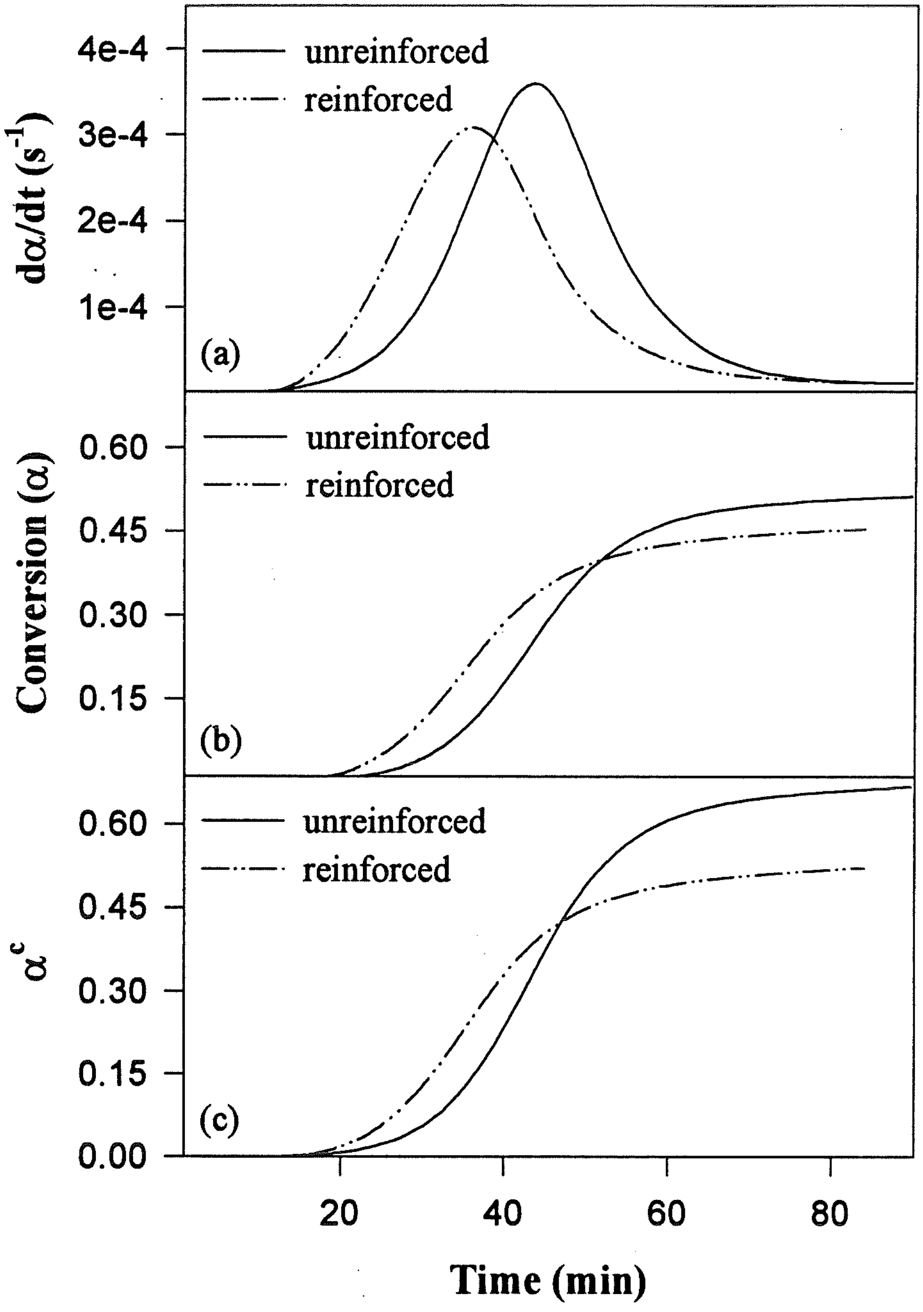

Fig. 5.2 Profiles of **(a)** cure rate and **(b&c)** degree of conversion for unreinforced and glass fiber reinforced (fiber content = 15 wt%) promoted vinylester resins obtained at 25°C by isothermal DSC. α^c represents degree of conversion corrected by Eq. 5.5.

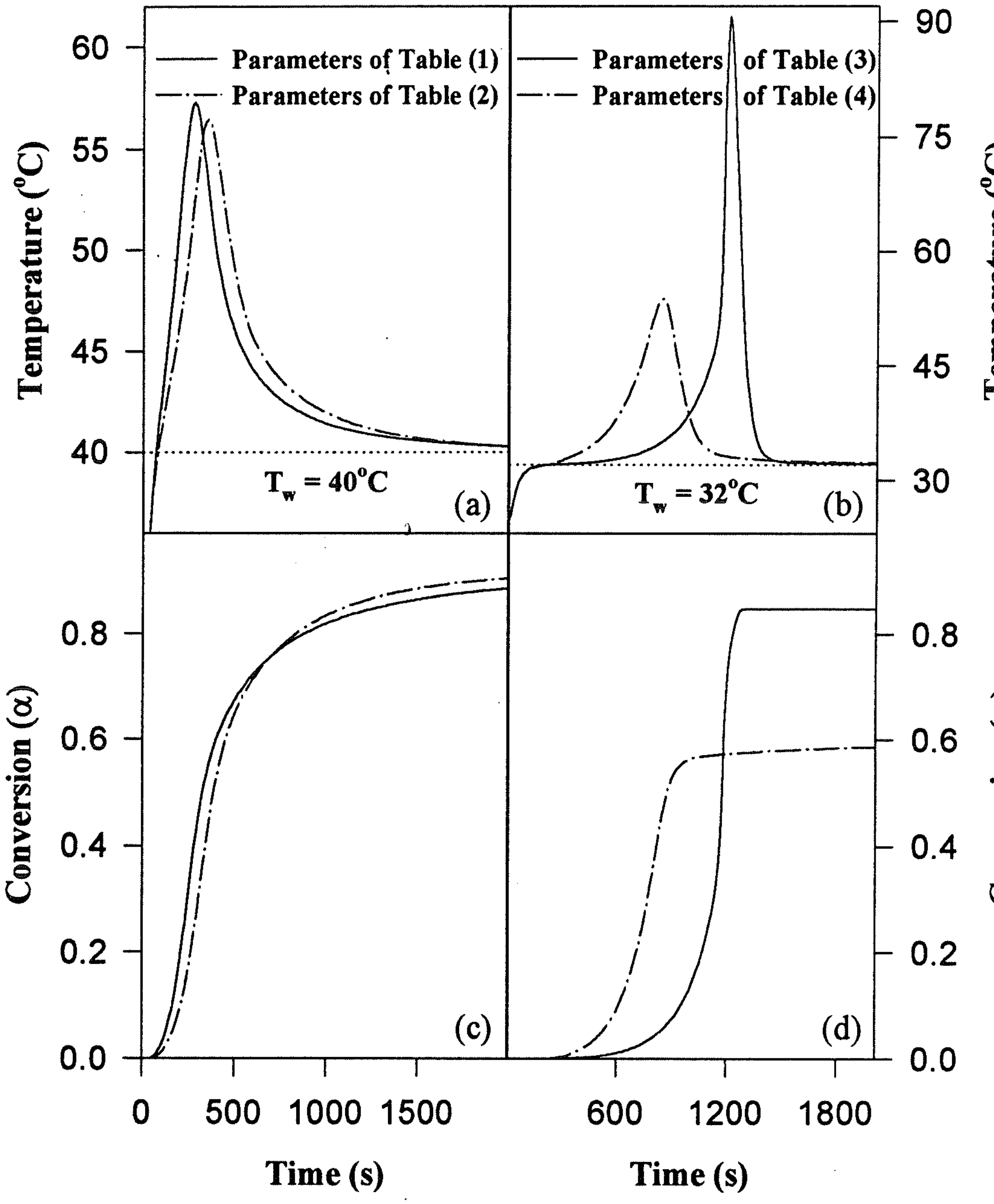

Fig. 5.3 Comparison of numerical results obtained by two different sets of parameters. **(a)-(b)** Centerline temperature for composites of polyester and vinylester reinforced by 15 vol% of glass fibers. T_0 = 25 °C; Part thickness = 8 cm.

(c)-(d) Corresponding extent of cure for Figs 3(a) and 3(b). The horizontal dotted lines represent mold wall temperature.

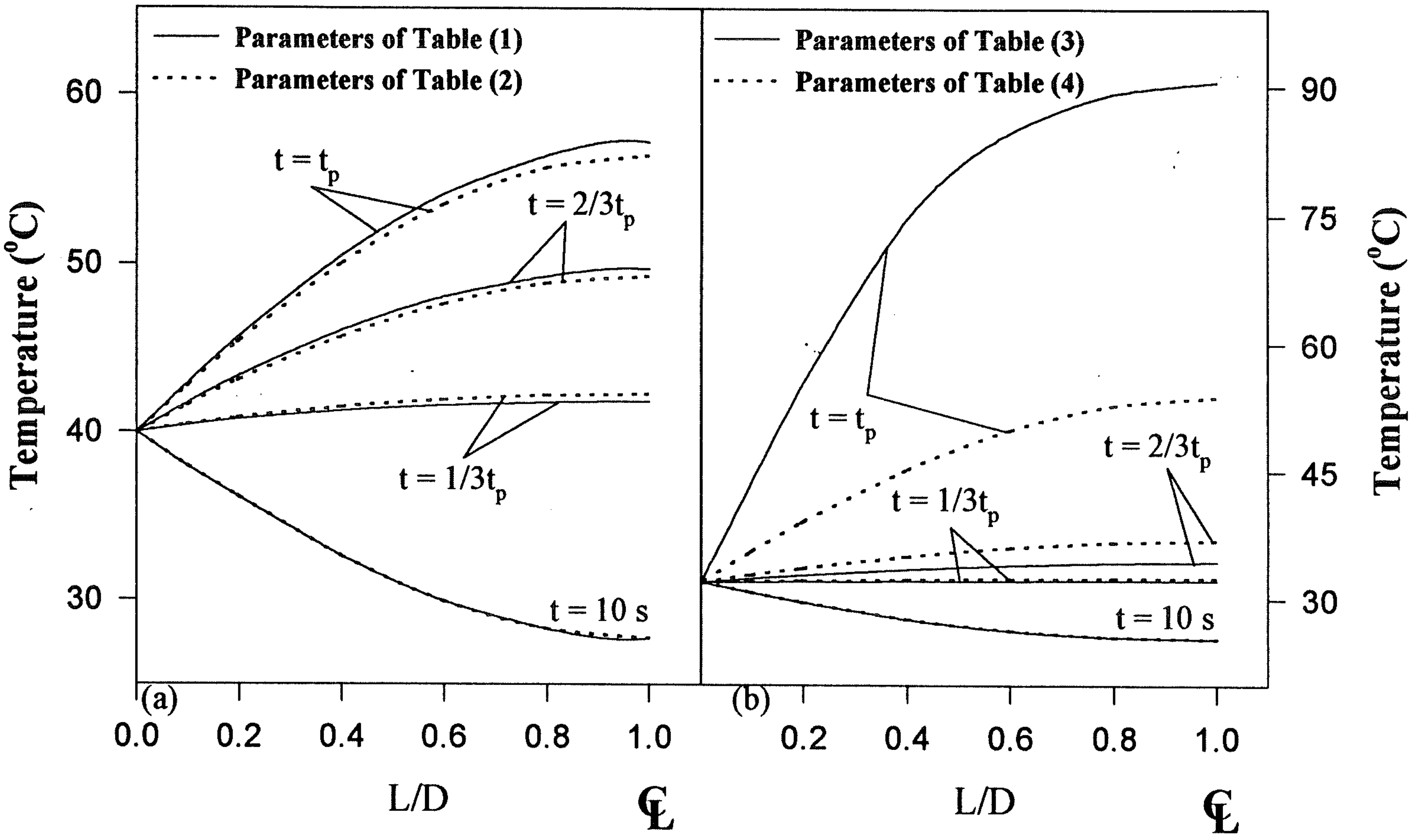

Fig. 5.4 Corresponding transient temperature profiles through the thickness of reinforced parts up to the peak time, obtained for figures **3(a)** and **3(b).** The molding conditions are the same as figures **3(a)** and **3(b)**.

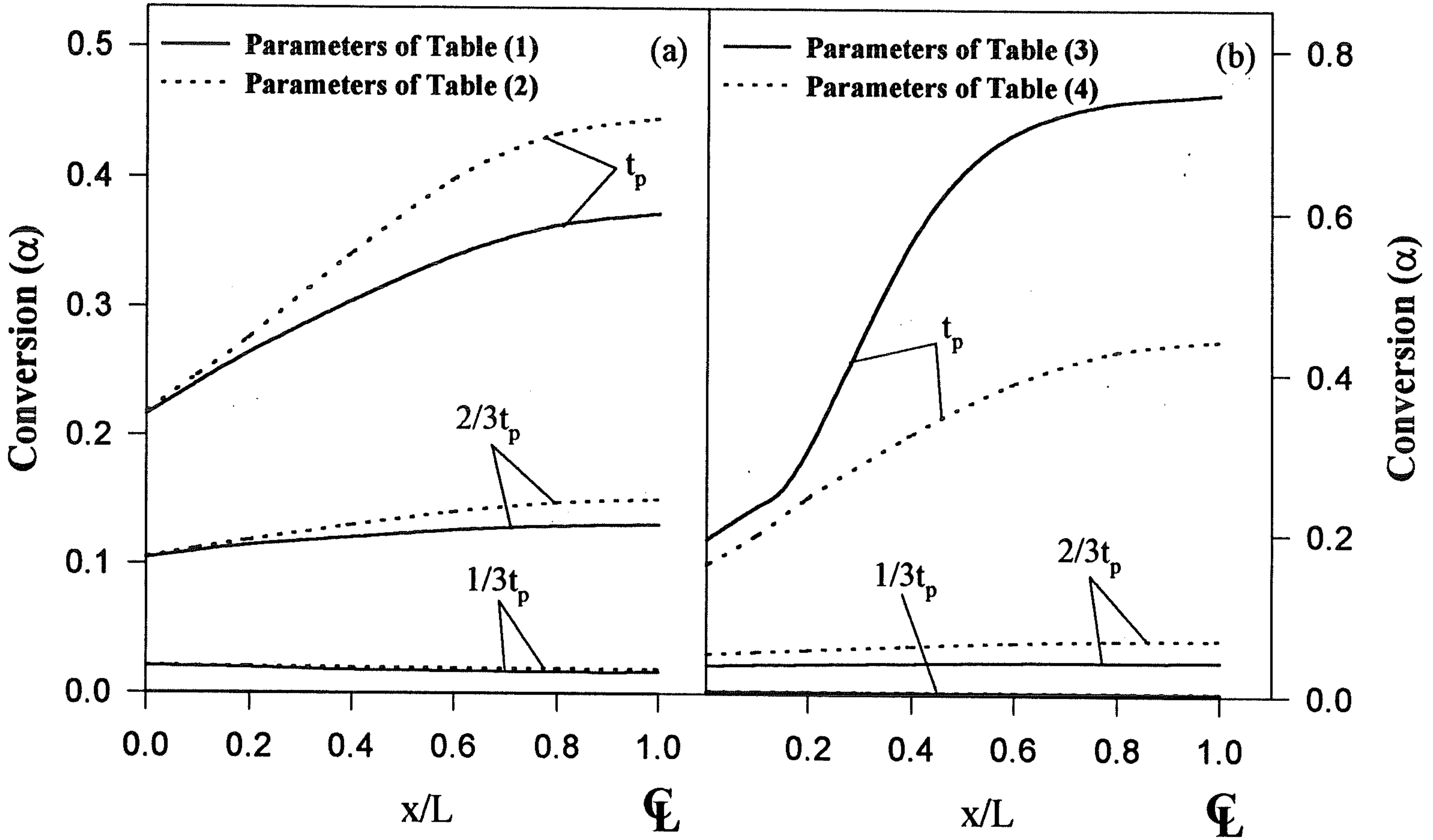

Fig. 5.5 Corresponding transient extent of cure profiles through the thickness of reinforced parts up to the peak time, obtained for figures **3(c)** and **3(d)**. The molding conditions are the same as figures **3(c)** and **3(d)**.

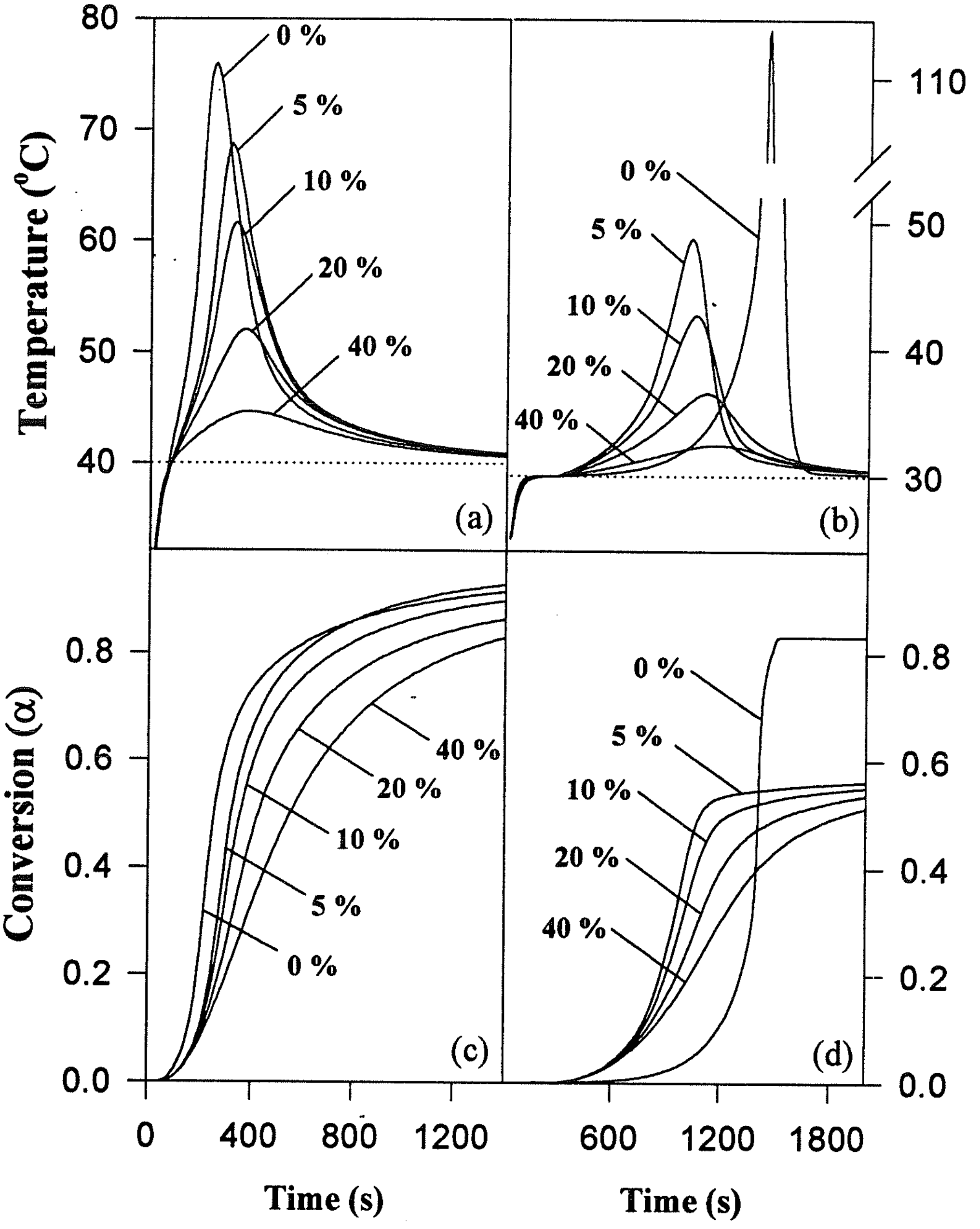

Fig. 5.6 The effect of fiber content on the centerline temperature and extent of cure for: **(a)** and **(c)** Polyester parts. Part thickness = 8 mm; T_0 = 25 °C; T_w = 40 °C.

(b) and **(d)** Vinylester parts. Part thickness = 7 mm, T_0 = 25 °C; T_w = 30 °C. Numbers indicate fiber content in vol%.

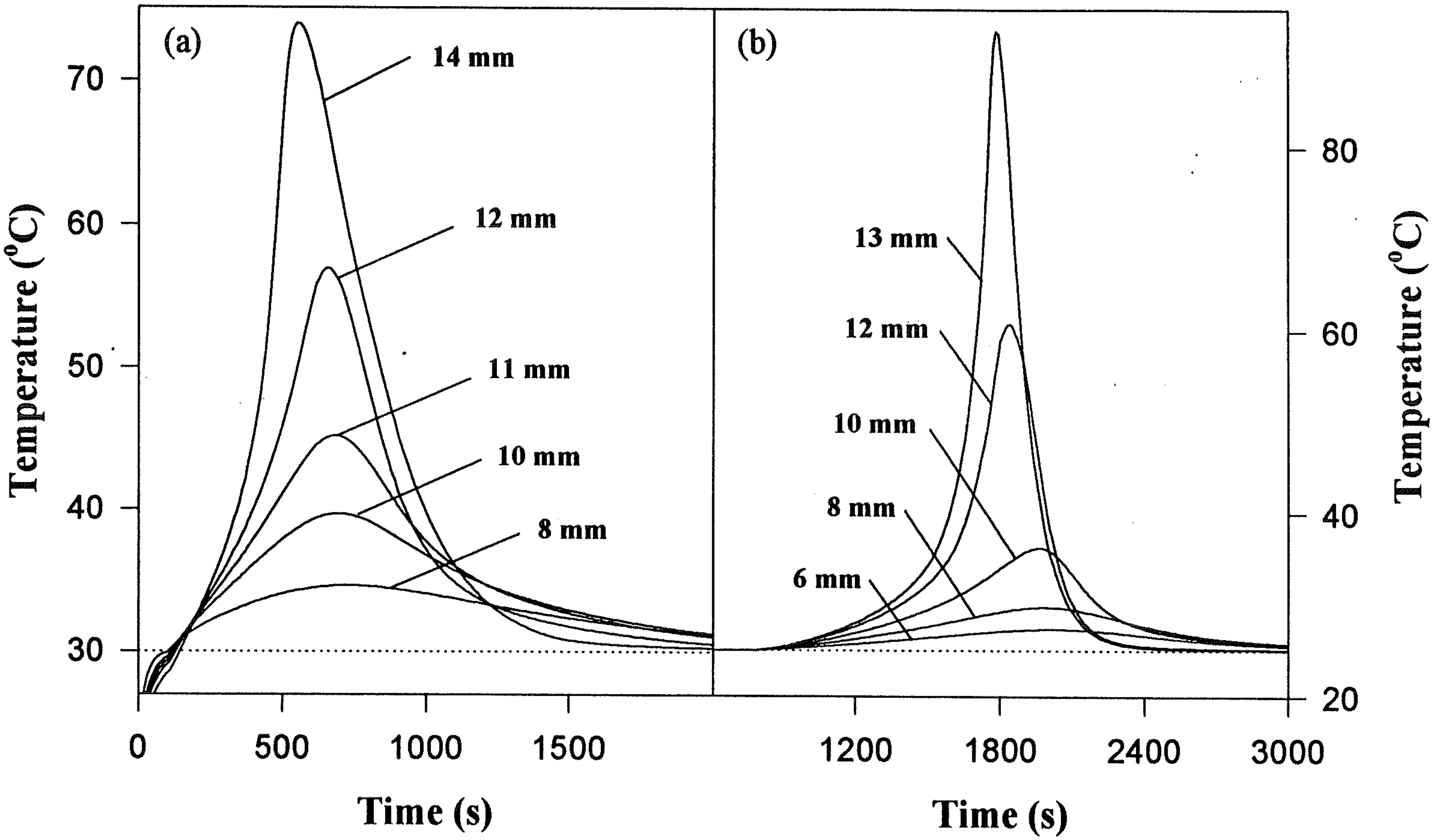

Fig.5.7 The influence of slab thickness on the centerline temperature of:

(a) Polyester Parts containing 15 vol% of glass fiber reinforcement; $T_0 = 25$ °C; $T_w = 30$°C.

(b) Vinylester Parts containing 20 vol% of glass fiber reinforcement; $T_0 = T_w = 25$ °C.

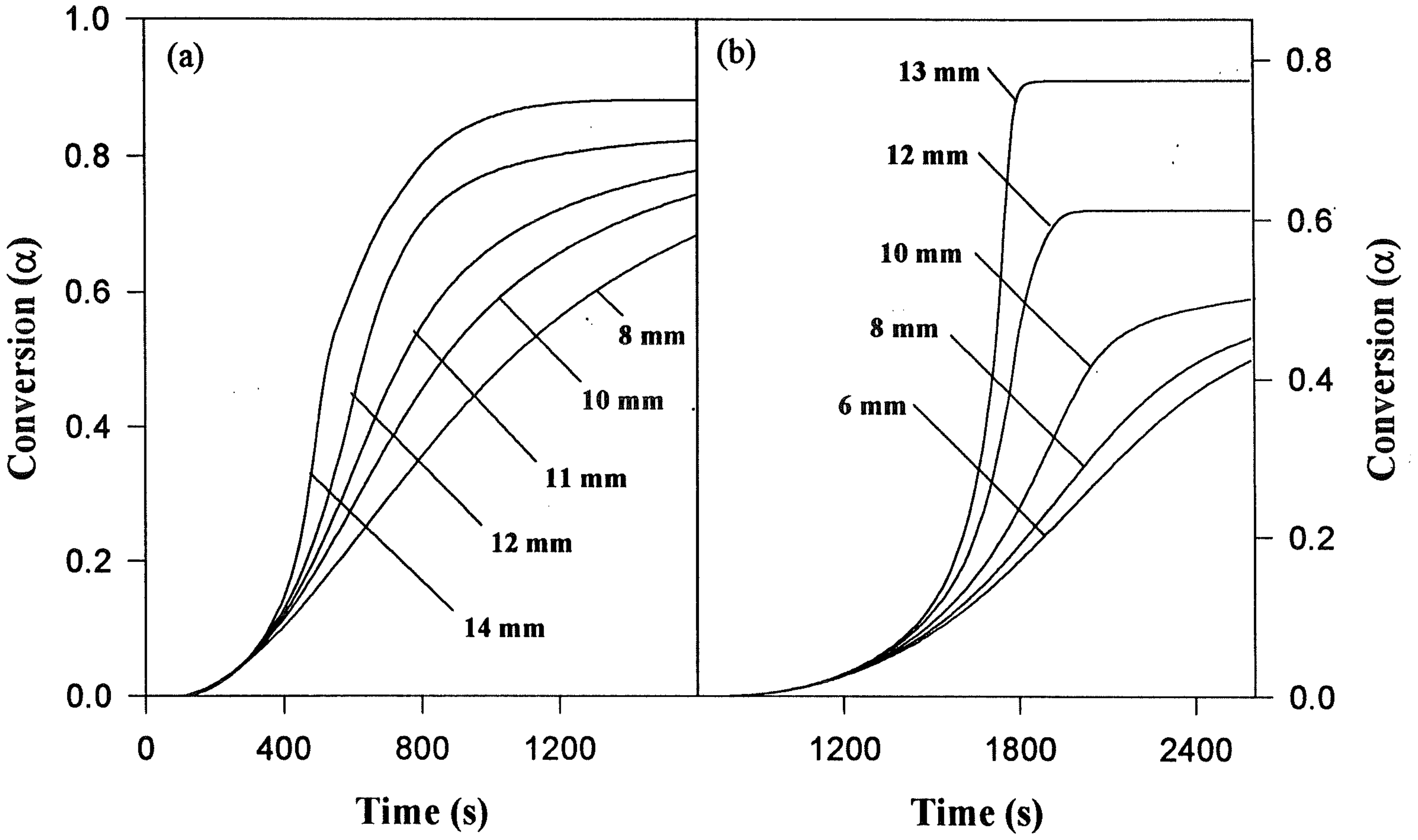

Fig. 5.8 The influence of part thickness on the centerline conversion profile of:
(a) Polyester parts containing 15 vol% of glass fiber reinforcement; $T_0 = 25°C$; $T_w = 30°C$.
(b) Vinylester parts containing 20 vol% of glass fiber reinforcement; $T_0 = T_w = 25\ °C$.

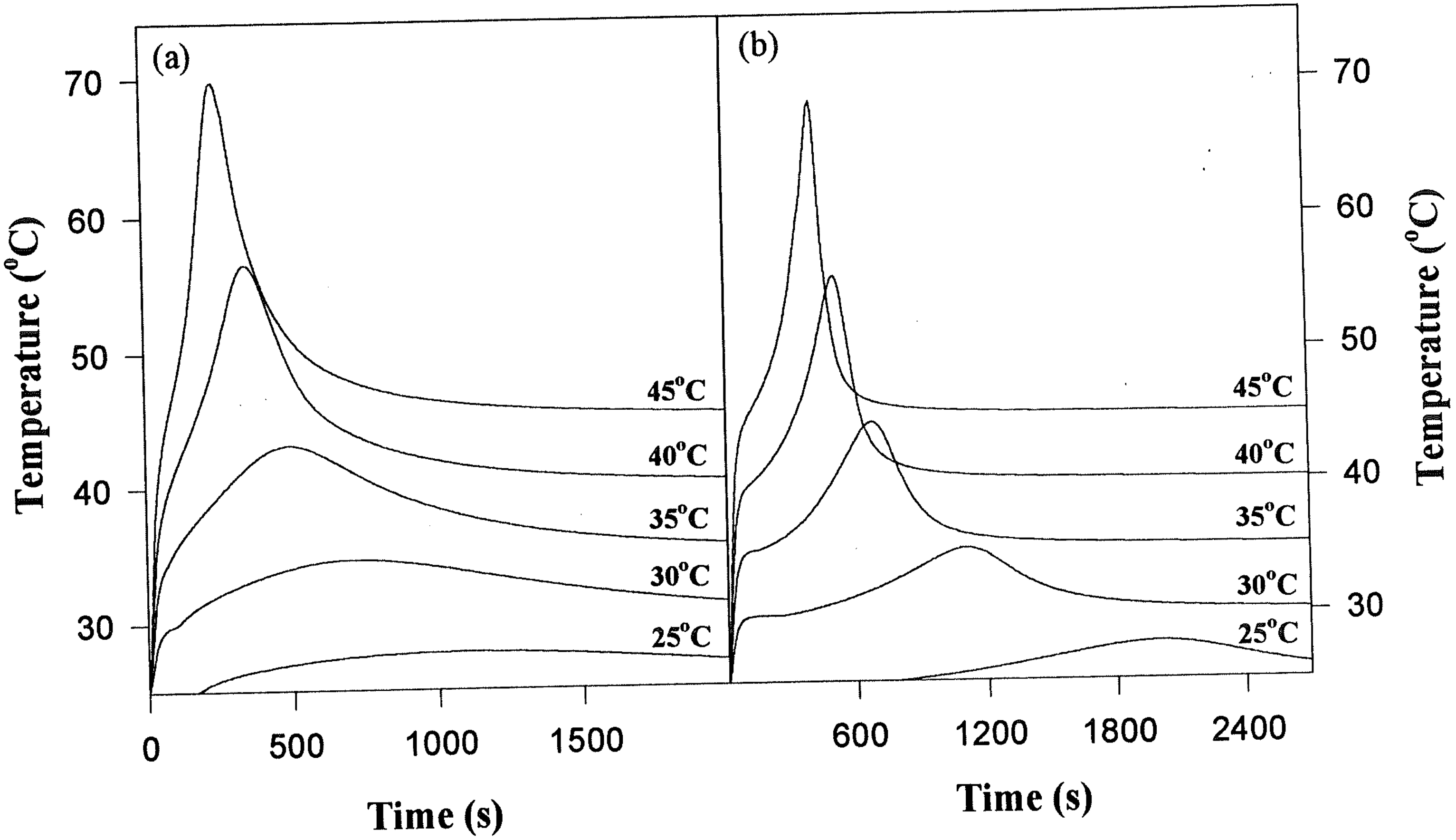

Fig. 5.9 The influence of mold wall temperature on the centerline temperature profile of:
(a) Polyester parts containing 15 vol% of glas fiber reinforcement; part thickness = 8 mm;
(b) Vinylester parts containing 15 vol% of glass fiber reinforcement; part thickness = 6 mm;
T_0 = 25 °C. Numbers represent mold wall temperature.

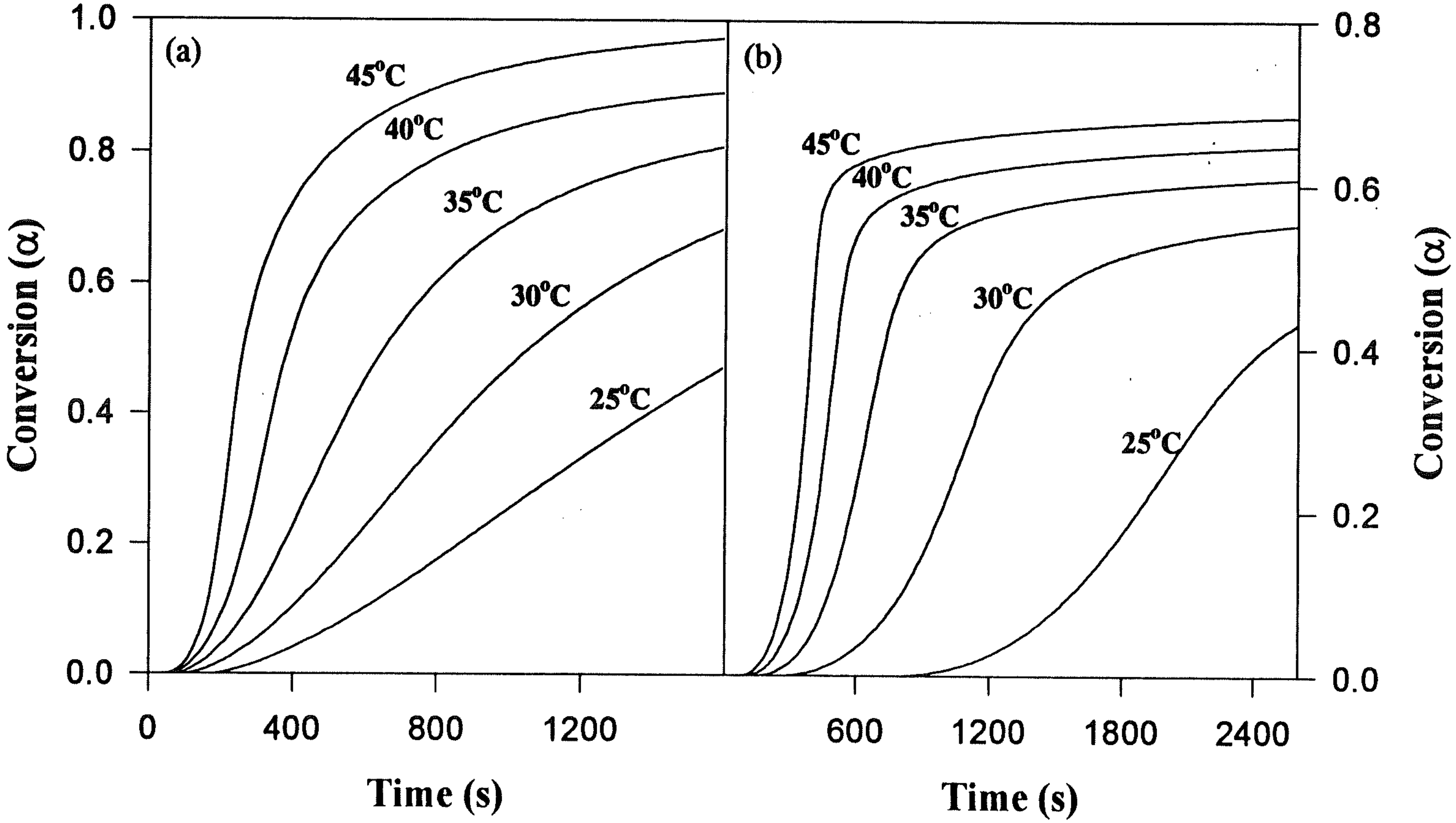

Fig. 5.10 Influence of mold wall temperature on the centerline conversion profile of:
(a) Polyester parts containing 15 vol% of glass fiber reinforcement; part thickness = 8 mm
(b) Vinylester parts containing 15 vol% of glass fiber reinforcement; part thickness = 6 mm. T_0 = 25 °C. Numbers represent mold wall temperature.

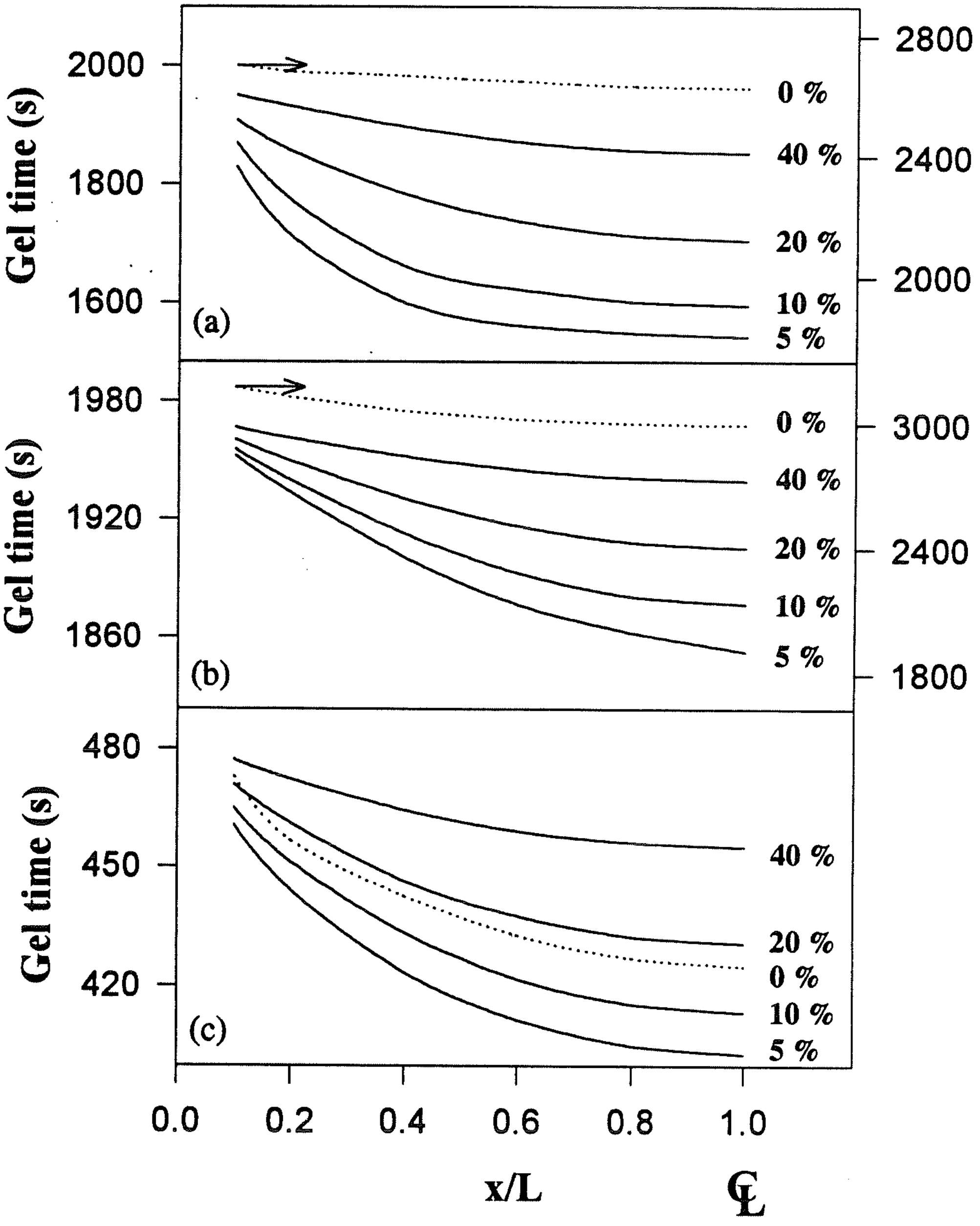

Fig. 5.11 Influence of part thickness (**a** and **b**) and mold wall temperature (**b** and **c**) on the gel time of vinylester parts containing various amounts of reinforcement.

(**a**) Part thickness = 11 mm (**b**) Part thickness = 6 mm; T_w = 25 °C.

(**b**) T_w = 25 °C (**c**) T_w = 40 °C; Part thickness = 6 mm.

T_0 = 25 °C. Numbers represent fiber content in volume percent.

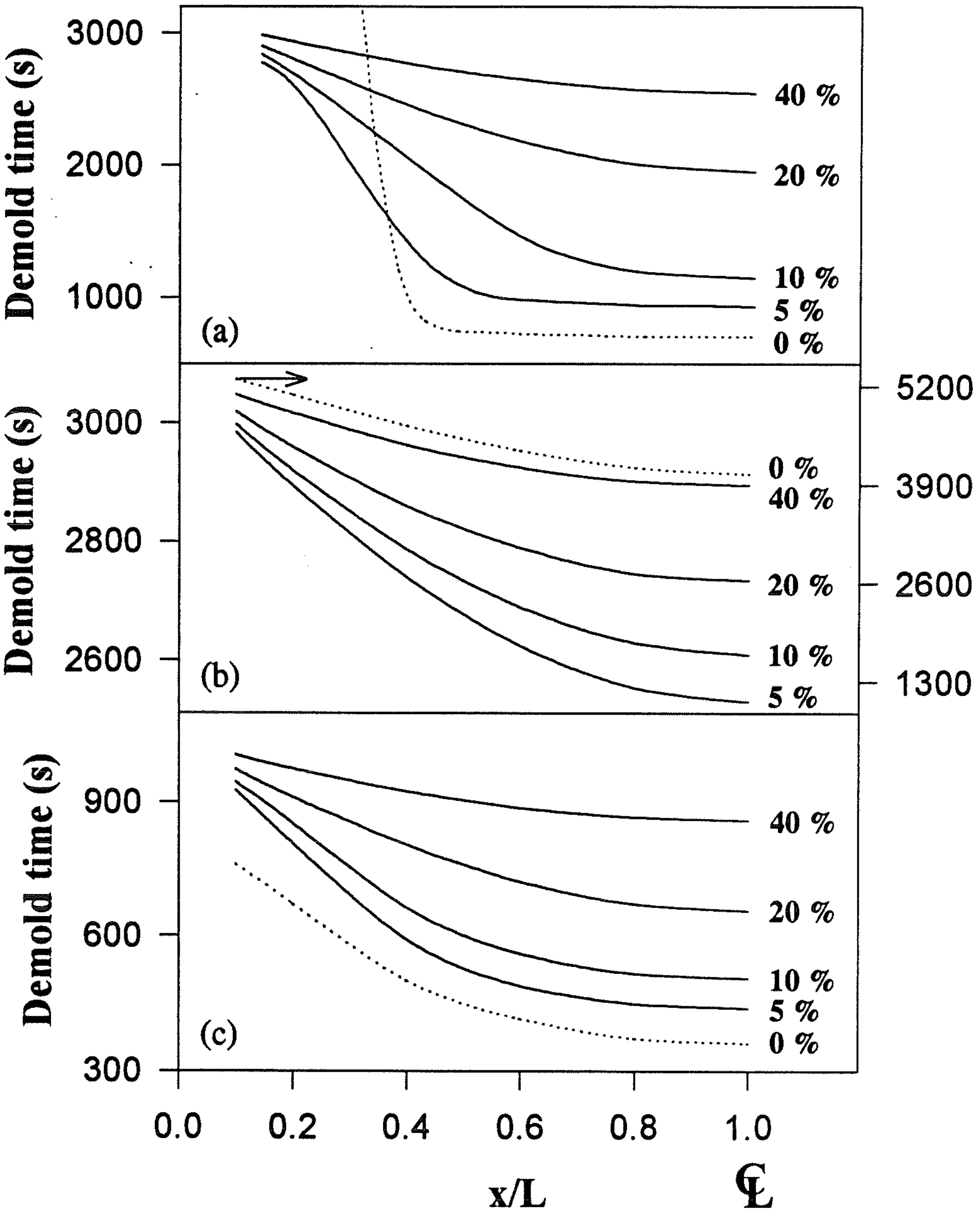

Fig. 5.12 Influence of part thickness (**a** and **b**) and mold wall temperature (**b** and **c**) on the demold time of polyester parts containing various amounts of reinforcement.

(**a**) Part thickness = 13 mm (**b**) Part thickness = 8 mm; T_w = 25 °C.
(**b**) T_w = 25 °C (**c**) T_w = 40 °C; Part thickness = 8 mm.
T_0 = 25 °C. Numbers represent fiber content in volume percent.

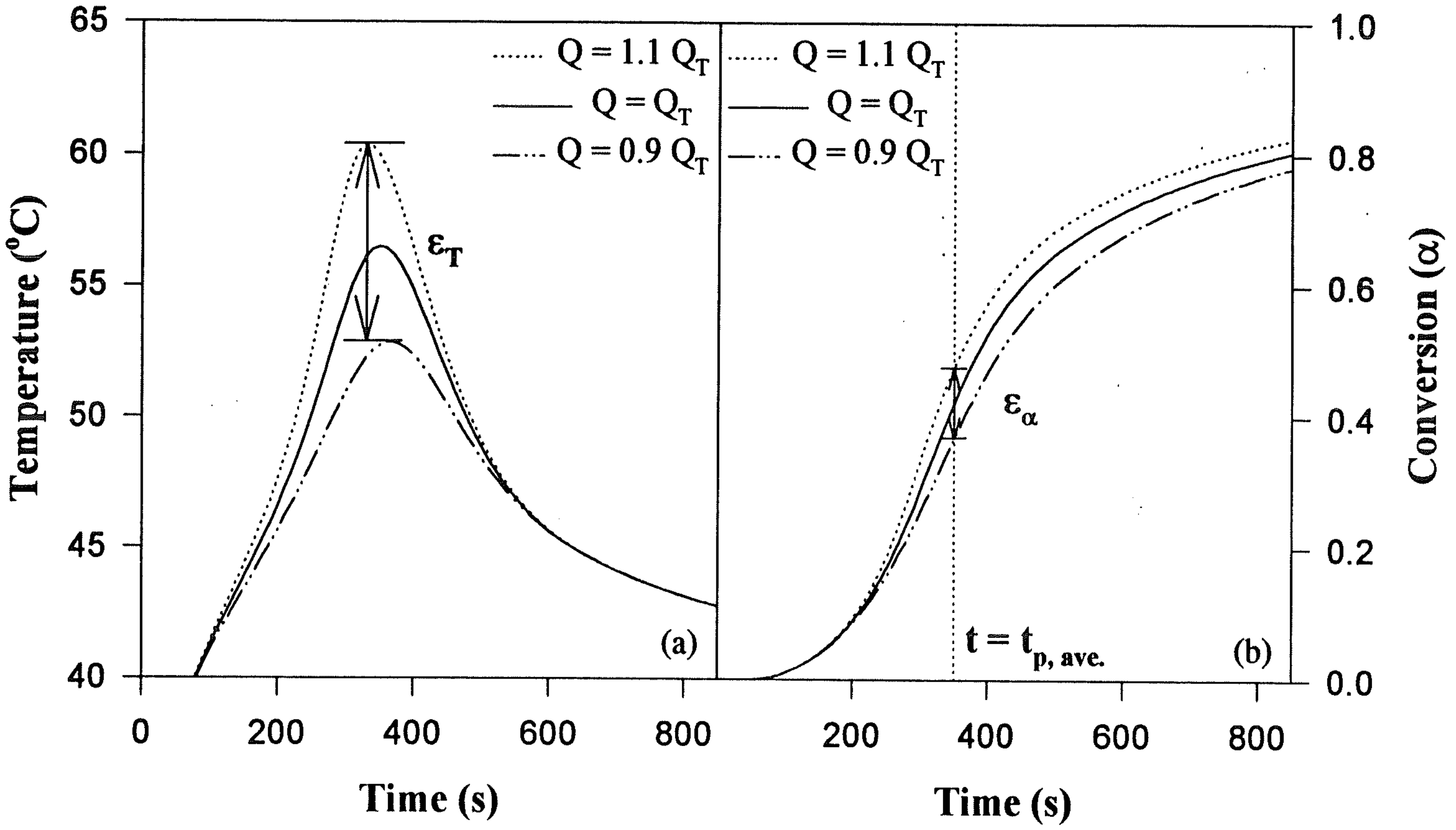

Fig. 5.13 Demonstration of error resulted in estimation of (a) temperature profile and (b) conversion profile at the centerof the part by inducing an arbitrary error in the evaluation of isothermal heat of cure for a polyester system.
T_0 = 25 °C; T_w = 40 °C; part thickness = 8 mm; fiber content = 15 vol %; $\varepsilon = 10\%\ Q_T$.

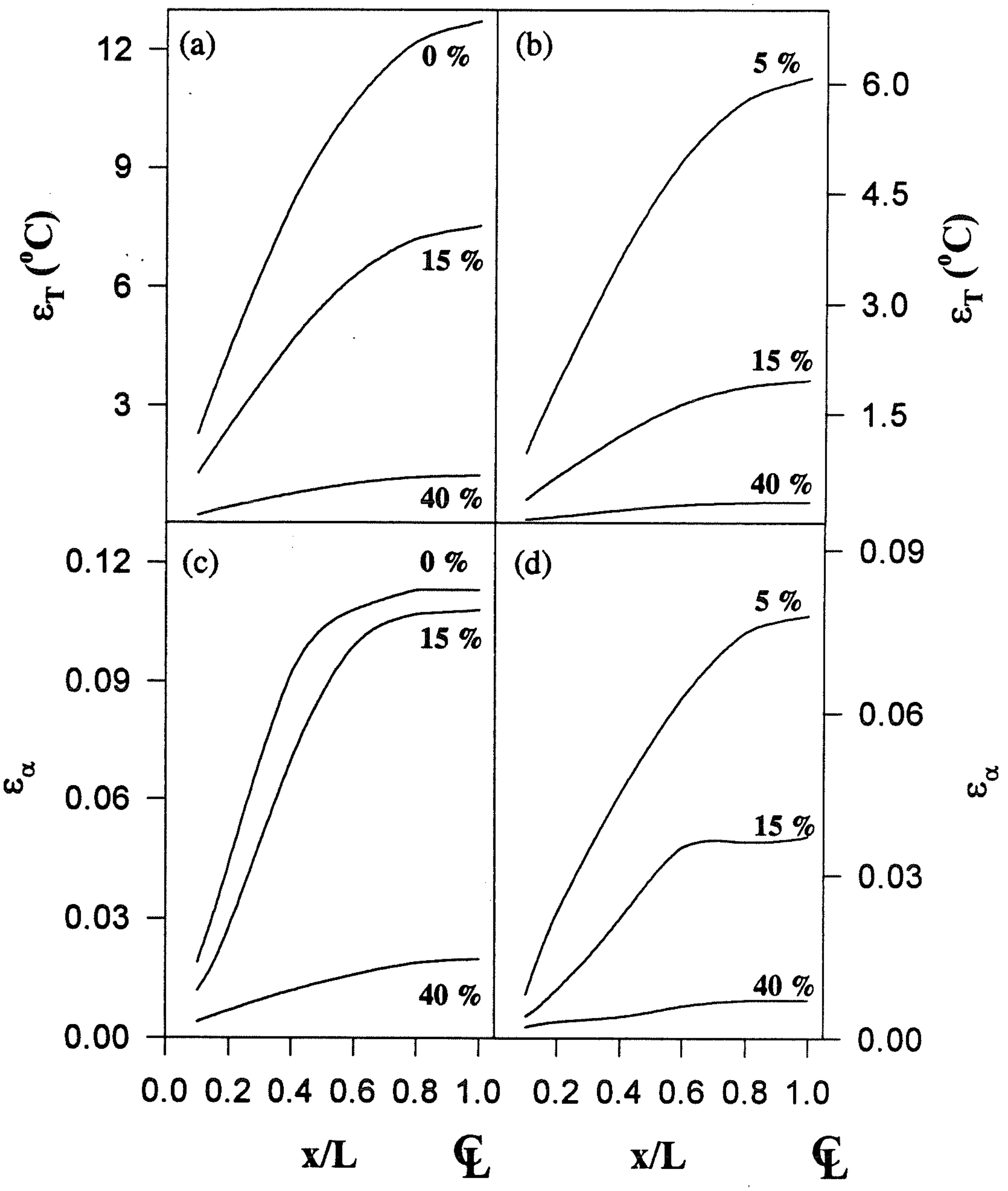

Fig. 5.14 Influence of the induced error in isothermal heat of cure, ε, on the extent of error resulted in the estimation of temperature and conversion at the peak, through the thickness of the part. T_0 = 25°C

(a) & (c) Polyester parts; T_w = 40°C; part thickness = 8 mm; ε = 10 % Q_T.

(b) & (d) Vinylester parts; T_w = 30°C; part thickness = 7 mm; ε = 5 % Q_T.
Numbers represent fiber content in vol %.

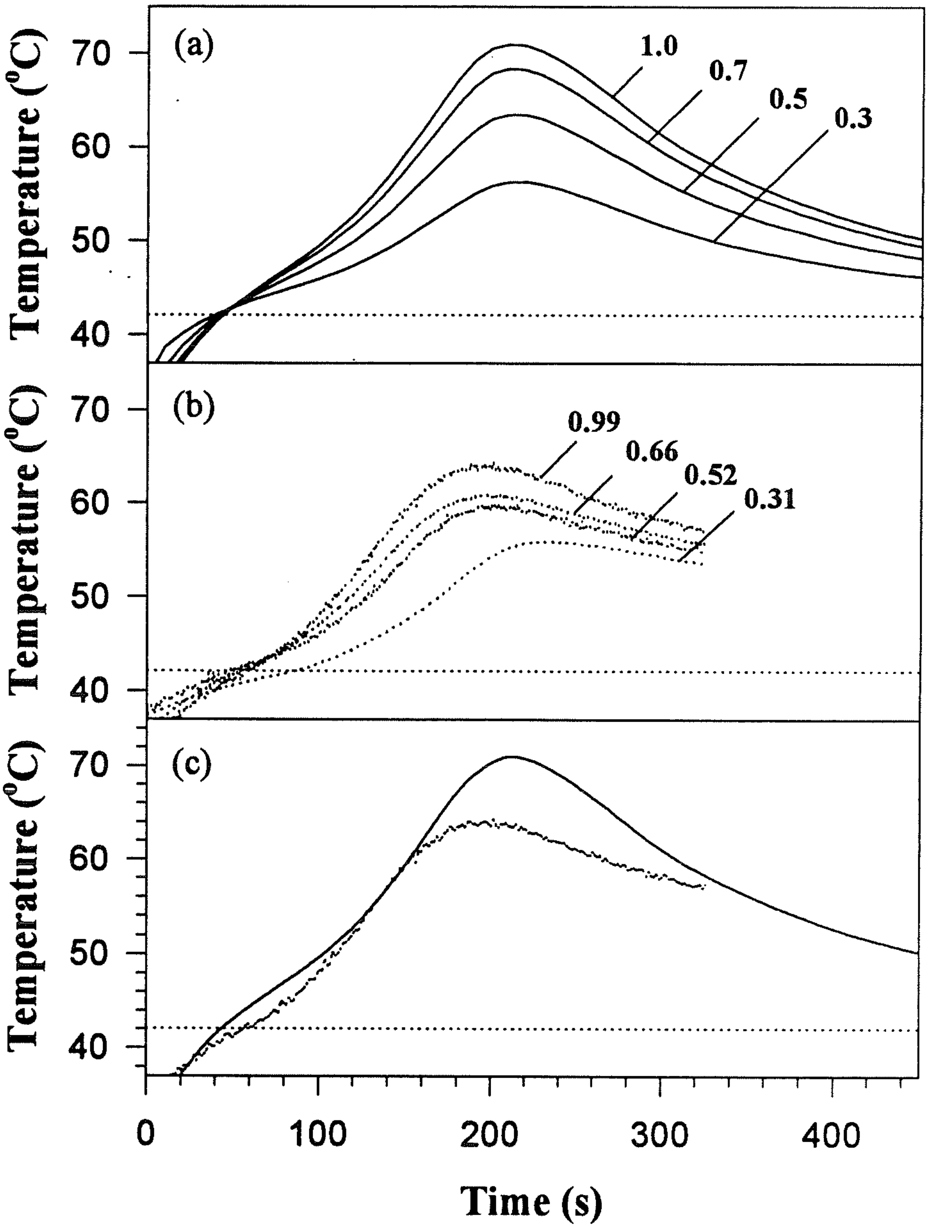

Fig. 5.15 Temperature profiles in different locations through the thickness of a polyester part. Fiber content=15 vol%; part thickness = 9 mm; T_0 = 25 °C; T_w = 42.1°C

(a) Numerical results. **(b)** Experimental results obtained in a heated mold. **(c)** Comparison of numerical results and experimental data at the centerline. Numbers represent distance from mold wall (x/L).

GENERAL DISCUSSION

The kinetic parameters of the cure reactions were estimated by conducting isothermal DSC measurements. In the present work, a new procedures was implemented to account for the unrecorded extent of cure during stabilization period of the calorimeter. This procedure attempted to estimate the kinetic parameters in a certain way to predict the Q_{M1}, instead of Q_{M2}, in Figs. 3.2-a and 3.2-b. It was also assumed that the first kinetic parameter, α_{max}, increased with cure temperature, passed through a maximum value, then decreased. To demonstrate the ability of the developed procedure, the results predicted using this procedure were compared with the predictions of an ordinary estimation procedure, where no attempt is made to correct for the unrecorded part of the cure exotherm.

To account for the complexity of the cure reactions in the presence of the promoter, the kinetic parameters of both promoted systems were considered temperature dependent. The temperature dependency of reaction exponents for the promoted polyester resin in Fig. 3.4-a was expressed using Eqs. 3.12 and 3.13. In spite of relatively complex variation of the reaction exponents, these expressions asymptotically approached the reaction exponents for nonpromoted polyester systems. The temperature dependency of kinetic parameters was attributed to the way a promoter affects the cure mechanism. The cure reactions in the presence of the promoter can be chemically (at low temperatures) or thermally (at high temperatures) induced. Therefore, a variable cure mechanism justifies the existence of different kinetic parameters in different temperature ranges. On the other hand, the kinetic exponents of the filled polyester samples were assumed to follow an Arrhenius temperature dependency. The comparison between Figs. 3.4-a and 3.4-b indicates that the incorporation of glass fibers in the promoted polyester system does not appreciably affect the reaction exponents at temperatures below 60°C. This implies that the effect of the promoter on the cure reactions was probably more significant than the potential effect of glass fibers.

The Arrhenius plots of reaction rate constants *versus* reciprocal cure temperature for the promoted polyester resin, Fig. 3.5-a, indicates that the presence of the promoter causes a significant increase in the rate constant at temperatures below 60°C; whereas, at higher temperatures a considerable decrease is observed. Fig. 3.5-a also shows that at low temperatures, the value of Arrhenius frequency factor for glass fiber filled samples is somewhat lower than that of unfilled ones. This decelerating effect was attributed to the inorganic radicals produced in the cure system. On the basis of experimental results, it was also found that the incorporation of glass fibers in the cure system at low temperatures, up to 60°C, caused a longer induction period of cure.

Fig. 4.4 demonstrates a significant discrepancy between the experimental data and the expected bell-shaped rate profile predicted by Eq. 4.1 for the promoted vinylester resin. Experimental cure data also indicated that the magnitude of this deviation was strongly dependent on the cure temperature. This behavior suggested that an additional kinetic parameter accounting for the deviation of cure exotherm from a bell-shaped rate profile should be introduced in Eq. 4.1. Consequently, Eq. 4.2 was used to predict the cure behavior of the vinyl ester resin in the presence of the promoter.

The temperature dependency of reaction exponents for the promoted vinylester resin in Fig. 4.6 was expressed using Eqs. 4.11 to 4.13. In spite of the relatively complex form assigned to the reaction exponents, at elevated temperatures these expressions asymptotically approached the reaction exponents of non-promoted vinylester systems. For the glass fiber filled vinylester samples, Fig. 4.6 to 4.8 show that the first reaction exponent, m, is a constant value independent of cure temperature, and the two other exponents, n and p, show linear dependencies with cure temperature up to 60°C and become temperature independent at higher temperatures. These major differences between unfilled and glass fiber filled systems were mainly attributed to counterbalancing of the acceleration effect caused by the promoter and the deceleration effect of glass fibers. To represent the variation of viscosity during the cure period of the promoted vinylester resin, Eq. 4.4 was modified to account for the acceleration effect of the promoter particularly at the start of cure (see Eq. 4.18).

Figs. 5.1 and 5.2 give the plots of estimated rate of conversion and extent of cure for the promoted polyester and vinylester resins, respectively. It can be seen that the inhibition effect of glass fiber reinforcement on the cure behavior of the promoted polyester resin is not significant; however, a severe inhibition of cure is observed in the case of promoted vinylester resin at high extent of cure (*e.g.* $\alpha > 0.5$). The centerline temperature and conversion profiles for polyester and vinylester parts containing 15 vol% of reinforcement are shown in Fig. 5.3. These profiles were obtained by applying the two different sets of kinetic parameters estimated for unreinforced and glass fiber reinforced systems (see tables 5.1 to 5.4). Comparing the temperature profiles in Fig. 3-b, obtained for vinylester composites, indicates that the set of kinetic parameters estimated for the unreinforced cure system significantly overestimate the heat evolution in the center of a reinforced composite part. As a consequence, applying a specialized kinetic model accounting for the inhibition effect of glass fibers is necessary in the modeling of composite manufacturing processes. The significant difference between the two predicted curves was attributed to the production of inorganic free radicals which lack adequate reactivity to initiate other radicals at low temperatures. Since oxide surfaces inhibit free radical polymerization by terminating growing chains, the significant inhibition of cure in the case of vinylester resin was found to be due to the surface treating agent of the reinforcement which was formulated for a polyester resin. The centerline temperature rise and cure profiles in Figs. 5.6-a to 5.6-d indicate that the peak temperature decreases due to the presence of glass fibers, and it is delayed because the thermal conductivity of the polymer is smaller than that of glass fibers.

A sensitivity analysis was performed based on the variation of the isothermal heat of cure. The extent of resulting error in the estimation of temperature and conversion profiles, shown in Figs. 5.14-a to 5.14-d, indicate the importance of precision and accuracy in evaluation of isothermal heat of cure. In order to verify the versatility of the applied kinetic models throughout this work, the temperature evolution during the curing phase of the promoted polyester resin was measured by conducting some molding experiments in a RTM mold. It was stated that a better agreement could be obtained between numerical predictions and experimental data in Fig. 5.15 if better kinetic information was available for the reinforced polyester system at temperatures higher than 55°C. Moreover, the limited precision of thermocouples in recording sudden temperature changes was found partly responsible for the observed discrepancy.

CONCLUSION

Thermosetting resins frequently used in engineering composites contain a variety of additives, including promoters and fillers. Since the molding time of a composite part is mainly determined by the resin formulation, understanding the influence of different additives on the kinetics of cure is of great importance in mathematical modeling of composite manufacturing processes. By combining the impregnation model with the specialized cure model, a prediction can be made for temperature history of the entire cycle.

In the present work, a new estimation procedure, compensating for the unrecorded part of the cure exotherm at high temperatures, was implemented to evaluate the kinetic parameters of the cure reactions. The effects of both promoter and glass fibers on the cure kinetics of polyester and vinylester resins were discussed with regard to the changes in the kinetic parameters. In spite of the fact that nonpromoted polyester and vinylester resins show constant kinetic parameters, in the case of the promoted resins, kinetic parameters were considered temperature dependent to account for the complexity of the cure mechanism in the presence of the promoter. It was found that this complexity was caused by the promoter which chemically induced the cure reactions at low temperatures. Our results also indicated that the sum of reaction exponents was not a constant value due to the changes caused by the promoter in the cure characteristics of the polyester and vinylester systems. Moreover, the total isothermal heat of reaction was almost identical for both filled and unfilled promoted polyesters.

On the basis of estimated kinetic data in Chapter 3, it was found that at low temperatures, below 60°C, the essential role of the promoter was to increase the overall reaction rate of the polyester resin through the Arrhenius frequency factor. The promoter also affected the reaction exponents in the entire temperature range. The primary effect of the glass fibers on the curing behavior of the promoted polyester resin was a slight decrease in the overall reaction rate at low cure temperatures. Acting as heat sinks, glass fibers absorbed the heat of reaction, and yielded a longer induction period of cure at temperatures below 60°C. Unlike promoter, glass fibers did not appreciably affect the reaction exponents.

At temperatures above 60°C, a significant decrease was noticed in the reaction rate constant of the promoted polyester resin through the changes in both the Arrhenius frequency factor and the activation energy of cure. The reaction exponents, m and n, asymptotically approached the values reported in the literature for nonpromoted polyester systems. For glass-fiber-incorporated samples, some increase in the reaction rate constant was observed. This event was attributed to the inorganic free radicals produced in the presence of glass fibers which were adequately active at high cure temperatures.

It was shown that for promoted vinylester resins, the mechanism of cure was too complicated to be presented by an ordinary autocatalytic kinetic model. To take into account the deviation of cure exotherm from the bell-shaped profile, caused by the addition of the promoter, a modified kinetic model was used in Chapter 4 to represent the cure behavior of the promoted vinylester resin. The latter model introduced an additional rate exponent, accounting for the complexity of the cure reactions. The estimated kinetic parameters for the cure system of the promoted vinylester resin revealed a temperature dependent characteristic within the temperature range studied in this work (25-90°C). This characteristic was attributed to the different cure mechanisms governing in different temperature ranges. The effect of promoter was found to be more pronounced at low temperatures where the cure reactions were chemically induced. The temperature dependent kinetic parameters in the presence of the promoter are also reported in the literature.

By incorporation of glass fiber reinforcement to the cure formulation of vinylester resin, a severe inhibition of cure was observed. This inhibition was attributed to the high population of inorganic radicals produced in the presence of glass fibers. It was also pointed out that a proper selection of surface treating agent could overcome the inhibition of cure caused by oxide surfaces in the case of glass fiber reinforced composites. Consequently, the inhibition was attributed to the sizing agent of the reinforcement which was formulated for a polyester resin. Comparing the results obtained for the polyester and vinylester resins in the presence of the glass fibers with the results reported in the literature indicates that the inhibition of cure caused by the glass fibers is generally manifested in some modifications in the reaction rate constant. In the case of the promoted vinylester resin, the significant decrease in the ultimate heat of cure for the glass fiber reinforced samples is in good agreement with the results reported in the literature for the inhibition of cure caused by an unproper surface treating agent.

A modified chemorheological model accounting for the accelerating effect of the promoter was introduced. Two sets of values were assigned to the rheological parameters from the onset of reaction up to the gel point. It was inferred that a chemorheological model with conversion dependent activation energy was able to represent adequately the chemoviscosity of a promoted system.

A one-dimensional numerical analysis for the post-filling phase of RTM process was presented in Chapter 5. The kinetic parameters estimated with regard to the influence of the cobalt-based promoter and glass fiber reinforcement were used in the numerical analysis. The influence of these additives on the process variables, such as cure time and demold time, and on the distributions of temperature and extent of cure was studied in through-the-thickness direction. It was shown that in the case of promoted vinylester resin, the presence of glass fibers gave rise to lower cure exotherms inside the composite part. The delayed exotherm peak in reinforced polyester parts was mainly attributed to the thermal effects induced in the presence of glass fibers.

Numerical results and experimental data were compared for a reinforced polyester part cured in a heated mold. The discrepancy between the theoretical and experimental results was attributed to some uncertainties associated with the estimation of kinetic parameters at high cure temperatures as well as to the delay time of thermocouples in response to sudden temperature changes. It was established that in the case of reinforced promoted vinylester composites, containing an unproper sizing agent, the set of kinetic parameters accounting for the inhibiting effect of glass fibers should be used in composite manufacturing processes.

The parameter estimation procedure applied in the present work was found to be reliable for evaluation of kinetic parameters. Considering the complexities involved in the cure process of promoted thermosetting resins, it was recommended to express the temperature dependency of kinetic parameters in a precautious manner to obtain reasonable values outside the temperature range in which the cure data were acquired.

RECOMMENDATIONS

On the basis of the results obtained in the present work, there are some areas that are worth further investigation.

1. Introducing a proper transformation technique to estimate the kinetic parameters from transformed dynamic DSC cure data in order to avoid time consuming isothermal measurements.

2. Extending the procedure developed in the present study to higher temperatures by applying the expressions recommended in Chapter 5 to represent the temperature dependency of the kinetic parameters.

3. Extending the DSC cure data to include the effect of the quantity of reinforcement in the developed kinetic models.

4. Investigating the effect of the promoter at different temperatures on the chemoviscosity of the promoted systems by incorporating an inhibitor in the cure formulation allowing the viscosity measurements at elevated temperatures.

5. Validating the versatility of the modified chemorheological model applied in Chapter 4

over a wide temperature range.

6. Evaluating the variation of the thermo-physical properties with the progress of cure by applying proper measuring techniques.

7. Conducting a sensitivity analysis on the estimated kinetic parameters and thermo-physical properties to evaluate the effect of ignoring their temperature, or conversion, dependencies on distributions of temperature and cure and on the estimated gel time and demold time inside a molded part.

8. Verifying the practical aspects of applying temperature dependent parameters by examining the time consumed to estimate the distributions of temperature and cure inside a molded part by a well-established program.

CLAIMS FOR ORIGINAL WORK

The present study represents the original contributions to the understanding of the different aspects affecting the post-filling phase of the RTM process. These contributions may be summarized as follows:

1. The extensive review of the literature in Chapter 2 indicates that previous works have generally ignored the acceleration and inhibition aspects of the promoter and glass fiber reinforcement. The realistic kinetic models derived in the present work describe adequately the role of the promoter in the cure system as well as the inhibition of cure caused by the formulation of the glass fiber reinforcement.

2. The main uncertainty associated with the DSC cure data is the weakness of this technique in recording the first part of the cure exotherm during the stabilization period of the calorimeter at high temperatures. Since the accelerating effect of a promoter is more pronounced at low temperatures particularly at the beginning of the cure period, the ordinary parameter estimation procedures are not capable of accounting for the unrecorded part of the cure exotherm. The new procedure implemented in the present study fulfil this task by introducing a well-defined correction factor.

3. The new way of expressing the temperature dependency of the kinetic parameters allows

the prediction of the kinetic parameters at high temperatures where the accelerating effect of the promoter is less pronounced.

4. In Chapter 4 it was demonstrated that the ordinary chemorheological models generally underestimate the viscosity rise at the beginning of the cure period. The modified chemorheological model, applied in Chapter 4, features a conversion dependent activation energy of flow which takes into account the accelerating effect of the promoter at the beginning of the cure.

5. The numerical analysis presented in Chapter 5 is the first work which places the emphasis on the precautious selection of the proper kinetic models, accounting for the individual effects of the additives, by comparing the predicted temperature and cure profiles obtained by each set of the estimated kinetic parameters.

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APPENDIX I

Thermal conductivity measurements

To predict the thermal conductivity of the solid filled polymers numerous theoretical and empirical correlations exist in the literature. In the present work, some of these models were applied to fit the experimental data obtained for polyester composites containing different quantities of the glass fiber reinforcement. The thermal conductivity of the reinforcement was estimated by extrapolating all the applied correlations to 100 % fiber content. Consequently, the estimated values were compared with the values reported in the literature in order to find the most reliable correlation which adequately predicts the thermal conductivity of the reinforcement.

The thermal conductivity measurements were conducted based on the ASTM C177-85 standard by the guarded heat flow meter method. A test sample is placed between two plates controlled at different temperature, resulting in a flow of heat from the hotter to the colder plate. At thermal equilibrium, the Fourier heat flow equation applied to the test stack becomes[1] :

$$R_s = N\frac{T_u - T_l}{Q} - R_o \tag{I.1}$$

---

[1] Thermal Conductivity Analyzer: Operation & Maintenance Manual

where :

R_s	sample thermal resistance
N	proportionality constant
T_l	lower surface temperature
T_u	upper surface temperature
Q	heat flux transducer out put
R_o	contact thermal resistance

The sample thermal resistance is defined as:

$$R_s = \frac{d}{k_s} \tag{I.2}$$

where d is the sample thickness and k_s is its thermal conductivity .

In the present work, flat disk-shaped specimens of cured promoted vinylester and promoted polyester resins with diameter of 50 mm and average thickness of 9 mm were used. The glass fiber reinforced specimens were prepared from the molded parts. The measurements were conducted at an average specimen temperature of 53°C.

Fig. I.1 shows the calibration curve obtained using Pyrex and Vespel as the standards. Each data point in this figure is the average value of at least three measurements. The error bars

Table I.1. Comparison of measured and predicted values of thermal conductivity for the cured resins and glass fiber reinforcement.

Correlation	**Glass fibers**	**Polyester**	**Vinylester**
Rule of mixture, series [66]	0.596	0.194	
Rule of mixture, parallel [66]	2.62e+4	0.208	
Springer-Tsai, square filament [67]	5.64e+4	0.201	
Springer-Tsai, cylindrical filament [67]	0.089	0.203	
Spherical inclusion model [68]	1.180	0.194	
Measured in the present work†	0.94 - 1.04	0.194	0.179

† : In the case of glass fibers, the measured value is adopted from the literature [69].

indicate the extent of error for each set of measurements. Fig. I.2 gives the average thermal conductivity of the specimens as well as the associated error with each set of measurements. In Fig. I.3 the predicted curves for the thermal conductivity of glass fiber reinforced polyester composites obtained by different correlations are illustrated. The extrapolation of the curves to 100% fiber content yields a wide range of thermal conductivity for the glass fiber reinforcement as can be seen in Table I.1. The most reasonable value which is adequately consistent with the reported values in the literature is provided by the spherical inclusion model. Therefore, for the numerical analysis in the present work, the spherical inclusion model was used.

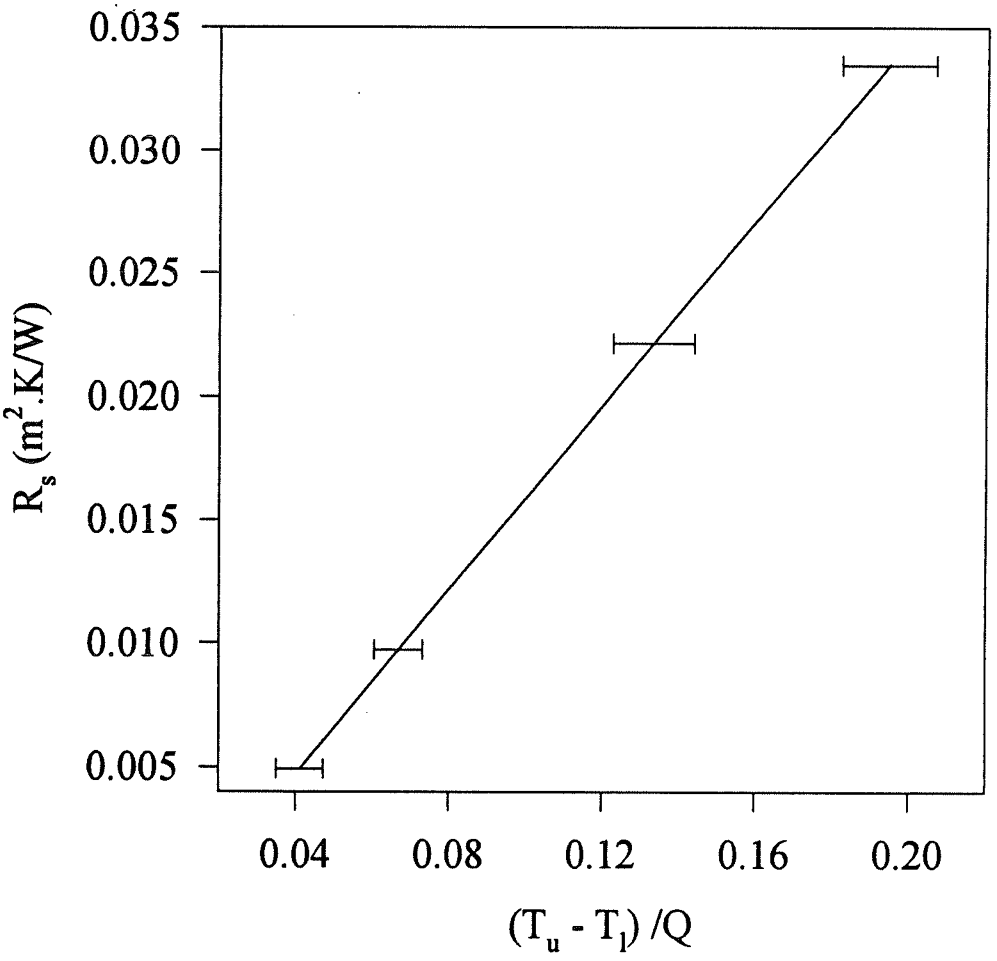

Fig. I.1 Calibration curve constructed using Pyrex and Vespel as the standards. Each data point represent at least 3 measurements.

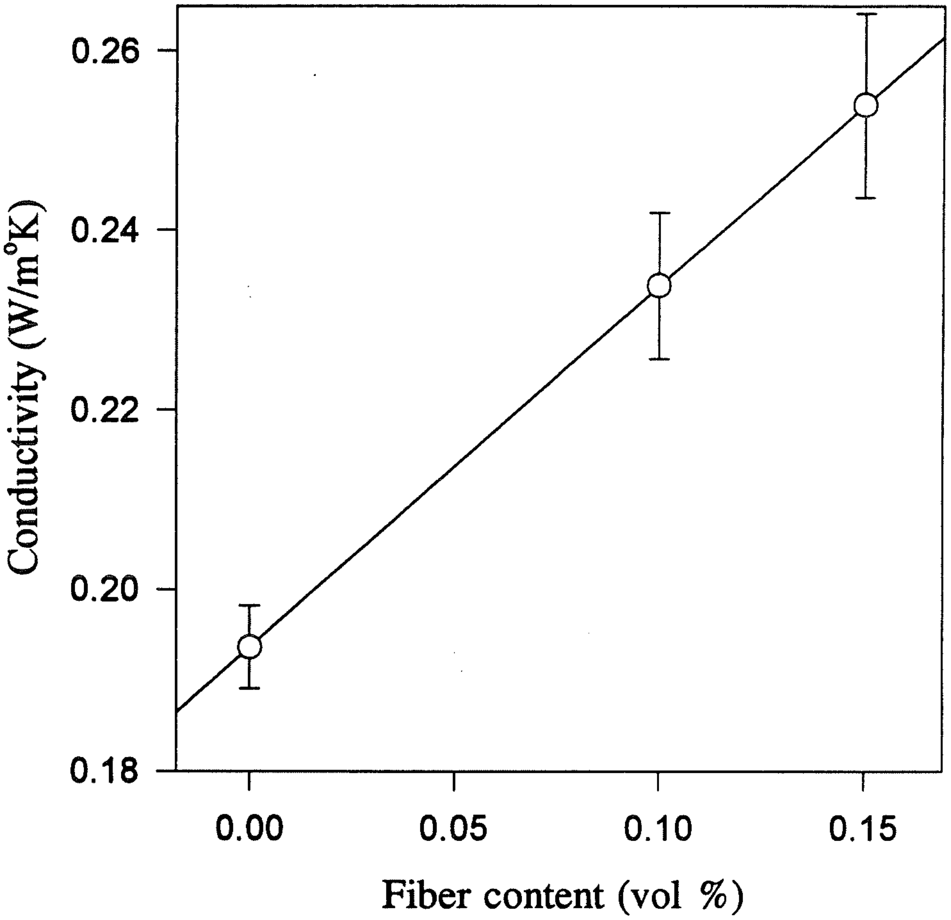

Fig. I.2 Thermal conductivity of polyester composites containing different amount of the glass fiber reinforcement.

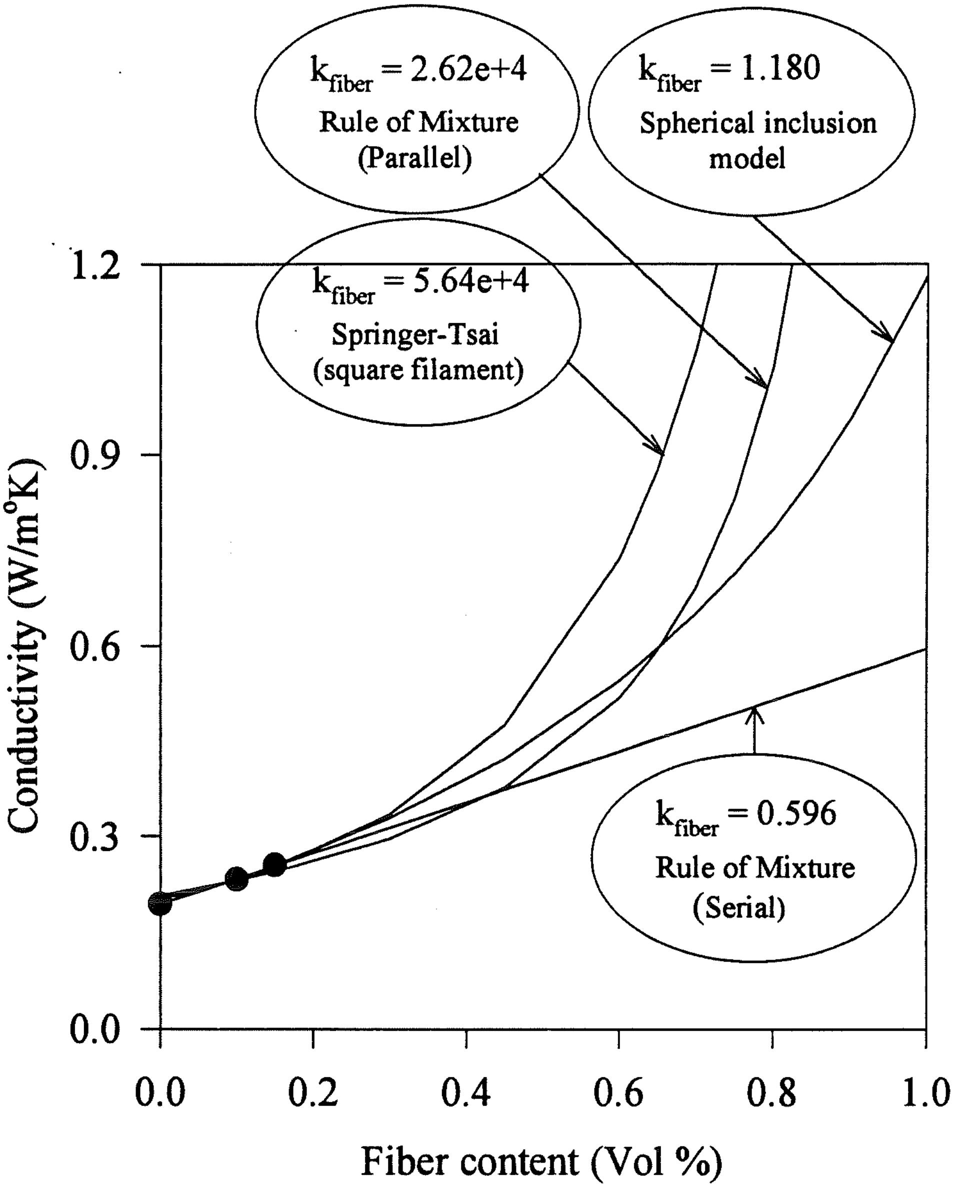

Fig. I.3 Thermal conductivity of polyester composites containing glass fiber reinforcement up to 15 vol% fitted to various correlations.

APPENDIX II

The developed cure analysis program

Based on some simplifying hypotheses (see Chapter 5), the governing equations for the cure process of the Resin Transfer Molding (RTM) may be written as follows:

Energy balance:

$$\rho_c C_{p,c} \frac{\partial T}{\partial t} = k_c \frac{\partial^2 T}{\partial x^2} + v_r \dot{Q}(t,x) \tag{II.1}$$

Mass balance:

$$\frac{\dot{Q}}{\rho_r Q_u} = \frac{d\alpha}{dt} = k_2 \alpha^m (\alpha_{\max} - \alpha)^n$$

(II.2 - II.3)

$$\frac{\dot{Q}}{\rho_r Q_u} = \frac{d\alpha}{dt} = k_2 \alpha^m (\alpha_{\max} - \alpha)^n (1 - \alpha)^p$$

where Eqs. II.2 and II.3 represent the rate of conversion for polyester and vinylester resins. In these equations, ρ, C_p , and k are the density, specific heat, and thermal conductivity, respectively, $\dot{Q}$ is the heat generation term, Q_u is the ultimate enthalpy of cure obtained for 100% monomer conversion, and subscripts "c", and "r" indicate the physical properties of the composite and polymer matrix, respectively.

The initial and boundary conditions used in this study, were:

$$T(x,0) = T_0 \quad , \quad \alpha(x,0) = 0 \qquad \text{(II.4 - II.5)}$$

$$\frac{\partial T(L,t)}{\partial x} = 0 \quad , \quad T(0,t) = T_w \qquad \text{(II.6 - II.7)}$$

here Eq. II.6 reflects the symmetry around the centerline, and Eq. II.7 is the boundary condition corresponding to constant wall temperature.

To place the governing equations into dimensionless form, the following dimensionless variables were defined:

$$t' = \frac{k_c t}{\rho_c C_{p,c} L^2} \quad , \quad x' = \frac{x}{L} \qquad \text{(II.8 - II.9)}$$

$$T' = \frac{T - T_0}{T_{ad} - T_0} \quad , \quad \dot{Q}' = \frac{v_r \dot{Q} L^2}{k_c (T_{ad} - T_0)} \qquad \text{(II.10 - II.11)}$$

here L is the half thickness of the part, T_0 is the initial temperature, and T_{ad} is the adiabatic temperature estimated as:

$$T_{ad} = T_w + \frac{Q_u}{C_{p,c}} \tag{II.12}$$

In general, T_{ad} represents the maximum temperature which may occur inside a composite.

The program was developed for a two dimensional heat transfer problem using 4-noded square elements. Therefore, Eq. II.1 in a dimensionless form will have the following form in a two dimensional analysis:

$$\frac{\partial^2 T'}{\partial x'^2} + \frac{\partial^2 T'}{\partial y'^2} + \dot{Q}'(T') - \frac{\partial T'}{\partial t'} = 0 \tag{II.13}$$

$$T' = 0 \quad on\ \Gamma \tag{II.14}$$

where the boundary condition in Eq. II.14 corresponds to that of a specified temperature which was used throughout the numerical analysis in the present work.

To apply the finite element analysis we assume that the region of interest, Ω, is divided into a finite number of subregions. Consequently, at the interconnections of elements, nodal-point values of the dependent variable, T', is defined. So, the variation of T' within an element may be defined by the shape functions [70]:

$$T'(x',y') = \sum_{i=1}^{n} N_i(x',y')T_i' \tag{II.15}$$

where n is the number of element nodal points. Popular choices of shape functions for two dimensional field problems are linear shape functions. So, for the problem treated in this work linear shape functions were chosen which preserve continuity of T' across the interface of adjacent 4-noded square elements.

To obtain the discretized equations on the element levels Galerkin method was used. Assuming that the right-hand side of Eq. II.13 is not zero, R_Ω was considered as the residual of Eq. II.13 in Ω. Set to zero the sum of the weighted residuals:

$$\int_{\Omega} N_i R_\Omega \, d\Omega = 0, \quad i = 1, 2 \ldots n \qquad \text{(II.16)}$$

Inserting Eq. II.13 into Eq. II.16 gives contributions to nodal point residuals:

$$\int_{\Omega^e} N_i \left[\frac{\partial^2 T'}{\partial x'^2} + \frac{\partial^2 T'}{\partial y'^2} + \dot{Q}'(T') - \frac{\partial T'}{\partial t'} \right] d\Omega = R_i, \quad i = 1, 2 \ldots n \qquad \text{(II.17)}$$

Using Green's theorem on the first two terms and multiplying through by -1 then yields:

$$\int_{\Omega^e} \left[\frac{\partial N_i}{\partial x'} \frac{\partial T'}{\partial x'} + \frac{\partial N_i}{\partial y'} \frac{\partial T'}{\partial y'} - N_i \dot{Q}'(T') + N_i \frac{\partial T'}{\partial t'} \right] d\Omega = R_i, \quad i = 1, 2 \ldots n \qquad \text{(II.18)}$$

Finally, Eq. II.15 is substituted into Eq. II.18 with the understanding that the nodal-point values T'_i now depend on time, $T'_i = T'_i\,(t')$:

$$\int_{\Omega^e}\left[\frac{\partial N_i}{\partial x'}\sum_{j=1}^{n}\frac{\partial N_j}{\partial x'}T'_j(t') + \frac{\partial N_i}{\partial y'}\sum_{j=1}^{n}\frac{\partial N_j}{\partial y'}T'_j(t')\right]d\Omega$$

$$- \int_{\Omega^e} N_i \dot{Q}'(T')\,d\Omega + \int_{\Omega^e} N_i\sum_{j=1}^{n} N_j \dot{T}'(t')\,d\Omega = R_i,\quad i = 1,2\ldots n \qquad \text{(II.19)}$$

which is written in formal matrix notation as:

$$[K]^e\{T'\}^e + [C]^e\{\dot{T}'\}^e - \{F\}^e = \{R\}^e \qquad \text{(II.20)}$$

In Eq. II.20 {T'} and $\{\dot{T}'\}$ are the element nodal point vector and its time derivative, $[K]^e$ and $[C]^e$ are element matrices, and $\{F\}^e$ is a vector. The elemental equations are then assembled to give the nonlinear set of equations for the nodal point vector {T}:

$$[K]\{T'\} + [C]\{\dot{T}'\} - \{F\} = 0 \qquad \text{(II.21)}$$

where [K] and [C] are global system matrices. To solve Eq. II.21 a time marching algorithm based on the finite difference method was used. The algorithm represent the first order matrix equation by finite difference approximations at an intermediate time, t'_θ, within each time step [71,72]:

$$t'_\theta = t'_n + \theta \Delta t', \qquad 0 \le \theta \le 1 \tag{II.22}$$

Then, we write Eq. II.21 at time t'_θ as:

$$[K]\{T'\}_\theta + [C]\{\dot{T}'\}_\theta = \{F(t'_\theta)\} \tag{II.23}$$

and introduce the approximations:

$$\{\dot{T}'\}_\theta = \frac{\{T'\}_{n+1} - \{T'\}_n}{\Delta t'} \tag{II.24}$$

$$\{T'\}_n = (1-\theta)\{T'\}_n + \theta\{T'\}_{n+1} \tag{II.25}$$

$$\{F(t_{\theta'})\} = (1-\theta)\{F\}_n + \theta\{F\}_{n+1} \tag{II.26}$$

Substituting Eqs. II.24 to II.26 into Eq. II.23 gives:

$$\begin{aligned} &\left[\theta[K] + \frac{1}{\Delta t'}[C]\right]\{T'\}_{n+1} + \theta\{F\}_{n+1} = \\ &\left[-(1-\theta)[K] + \frac{1}{\Delta t'}[C]\right]\{T'\}_n + (1-\theta)\{F\}_n \end{aligned} \tag{II.27}$$

where the right-hand side is known since $\{T'\}_n$ is known at t'_n. Thus, the global system to be solved is:

$$[C']\{T'\}_{n+1} = \{F'\}_{n+1} \tag{II.28}$$

where:

$$[C'] = \theta[K] + \frac{1}{\Delta t'}[C] \tag{II.29}$$

$$\{F'\}_{n+1} = \left[-(1-\theta)[K] + \frac{1}{\Delta t'}[C]\right]\{T'\}_n + (1-\theta)\{F\}_n + \theta\{F\}_{n+1} \tag{II.30}$$

If $\theta = 0$, the algorithm is the forward difference method (Euler method); if $\theta = ½$, the algorithm is the Crank-Nicolson method; if $\theta = ⅔$, the algorithm is Galerkin method; and if $\theta = 1$, the algorithm is backward difference method [71].

The direct integration of the first-order matrix equations by the recurrence formula, Eq. II.27, introduces numerical errors in the computed transient response because of the finite difference approximations in Eqs. II.24 to II.26. The transient response will approach the exact solution closely as $\Delta t' \rightarrow 0$. In contrast, for large $\Delta t'$ the transient response may exhibit oscillations, and in some instances may become unstable. The Euler forward difference algorithm is stable only if the time step is less than a critical value, but the Crank-Nicolson, Galerkin, and backward difference algorithms are unconditionally stable. However, if the time step is too large, the Crank-Nicolson and Galerkin algorithms will exhibit oscillations. The backward difference method always predicts a smooth decay [71]. In a more detailed study with comparisons to other integration algorithms, Hogge [73] recommended the Crank-Nicolson scheme ($\theta = ½$), as being the most accurate one step (t_n , t_{n+1}) integration scheme for nonlinear heat transfer. Moreover, error growth is the least for $\theta = ½$, establishing this choice of θ to be the most accurate scheme of the θ family.

Since in the present work Eq. II.21 is highly nonlinear with [K], [C], and [F] depending on {T}, for the numerical analysis , $\theta = ½$ was selected. To model the post-filling period of the RAM process, a one-dimensional through-the-thickness heat transfer analysis was found to provide satisfactory results. The specific heat and thermal conductivity of composite were treated as being temperature dependent and conversion dependent, respectively. Taking a constant time step, $\Delta t = 1$ s, and 10 elements for a half thickness of 10 mm provided a stable transient response for the problem. To verify the developed program, the temperature profiles for a cure process predicted by the program were compared with those produced by Progelhof [74] using a finite differences method. Fig. II.1 shows a reasonable concordance between these two methods.

The developed program also accounts for the induction time of the cure reactions. As a consequence, the reaction at each nodal point starts after elapsing the induction time calculated at the nodal temperature. This aspect becomes important when the mold filling time is long enough to be a limiting factor in selecting the process variables, *e.g.* mold wall temperature. To avoid premature gelling during the mold filling period, the induction time of the cure reactions should be long enough to provide a complete mold filling. In the developed program, assuming that the temperature at each thermocouple position is constant throughout the mold filling period, the extent of cure at the end of this period is calculated by accounting for the induction time of the cure system. This aspect of the program was used to compare the numerical predictions and experimental data in Chapter 5, Fig. 5.15.

Since the kinetic parameters of the promoted systems were mostly temperature dependent, in this program the parameters are evaluated at the nodal temperature within each time step. The thermal conductivity and specific heat of the composite are calculated based on the degree of conversion attained at each nodal point and the nodal temperature, respectively. The flowchart for the cure analysis program is given in Fig. II.2 where the entire calculation procedure is summarized.

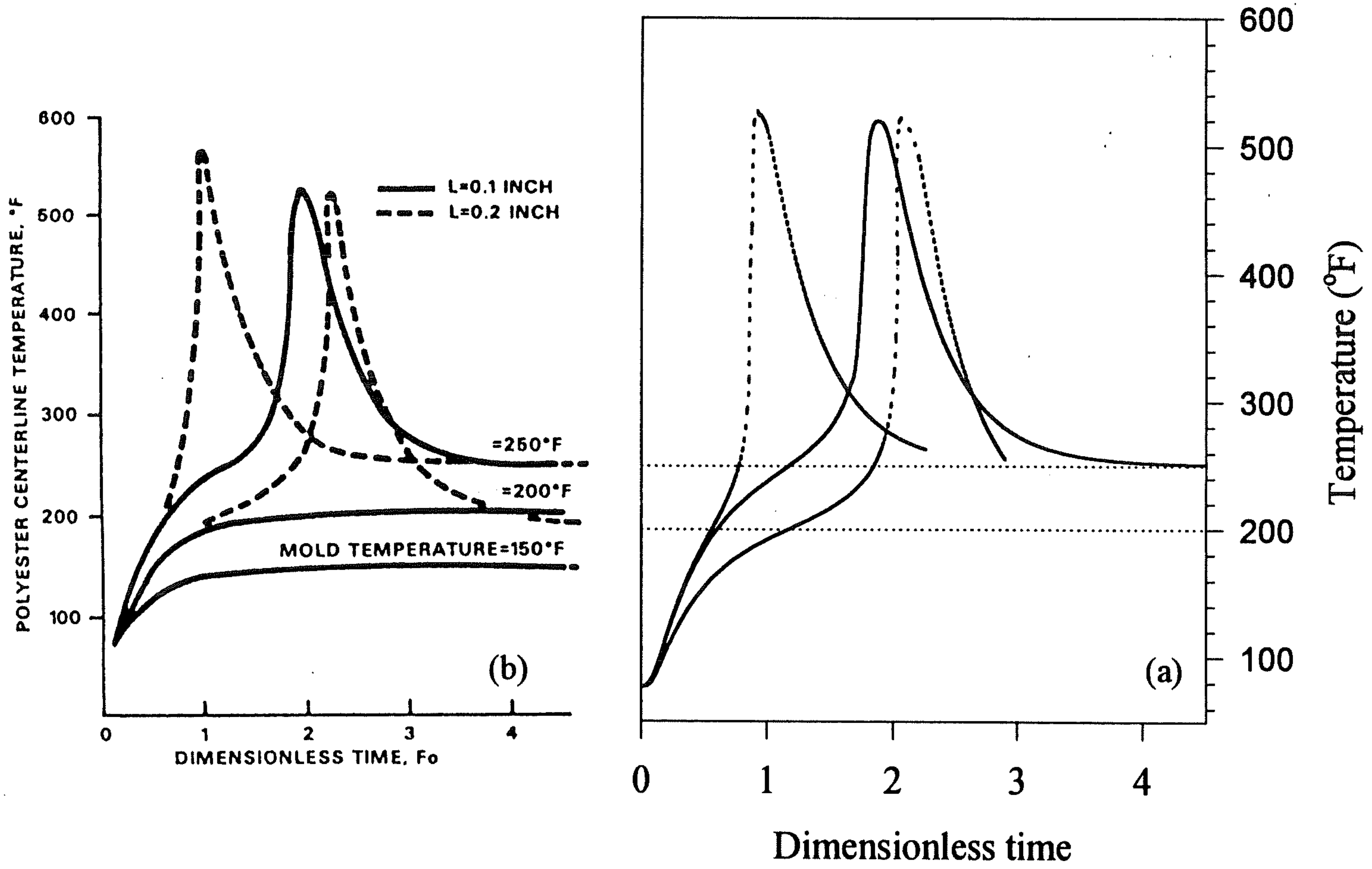

Fig. II.1 Comparison of temperature profiles predicted by the **(a)** finite difference method **(b)** finite element method.

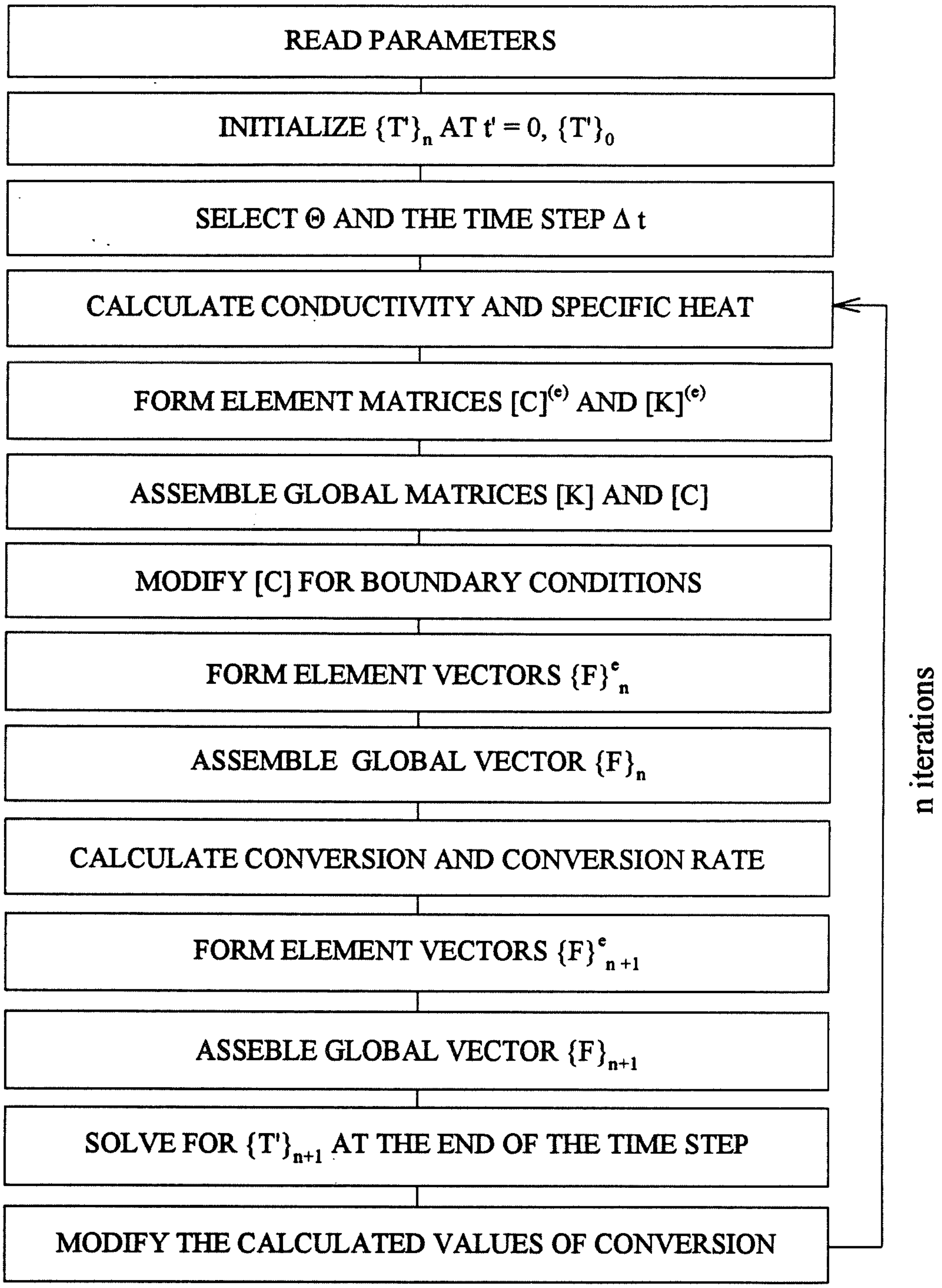

Fig. II.2 Flowchart of the cure analysis program