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UNIVERSITÉ DE MONTRÉAL

EARLY DEVELOPMENT OF AN ENERGETIC BIODEGRADABLE THERMOSET ELASTOMER

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Ce mémoire intitulé:

EARLY DEVELOPMENT OF AN ENERGETIC BIODEGRADABLE THERMOSET ELASTOMER

présenté par: COSSU Claudia
en vue de l'obtention du diplôme de: Maîtrise ès sciences appliquées
a été dûment accepté par le jury d'examen constitué de:

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M. LUSSIER Louis-Simon, Ph.D, membre et codirecteur de recherche
M. AJJI Abdellah, Ph.D., membre

To my family

Bestial as always before, carnal, self seeking as always before,
selfish and purblind as ever before,
Yet always struggling, always reaffirming, always resuming their
march on the way that was lit by the light;
Often halting, loitering, straying, delaying, returning, yet
following no other way.
(T.S. Eliot)

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RÉSUMÉ

L'accumulation de plastique dans les dépotoirs ainsi que dans les milieux naturels entraîne des impacts écotoxicologiques connus et bien réels. L'intérêt de ces dernières années porté aux polymères biodégradables s'est donc élargi en dehors du domaine médical. Ce nouveau type de matériau sera amené à résoudre cette problématique à grande échelle.

Bien que disponibles depuis plusieurs décennies, la production de polymères continue d'augmenter. Ces derniers ont des applications dans un grand nombre de domaines allant du biomédical au militaire. Toutefois, l'épuisement des ressources pétrolières et les préoccupations environnementales grandissantes, ont engendré un fort intérêt envers les polymères qui sont non-seulement biodégradables, mais aussi fabriqués à partir de ressources renouvelables. Divers polymères biodégradables, synthétiques et naturels, ont été développés afin d'obtenir des propriétés physiques et mécaniques particulières. Différentes techniques de fabrication ont été testées : copolymérisation, mélanges de polymères et réseaux composites ou réticulés afin d'améliorés les produits.

En raison de ce contexte, une nouvelle tendance a émergé en la production de polymères énergétiques biodégradables pour des applications tant civiles que militaires. Ces derniers représentent une nouvelle génération de liants énergétiques qui ont comme avantages une performance accrue et une vulnérabilité réduite. L'énergie qu'ils dégagent en se décomposant est due à la présence de groupements azides ou nitro dans la chaîne latérale. Les élastomères thermodurcissables biodégradables sont une alternative intéressante en tant que précurseurs de polymères énergétiques en raison de leur faible viscosité et basse température de mise en forme.

Au cours des dernières années, les chercheurs ont développé de nouveaux matériaux biodégradables contenant des hétéroatomes dans leur squelette. L'intérêt de ces matériaux réside dans la présence de liens éther, ester ou amide. Ces liens sont facilement susceptibles à des réactions d'hydrolyse et libèrent des sous-produits facilement biodégradables dans un sol ou dans un compost.

L'étude des polyéthers et des polyesters a joué un rôle important puisqu'ils sont les polyols les plus utilisés dans la fabrication d'élastomères. La différence entre les polyesters aromatiques et aliphatiques est très grande: les aromatiques ont de bonnes propriétés physiques et mécaniques mais résistent à toute attaque bactérienne et ne sont pas biodégradables. D'un autre côté, les polyesters aliphatiques tels que le poly (ε-caprolactone) et le poly (L-lactide) sont reconnus pour leur biodégradabilité. Par contre, ils ont des propriétés physiques et mécaniques généralement plus faibles que les polyesters aromatiques. La littérature indique que les polyuréthanes dérivés de la lysine se dégradent en composés non toxiques.

L'objectif principal de ce travail était la conception d'un réseau poly (ester/éther-uréthane) énergétique biodégradable, se dégradant en composés non-toxiques, servant de propulsif ou générateur de gaz. L'impact des groupements azides sur la biodégradabilité du polyuréthane sera comparé avec un polyuréthane non-énergétique.

La première étape consistait en la synthèse d'un polyol en faisant réagir du polyepichlorohydrine avec du chlorure de sébacoyle et l'azidation subséquente afin d'introduire un groupement N_3. Par la suite, la formulation et la préparation de réseaux polyuréthane ont été effectuées grâce à la réaction entre les terminaisons hydroxyle du poly (ester/éther), un diisocyanate biodégradable, le L-Lysine diisocyanate et du poly-caprolactone triol.

Les polyuréthanes ont été caractérisés chimiquement, mécaniquement et des mesures de dégradation ont été effectuées dans du compost à 55 °C. Une température de transition vitreuse de -14 et de -23 °C a été trouvé pour les polyuréthanes non-énergétique et énergétique, respectivement. Au cours du séjour dans le compost, la perte en masse des polyuréthanes a été mesurée et semble montrer une relation quasi linéaire

avec le temps et cela pour les deux types de matériaux. Après 20 jours, les polyuréthanes non-énergétiques ont perdus environ 50% de leur masse en raison du mécanisme de dégradation. Ce n'est cependant pas le cas des élastomères énergétiques qui eux n'ont perdu que 25% de leur masse initiale après 25 jours. Ces résultats expérimentaux montrent bien que la présence du groupe ramifié azide dans la partie souple du polyuréthane est le principal facteur qui contrôle les propriétés physiques, mécaniques et de dégradation des réseaux polyuréthanes.

ABSTRACT

In the last years plastics have gained a large fame as fascinating materials available for a large number of applications, from biomedical to military [1-3]. However, the expected depletion of oil resources and a greater awareness for the environmental impact of plastic products have created a strong interest towards polymers that are not only biodegradable but also obtained from renewable resources. Various natural and synthetic biodegradable polymers have been developed in order to satisfy specific mechanical and physical requirements and different techniques have been tried such as copolymerization, polymer blending, composite formulations and cross-linking networks in order to improve the product properties [4].

In these interesting surroundings a new trend has emerged in the production of energetic polymers for specialized civil and military applications. They represent the new generation of energetic binders with the double advantage of improved performance and lower vulnerability (LOVA). The explosive energy they release during the decomposition is due to the presence of an azido or nitro group in the side chain.

Biodegradable polyurethanes based on lysine have been reported in the literature to transform into non-toxic decomposition products [5, 6]. For those reasons polyurethane elastomers can be attractive materials for the preparation of composite solid propellants, in which the elastomer can act as a rubbery phase intimately mixed, and it can be used as a binder for other materials like ammonium perchlorate or other oxidizers, aluminum or other metallic fuels.

In the last years the researchers have developed new biodegradable materials which contain hetero-atoms in their backbone. Ether bonds, amide bonds or ester bonds can easily undergo a hydrolytic attack: in this way they are able to release low molecular weight by-products which are easily biodegradable in the soil or in the compost. Aliphatic polyester, like poly (ε- caprolactone), poly (L-lactide) are well known for their biodegradability, but they do not stand the comparison in terms of physical and mechanical properties.

The main objective of this work has been the design of a biodegradable and energetic co- poly (ester/ether-urethane) network, in order to be used as propellant or gas generator. The impact of the azide group on the biodegradability of the polyurethane is compared with a non-energetic polyurethane.

The first step has been the synthesis of a co-poly(ester/ether) from polyepichlorohydrin (PECH) and sebacoyl chloride (SC) using pyridine as catalyst and HCl acceptor. Consequently, the chlorinated co-polymer was azidified with NaN_3 in dimethyl sulfoxide solutions to produce an energetic co-polymer. The success of the reaction was confirmed by H-NMR, ^{13}C-NMR and FTIR techniques. The azide groups replaced 80% of the initially present chlorine atoms. Both non-azidified (non-energetic) and azidified (energetic) co-polymers were cross-linked in the presence of polycaprolactone triol (PCL) and L-lysine diisocyanate (LDI) as a non toxic coupling agent to form a soft thermoset polyurethane network. Subsequently, the chemical and mechanical properties of the produced polyurethanes along with the water uptake and biodegradation in compost of these materials were characterized. The non-energetic polyurethane showed a glass transition temperature at -14 °C whereas the energetic one at -23 °C. The weight loss of the polyurethanes after composting was traced and was shown to increase almost linearly with time for both materials: after 20 days the non-energetic binders had lost about 50% of their mass due to biodegradation; whereas, the energetic binders had lost only about 25% of their initial mass after 25 days. The experimental results revealed that the azide pendant group in the soft segment is the main factor that controls the physical, mechanical, and degradation properties of these polyurethane networks.

CONDENSÉ EN FRANÇAIS

L'accumulation de plastiques dans les décharges et la nature entraîne des impacts éco- toxicologiques connus et bien visibles. L'intérêt porté aux polymères biodégradables s'est donc élargi et ce type de polymères sera amené à faire partie de la solution à cette problématique à grande échelle. Actuellement, on peut remarquer que les applications principales des polymères biodégradables sont plutôt à l'échelle du corps humain. Or ici, on recherche un élastomère qui se dégraderait dans la « nature » et plus précisément dans les sols pour une prévention contre l'écotoxicologie qui est devenue importante.

Au cours des dernières années, les matières plastiques se sont révélées d'un grand intérêt et peuvent être utilisées dans de multiples applications comme par exemple l'industrie biomédicale ou pour des applications militaires [1-3]. Toutefois, la diminution attendue des ressources pétrolières et la prise de conscience de l'impact environnemental des produits en matières plastiques ont créé un grand intérêt pour les polymères qui sont obtenus à partir de ressources renouvelables. Ainsi, divers polymères biodégradables naturels et synthétiques ont été développés afin de satisfaire des exigences mécaniques et physiques. Différentes techniques ont été développées afin d'améliorer les propriétés des produits telles que la copolymérisation, le mélange de polymères, la fabrication des composites et la réticulation [4].

Aujourd'hui, il existe une tendance au développement de matériaux biodégradables pour des applications non-traditionnelles telles que les applications militaires. Compte tenu du fait que la majeure partie des produits fabriqués par un pays nécessite souvent l'extraction de ses matières premières et engendre généralement un problème environnemental, l'intérêt d'utiliser des matériaux énergétiques moins nocifs pour l'environnement devient indispensable.

Dans cette perspective, les polymères biodégradables peuvent être une bonne alternative, particulièrement suite aux progrès enregistrés dans la conception de ces polymères, et qui favorise à présent leur production en masse.

Le principal intérêt de ce travail est axé sur la synthèse d'un co-poly (ester / éther) approprié pour par la suite préparer un polyuréthane à partir de ce co-poly (ester / éther). Il est important de noter la différence entre aromatique et aliphatique : les polyesters aromatiques ont de bonnes propriétés physiques et mécaniques, mais ils résistent à tous types d'attaques de bactéries et sont donc non biodégradables [5]. Quant aux polyesters aliphatiques tel que la poly (ε-caprolactone) ou l'acide polylactique, ils sont bien connus pour leur biodégradabilité [6], mais en comparaison avec les polyesters aromatiques, ils affichent de faibles propriétés physiques et mécaniques.

L'existence de polyuréthanes biodégradables obtenus à partir des dérivés de la lysine est rapportée dans la littérature et il est intéressant de voir que leur décomposition ne comporte aucun produit toxique [7]. La lysine diisocyanates (LDI) est essentiellement synthétisée par phosgénation de l'amine-lysine ester et possède une tension de vapeur faible par rapport aux autres diisocyanates aliphatiques (par exemple, hexaméthylène diisocyanate, l'HDI) [8]. Cette basse pression de vapeur de LDI est un point clé dans la manipulation et le traitement du procédé car à plus haute température, la manipulation du produit peut être dangereuse d'un point de vue santé et sécurité (toxicité à l'inhalation). Toutefois, la production d'un liant d'élastomère de polyuréthane biodégradable à partir de lysine diisocyanate est actuellement étudiée en particulier pour des applications biomédicales [9]. Dans une des étapes du procédé, le polyisocyanate est mélangé avec un polyol conduisant à un liquide réactif qui est ensuite coulé et durci pour finalement obtenir un produit solide.

La formulation des matériaux énergétiques contemporains nécessite l'utilisation de méthodes plus écologiques, avec des oxydants moins fort tels que le nitrate d'ammonium. Afin de compenser l'énergie perdue en changeant l'oxydant, de nouveaux polymères énergétiques ont vu le jour pour des applications spécialisées dans les domaines civils et militaires. Ils représentent la nouvelle génération de liants énergétiques avec le double avantage d'améliorer les performances et de réduire la vulnérabilité. La libération de l'énergie au cours de leur décomposition thermique est due à la présence d'un groupe nitro ou azide sur la chaîne latérale. En outre, les élastomères thermodurcissables biodégradables sont une alternative intéressante en tant que précurseurs de polymères énergétiques en raison d'une faible viscosité et de leur faible température de transformation.

Pour créer des matériaux énergétiques, deux options sont discutées dans la littérature: il est possible de produire des précurseurs de ce type de polymères à partir de monomères énergitiques (avec les azides ou groupements nitro dans leurs chaînes). Il est également possible d'obtenir ces précurseurs à partir de monomères non-énergétiques, à qui il sera possible, après la polymérisation d'un pré-polymère, d'ajouter le group azide ou des groupes nitro à travers une réaction de substitution nucléophile [10].

Les poly (ester-éther) polyuréthanes dégradables ont été étudiés dans le but de produire des matériaux appropriés pour différentes applications: domestiques, industrielles et militaires, et également dans certaines formulations biodégradables [11,12]. Ils sont utilisés dans la formulation des peintures, des mousses de matelas, dans l'encapsulation électrique, comme instruments médicaux, rouleaux, semelles de chaussures et autres.

Pour ces raisons, les élastomères de polyuréthane polyester peuvent être intéressants pour la préparation des matériaux composites de propergols solides, dans lesquels les élastomères peuvent agir comme une phase caoutchouteuse intimement mélangée, et peuvent être utilisés comme liant pour les autres matériaux, par exemple le perchlorate d'ammonium ou d'autres oxydants, l'aluminium métallique ou d'autres combustibles. Un liant en polyuréthane est utilisé pour donner au produit final des propriétés physiques et mécaniques améliorées, et peut libérer de la chaleur par décomposition thermique [13]. Les plastifiants azides peuvent être également utilisés pour apporter de l'énergie supplémentaire aux liants, car chaque groupe N_3 peut fournir une énergie de 85 kcal /mol dans le système.

Dans le marché des propergols, il y existe un remplacement progressif des polymères inertes tels que le polybutadiène (HTPB) par des polymères énergétiques tels que le polyazoture de glycidyle (PAG) comme liant énergique. La plus utilisée des matières premières dans la science des matériaux énergétiques est la polyépichlorohydrine (PECH), car dans cette dernière, le groupe Cl peut être facilement échangé avec un groupe N_3 par la réaction de substitution nucléophile d'ordre 2 (SN2). Pisharath et al. [14] ont synthétisé un intéressant polymère énergétique à partir de polyépichlorohydrine à grand poids moléculaire qui est ensuite converti en un PAG.

En général, les fonctions des polymères PAG sont protégées par réaction de ses groupes hydroxyles avec des agents de durcissement, comme le diisocyanate de toluène, le diisocyanate isophorone (IPDI) ou d'un tri-isocyanate pour améliorer la structure réticulée du polyuréthane [15]. Mais un polymère à base de polyépichlorohydrine n'est pas biodégradable, et au cours de la dernière décennie, la question de l'impact du matériel énergétique sur l'environnement est devenue une source de préoccupations.

Dans la recherche militaire, la force motrice pour le développement des nouvelles technologies a toujours été la performance, sans oublier la sécurité. Toutefois, le changement de mentalité de la population concernant la production industrielle et l'élimination des déchets a aussi commencé à influencer le domaine des activités militaires. Pour augmenter la biodégradabilité d'un matériel énergétique à base de polyépichlorohydrine, une solution envisageable peut être l'insertion de certains liants, tels que les esters, qui peuvent promouvoir la biodégradabilité.

Ce type de polymères peut être produit par une réaction de polycondensation entre un acide carboxylique (comme le chlorure d'acyle ou ses dérivés, les esters ou anhydrides), de diols (ou polyols) et par échange ester-alcool ou alcoolyse. Kricheldorf et al. [14] ont effectué un remarquable travail de recherche afin de comparer ces trois méthodes de base pour produire des polyesters en vue de trouver la meilleure méthode de synthèse des co-poly (ester/éther) avec un bon rendement et de bonnes propriétés mécaniques. Ils ont réussi à produire un polyester aliphatique en utilisant la méthode de polycondensation catalysée de la pyridine: la réaction est réalisée à température ambiante entre le butène-1,4-diol et plusieurs acides dicarboxyliques aliphatiques dichlorides. De cette façon, l'acide activé réagit avec un alcool à des conditions moins agressives en accord avec le mécanisme de Schotten-Baumann, à température ambiante, la pyridine agissant comme catalyseur et accepteur de HCl, de manière à modifier l'équilibre de la réaction chimique. Toutefois, la réalisation de cette réaction est très délicate : la production du prépolymère dépend de la réactivité de la PECH elle-même; le durcissement des liants à l'aide d'un catalyseur spécifique n'est pas toujours facile car au cours de la réaction entre l'eau et le diisocyanate, il peut y avoir formation de CO_2. Une fois formé, le CO_2 peut être retenu dans le réseau de polyuréthane; si le phénomène se produit, les matériaux ne sont plus utilisables car même une petite quantité de bulles est suffisante pour produire des vides, ce qui provoque des taux d'explosions incontrôlables. Compte tenu de tous les aspects de la formulation des polyesters polyuréthanes, le point clé dans la production de propergols est le choix d'un catalyseur adéquat et l'indentification des conditions opératoires optimales pour la réaction.

L'objectif principal de ce travail est de concevoir un polymère biodégradable et un co-poly (éther / ester-uréthane) énergique qui soit en mesure de libérer des produits non toxiques non seulement dégradables, mais aussi pouvant être utilisés comme carburant ou générateur de gaz. L'analyse de la biodégradation du produit a été utilisée pour évaluer la capacité à la biodégradation du matériel synthétisé.

Dans le cadre de ce travail, la synthèse d'un co-poly (ester/éther) à partir de la polyépichlorohydrine (PECH) a été effectuée dans différentes conditions chimiques et à des températures variées. L'acide sébacique (SA) a été fait réagir avec la PECH dans le toluène et différents catalyseurs ont été utilisés pour faciliter la réaction. La réaction de polycondensation est une réaction d'équilibre qui produit l'eau comme sous-produit, et la suppression de l'eau s'est avérée nécessaire pour compléter la réaction. Cette élimination a été réalisée en utilisant un appareil de type *Dean Stark* en combinaison avec un condensateur à reflux. La réaction est conduite sous un reflux dans le toluène, qui est moins dense que l'eau, et dans lequel l'eau se melange pour former un azéotrope. L'appareil permet à l'eau de se séparer du condensé azéotrope, l'empêchant ainsi de retourner au mélange réactif originel. Lors des expériences, différents catalyseurs comme l'acide sulfonique p-toluène ou la pyridine hydrochloride, ont été testés sous des températures variant entre 120 et 145 °C.

La polycondensation directe entre le PECH et le SA n'a produit aucun copolymère de haut poids moléculaire. Le poids moléculaire le plus élevé ($M_n \approx 1500$ g/mol) a été obtenu en utilisant l'acide para-toluène sulfonique (PTSA) comme catalyseur, dans le toluène. Ces résultats peuvent être expliqués en analysant le mécanisme de la réaction. Durant la polycondensation entre un diacide et un diol, le proton acide du catalyseur réagit avec le diol, formant un complexe qui est alors capable d'attaquer le diacide. Le carbone terminal du groupe -COOH devient plus électrophile, et de là plus susceptible d'attaquer l'alcool. Un intermédiaire réactionnel est formé et seulement l'élimination d'une molécule d'eau peut faire cesser la réaction. Malheureusement, les réactions de polyesterification sont très sensibles aux températures élevées, et des réactions secondaires peuvent survenir menant à des sous-produits (des polymères de faible poids moléculaire) et à une perte de la fonctionnalité.

Une autre méthode pour produire un co-poly (ester/ethers) se situe dans la réaction entre les dichlorides dicarboxiliques en utilisant de la pyridine comme catalyseur et receveur de HC1. Ce type de réaction demeure cependant plus difficilement réalisable en raison du coût élevé des acides dicarboxiliques et des conditions expérimentales particulières (milieu non aqueux) requises pour la synthèse, mais les résultats sont néanmoins satisfaisants. Après 24 heures, un copolymère d'environ 6000 g/mol selon des standards de polystyrène a été produit. Après 48 heures, le poids moléculaire de ce copolymère a atteint une valeur d'environ 25 000 g/mol selon des standards de polystyrène. Ces résultats ont été obtenus dans des conditions parfaitement stochiométriques, en utilisant un excès de pyridine. Les poids moléculaires équivalents des deux copolymères ont été évalués par réaction acétylique suivie d'un titrage et par l'utilisation de la technique FTIR. Pour le copolymère à faible poids moléculaire, le poids équivalent a été estimé à environ 2000 g/équiv, alors que pour le copolymère à fort poids moléculaire, un poids équivalent d'environ 8200 g/équiv a été trouvé. L'étape de polycondensation entre la PECH et SC a été fondamentale afin de produire un polymère pouvant être azidé par la réaction nucléophile avec NaN_3. Dans l'industrie du propergol, le poids moléculaire absolu suggéré du polymère qui subit la réaction d'azidation doit être compris entre 2000 et 3000 g/mol. Dans le cas contraire, la viscosité serait trop élevée pour être contrôlée dans la réaction de production du polyuréthane.

L'azidation de 40g du polymère de bas poids moléculaire donne un produit jaune huileux avec un poids moléculaire équivalent d'environ 2230 g/equiv. Le succès de la réaction a été confirmé par C-NMR, H-NMR et FTIR. Toutes ces analyses ont confirmé la substitution de groupes Cl avec N_3 sur les chaînes polymères. Des expériences de calorimétrie différentielle à balayage (DSC) ont été réalisées sur le copolymère énergétique et sur le non-énergitique de bas poids moléculaire. Les balayages des deux copolymères ont montré un seul pic exothermique, confirmant la structure complètement amorphe. Le copolymère énergétique a montré une température T_{max}=176 °C associée à un énorme pic exothermique, avec un dégagement de chaleur de 7000 mW/g; le copolymère non énergitique a montré un pic plus petit à très haute température. Il est possible de conclure que l'adjonction de N_3 sur les chaînes de polymère a eu un effet important sur la stabilité thermique du copolymère.

Plusieurs méthodes ont été utilisées pour réaliser la synthèse de polyuréthanes élastomères thermodurcissables ayant les copolymères L- Lysine diisocyanate (LDI) et polycaprolactone triol (PCL) comme réactifs. La formation du polyuréthane avec le polyol de bas poids moléculaire a été satisfaisante. Cependant, le copolymère à haut poids moléculaire a montré quelques problèmes en raison de la production de bulles et de la dégradation du matériel pendant la réaction. Par conséquent il n'a pas permis la production d'un bon polyuréthane à l'échelle du laboratoire. La formation du polyuréthane énergétique a été réalisée en suivant la même méthode que pour le polyuréthane non-énergétique. Pour les deux élastomères, le temps de réaction et la température sont les paramètres clés pour préparer un polyuréthane avec une consommation complète du polyol et du diisocyanate.

Les polyuréthanes ont été caractérisés en utilisant la technique de *Dynamic Mechanical Thermal Analysis (*DMTA); les polyuréthanes énergiques (E) et les polyuréthanes non-énergétiques (NE) présentent une température de transition vitreuse T_g de -23 °C pour E et de -14 °C pour NE.
L'analyse du module élastique à basse température peut aider à évaluer la performance des matériaux. A température plus basse, le (E) a montré un module élastique d'à peu près 3300 MPa et le (NE) d'à peu près 1800 MPa. L'introduction de N_3 dans la structure peut affecter la mobilité moléculaire du réseau du polyuréthane. Remplaçant l'atome de Cl, N_3 représente un obstacle stérique plus grand et il réduit la flexibilité de la chaîne du polymère. Mais d'un autre côté, la présence de groupe azide augmentent le volume libre disponible pour les mouvements moléculaires, ajoutant un degré de liberté, ce qui a pour résultat une grande différence de T_g entre les deux produits (environ 10 °C).

La biodégradation de ces polyuréthanes a été évaluée par un test de dégradation de vingt-cinq jours, réalisé selon les normes ASTM D 5988-03 et ASTM D5338-98 (2003). Les échantillons ont été placés dans des boîtes remplies de compost et incubés pour une période de temps qui a varié entre dix et trente jours. Le contenu en eau a été régulièrement vérifié pour garantir 60% d'humidité et la température a été fixée à 55 °C. Le poids des échantillons a diminué presque linéairement avec le temps pour les deux matériaux, et cette diminution a été plus prononcée pour les NE : après 20 jours dans le compost, les échantillons ont perdus environ 50% de leur poids en raison du mécanisme de biodégradation. L'élastomère E, après 25 jours, a perdu environ 25% de sa masse initiale. Au début, la dégradation s'est produite surtout sur la surface de l'élastomère due à l'absorption d'eau, causant un changement de couleur des échantillons, qui ont perdu leur aspect transparent. Cependant le mécanisme de dégradation dépendait de la structure et de la configuration chimiques des chaînes polymériques. On peut affirmer que le groupe azide est plus stable et plus résistant à la dégradation que le groupe chlore; NE a pu subir plus facilement l'hydrolyse et l'attaque bactérienne après seulement 10 jours dans le compost.

Les propriétés physico-chimiques des échantillons dégradés ont été évaluées par analyse FTIR-Photoacoustique et l'extraction Soxhlet dans le dichlorométhane. Le solide a été lavé plusieurs fois avec ce solvant pour dissoudre correctement la partie soluble de l'échantillon. La dissolution spontanée du polyuréthane dans le dichlorométhane a augmenté avec le temps dans le compost. Cela signifie que la rupture spontanée arrive au hasard sur les chaînes de polymère dans le compost et, avec le temps, la présence de dérivés de bas poids moléculaires solubles dans les solvants organiques reste stable. La spectroscopie FTIR-PAS a été utilisée pour examiner la différence structurelle entre les échantillons dégradés et non-dégradés. Les régions spécifiques ont été contrôlées en fonction du temps : les groupements $C-N_3$ (2100 cm^{-1}) pour l'élastomère E, CH_2-Cl (750 cm^{-1}) pour le NE et les liens 'éther/uréthane' (entre 1700 et 1800 cm-1) pour les deux élastomères ont été identifiés. L'intensité de tous ces pics a diminué avec le temps. Ces analyses ont confirmé la dégradation des échantillons. Au cours de travaux futurs, il pourrait être intéressant de varier les conditions chimiques utilisées afin de produire des copolymères avec des poids moléculaires différents et avec différents liens chimiques. On pourrait utiliser d'autres types d'alcools avec différentes fonctionnalités. Pour les analyses de dégradation, une étude du degré de réticulation par solubilité pourrait être conduite.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

DBTL	*Dibutyl* tin *dilaurate*
ECH	*epichlorohydrin*
ε	*Deformation*
$\dot{\epsilon}$	*Rate of deformation*
FTIR	*Fourier Transform Infrared Spectroscopy*
GAP	*Glycyl azide polymer*
HDI	*Hexamethylene diisocyanate*
HS	*Hard segment*
HTPB	*Hydroxyl-terminated polybutadiene*
IM	*Insensitive Munitions*
LDI	*Lysine diisocyanate*
LTI	*Lysine triisocyanate*
LVE	*Linear Viscoelastic Region*
M_o	*Molecular weight of repeating unit*
Mn	*Number average molecular weight*
p	*Conversion*
PAS	*Photoacoustic Spectroscopy*
PECH	*Polyepichlorohydrin*
PCL	*Polycaprolactone triol*
PGA	*Polyglycolide*
PLA	*Polylactide*
PLGA	*Polylactide-co-glycolide*
PolyGLYN	*Poly(glycidyl nitrate)*
PolyNIMMO	*Poly(3-nitratomethyl-3-methyloxetane)*

PyH	*Pyridine hydrochloride*
PU	*Polyurethane*
PTSA	*P-toluene sulfonic acid*
σ	*Stress*
SA	*Sebacic acid*
SC	*Sebacic chloride*
SS	*Soft segment*
TEA	*Tetraethylamine*
TDI	*Toluene diisocyanate*
T_g	*Glass transition temperature*
T_m	*Melting point Temperature*
TPEs	Thermoplastic elastomers
TSEs	*Thermoset elastomers*
X_n	*Degree of polymerization*

Chapter 1 : INTRODUCTION

1.1 BACKGROUND

Despite having been available for a few decades, the production and use of plastic materials continue to increase steadily. Their applications range over many fields, from biomedical to military. However, the expected depletion of oil-resources and a greater awareness for the environmental impact of plastic products have created a strong interest towards polymers that are not only biodegradable but also obtained from renewable resources.

Various natural and synthetic biodegradable polymers have been developed in order to satisfy specific mechanical and physical requirements and different techniques have been tried such as copolymerization, polymer blending, and composites or cross-linking networks in order to improve the product properties [4]. In the last few years, there has been a great interest in biodegradable synthetic polymers for biomedical and pharmaceutical application [7]. Nowadays there is a tendency towards the development of possible applications for biodegradable polymers in less traditional applications such as military.

Contemporary energetic materials formulations tend to use greener but less powerful oxidisers such as ammonium nitrate. In order to compensate the energy lost from the change in the oxidiser, novel energetic polymers have emerged for specialized applications in the civilian and military domains. They represent the new generation of energetic binders with the double advantage of improved performance and lower vulnerability (LOVA). The energy they release during their thermal decomposition is due to the presence of an azide or nitro group on the side chain.

Over the last 40 years, several attempts have been done to synthesize energetic polymers for the production of energetic solid propellants, but yet there are some problems in the formulations e.g. chemical incompatibilities with other ingredients, instabilities of energetic groups in the polymeric chains. Also, the cost of these raw materials is significant and the research is still being done in order to improve the mechanical properties of energetic binders [8]. Furthermore, the introduction of new pyrotechnic systems requires structured and progressive safety assessments.

For the synthesis of such energetic matrix, a solution can be represented by biodegradable polyurethane elastomers. Urethane structure presents intermolecular hydrogen bonds. If stress is applied, the hydrogen bonds can be separated, absorbing energy. When the stress is removed, hydrogen bonds are reformed. This behaviour provides excellent mechanical properties to the materials. The synthesis of polyurethane requires at least two reagents: a diisocyanate and a polyol. The choice of the polyol and diisocyanate will have an impact on the final physic-mechanical properties and also on the biodegradability of the polyurethane.

The most used polyols for this kind of applications are GAP (glycidyl azide polymer) and poly 3,3-bis (azidomethyl) oxetane. Unfortunately they are neither biodegradable nor even recyclable.

The major problem of these new applications is the synthesis of a polyol with improved biodegradable tendency, which could provide also optimal mechanical properties. The polyol should be cured with aliphatic diisocyanates (e.g. Lysine diisocyanate) which can enhance the biodegrability of the final product.

1.2 RESEARCH OBJECTIVES

The main objective of this work is to design a biodegradable and energetic co-poly (ether/ester-urethane) network, which is able to release only non-toxic degradation products, in order to be used in an environmentally friendly propellant or gas generator formulation. Insertion of ester bonds on polymer backbone should improve the biodegrability tendency of the final polyurethane without affecting too much the mechanical properties. Poly(ester/ether) based polyurethane can easily undergo a hydrolytic attack; and in this way release low molecular weight by-products which are easily biodegradable in the soil or in the compost. These assumptions are verified by a systematic task of chemical and mechanical characterization and biodegradation measurements. Energetic and non energetic polyurethanes are compared in terms of weight loss and available soluble in order to verify the impact of the azide group in the final product.

The choice of thermoset polyurethane elastomers for this task is motivated in part by the fact that they can present brilliant mechanical properties over a large range of temperature, consisting of alternating roughly short sequence of soft and hard segments.

1.3 CONTENT

This master's thesis is divided into six chapters. After the first introductive chapter, the second chapter reviews concepts of energetic materials, polymer synthesis, polymer characterisation and also biodegradation processes. The third chapter presents a description of the methodology of the research: the steps followed for the synthesis of energetic and non energetic binders, starting from the polycondensation reaction to produce the pre-polymer polyol going through the polyurethane reaction. General discussions of the methods followed and technical information on the experiments realised are presented. The fourth chapter contains the article: "Early Development of energetic thermoset elastomer" submitted to Applied Polymer Science in June 2009. In this article the main results are presented: GPC, H-NMR, ^{13}C-NMR, FTIR, along with mechanical and chemical properties of the two polyurethanes. The early stages of biodegradation measurements are also discussed. The fifth chapter presents a general discussion of the study performed and the sixth chapter shares some conclusions and recommendations for future work, based on the results obtained in the present study. Finally bibliography and a appendices are presented.

Chapter 2 : LITERATURE REVIEW

2.1 INTRODUCTION

Over the past two decades the most used keywords in the plastic industry were 'biopolymer', 'biodegradability', 'biocompatibility', 'compostability', 'environmental friendliness'. These keywords are currently reflecting world's concern on the environmental pollution.

Biomaterials can be divided into two groups: natural and synthetic. Among the natural biomaterials, polysaccharides, also known as starch, are the most common natural biopolymers [9]. Starch can be refined from plants and can finally degrade in the environment. It can be used in combination with natural or synthetic materials and processed like thermoplastic elastomers. They possess low toxicity and they are biodegradable but their mechanical properties are still poor.

Between synthetic biomaterials, polyglycolide (PGA), polylactide (PLA) and polylactide-co-glycolide (PLGA) are most used and they are suitable for different applications. Among the synthetic biopolymers, aliphatic polyesters represent the most attractive materials due to their ease of degradation through hydrolysis of the ester bonds and subsequent bacterial attack. However other biodegradable polymers have showed up in recent years, such as polyorthoesters, polyanyhdrides, polyphosphazenes and polyurethane (PU), as promising materials.

This literature review concentrates on polyurethane formulations. Biodegradable polyurethanes are a family of block co-polymers which have been used as fibers, elastomers, coating and for biomedical applications for over three decades [10, 11]. At this stage, their possible applications have been expanded covering different fields of research, e.g. military and civil. Due to their good biocompatibility and inherent elastomeric properties, it is expected that energetic biodegradable polyurethanes would be more suitable than inert polyurethanes like hydroxyl-terminated polybutadiene (HTPB) for military application systems.

2.2 BIODEGRADABLE ENERGETIC ELASTOMERS

By definition an elastomer is an elastic material which is able to recover its original shape after being stretched to great extents. Elastomers are either thermoplastic or thermoset. Under rest conditions, the long molecules are randomly coiled. However, when a force is applied, the molecules straighten out in the direction in which they are being pulled. Upon release, the molecules spontaneously return to their initial random coil state.

New biodegradable elastomers containing hetero-atoms in their backbone have been developed in the last 40 years [12, 13] and poly(esters/ether) based elastomers have played an important role in this respect. Not only natural polyesters, but also synthetic polyesters can show the same biodegradability tendency if they have aliphatic chains in their backbone. They can be synthesized by the polycondensation of bifunctional monomers, and later used as pre-polymers in polyurethane formulation.

For these reasons, polyester polyurethane elastomers can be attractive materials for composite solid propellants in which the elastomers act as the rubbery phase; they can also be used as binders for other materials like oxidizers (e.g. ammonium perchlrorate) and aluminum or metallic fuel.

One of the most used prepolymers for propellant formulations is a glycidyl azide polymer (GAP). GAP is obtained from Polyepichlorohydrin (PECH), where the Cl group on the polymer repeating units can be easily exchanged with a N_3 by azidation reaction according to the well known Frankel procedure [14].

In general the GAP polymer is subsequently cured by the reaction with diisocyanate curing agents like toluene diisocyanate (TDI, isophorone diisocyanate

(IPDI) or other triisocyanates to produce an energetic polyurethane network structure [15]. A polyurethane energetic binder adds superior physical and mechanical properties to the final product that can release heat (about 685 kJ/mol) by decomposition [16].

To increase the biodegradability of a polyether based energetic material, such as GAP, some specific linkages can be inserted, for example an ester bond. Furthermore, the diisocyanate involved in the curing reaction should be as well biodegradable. Accordingly, there is a progressive use of aliphatic diisocyanate instead of aromatic ones.

Considering all these aspects, the poly(ester/ether-urethane) formulation is the key material in the overall propellants production and it is important to choose the right catalyst and the optimal reaction conditions.

2.2.1 Historical development of biodegradable polyurethane elastomers

Polyurethanes represent a large family of polymeric materials with different chemical composition and physical properties in order to be used in several applications. In 1937, Friedrich Bayer synthesized the first prototype, Perlon U, reacting toluene diisocyanate and dihydric alcohols. However, polyurethanes started to be a suitable alternative to natural rubber between the two World Wars in Germany [11].

A polyurethane network is characterized by a repeating urethane group (Figure 2.1).

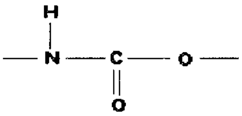


Figure 2.1: Urethane functional group

Polyurethanes can be either thermoplastic or thermoset. Thermoplastic polyurethanes can be softened if heated and hardened if cooled. Thermosets, on the contrary, are set into permanent shape by chemical cross-links that occur during cross-linking reaction. The process of hardening a thermoset in a certain shape is irreversible. Thermoset polyurethane elastomers, consisting of alternating approximately short sequences of soft and hard segments, can present good mechanical properties over a large range of temperatures for different applications (Figure 2.2).

The typical cross-linking reaction for the production of thermoset polyurethane elastomers occurs between a polyol and a diisocyanate. It might require chain extenders, catalysts and blowing agents. The soft segments (SS) which come from the polyol, add elastomeric characteristics to the polyurethane, whereas the hard segments (HS) with diisocyanate structure, provide the chemical cross-links. The final properties will depend on the phase separation between the soft and hard phases [17].

In general it is possible to distinguish three methods for polyurethane production: the one-shot method [18], the pre-polymer method [19], and the quasi pre-polymer method [20]. In the one-shot method, all the reactants are mixed together with catalyst and pigments [11]. In the pre-polymer method, the polyol is pre-reacted with an excess of diisocyanate and after it is mixed with all the other reactants. In the quasi pre-polymer method, only a part of the polyol is mixed with the diisocyanate and the other part is mixed with the rest of the reactants (chain extenders, blowing agents...) as a different system. At the very end they are mixed together.

Vegetal raw materials, like starch [21], castor oil [22], cellulose, etc can be added to help the biodegradation process. Depending on the polyol type in the polyurethane formulation, the biodegrability tendency decreases as follows:

oleochemical polyols, dimer acid based polyesters > polybutadiene polyols > PTHF > polyalkyleneoxide polyethers > PC-polyols > PCL-polyols > aliphatic polyesters based on diethylene glycol and adipic acid.

Over the last twenty years, an L-Lysine diisocyanate (LDI) has received growing attention in the development of biodegradable polyurethane. S. Guelcher et al. [5]

studied a polyurethane network from lysine polyisocyanate. In their work, they synthesized biodegradable and biocompatible networks out of poly (ε –caprolactone) and poly (ε –caprolactone co-glycolide co DL-lactide) triols, lysine diisocyanate (LDI) and lysine triisocyanate (LTI) in a two-step quasi prepolymer process [5]. When LDI based polyurethane degrades, it releases lysine which is a non-toxic amino acid also present in proteins.

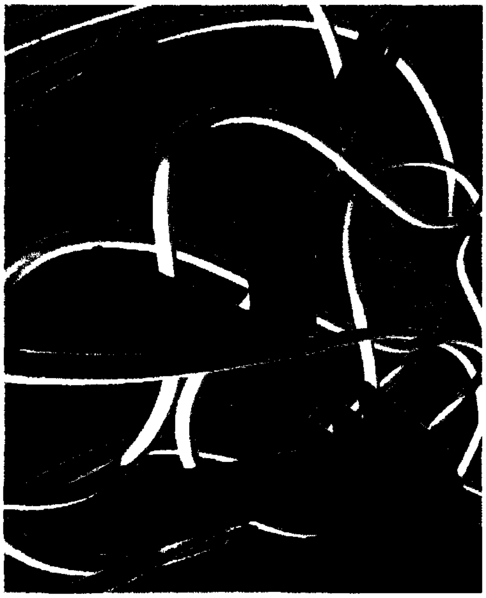


Figure 2.2: Structural model of PU elastomers [23]

2.3 SYNTHESIS OF THE POLYOL

2.3.1 Properties of the polyol

Polyols are multifunctional hydroxyl-bearing polymers. In polyurethane production, two different kinds of polyols are used:

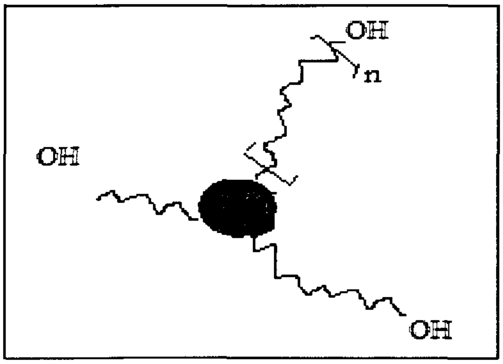
1. Polyether Polyol containing an ether group, ROR

2. Polyester Polyol: containg the ester group, RCOOR'

Polyether-based polyurethanes are not as strong and as tough as polyester-based ones. Compared to polyesters, they can resist better to hydrolysis attacks (which is favourable for biodegradation), while polyesters can provide a better oil resistance. Based on a review of current industry research, polypropylene ether glycol and polytetramethylene glycol are the most used polyethers in the polyurethane formulations [11]. Polyester polyols present high secondary forces inside their chains, (polyether polyols are normally amorphous) and they have higher thermal and fire resistance [24].

Apart from the polyesters that are obtained from the reaction between dibasic acid and diol, polycaprolactone and polycarbonate-based materials can be considered as polyesters. Polycaprolactone is synthesized through a ring opening polymerization of the caprolactone. Polycarbonate is the product of the reaction between either ethylene carbonate or propylene carbonate with an aliphatic diamine. However the most classic-based polyester is produced starting from dibasic acid and diol, with water as by-product.

A polyol for polyurethane production can have two up to eight hydroxyl group/mol (Figure 2.3).



Where
n=0,1,2,3...
∿∿ = oligomeric chain
-OH= terminal group
n= number of polymeric chain

Figure 2.3: General structure of a polyol

It is important to know the number of OH end-groups available for the reaction with diisocyanate. According to ASTM E222, the OH number can be calculated through an esterification reaction of the hydroxyl end groups with organic anhydrides (acetic anhydride or phtalic anhydride) in pyridine, followed by a titration of the excess acid reagent by a sodium hydroxide solution [25]. The hydroxyl number is expressed as milligrams of potassium hydroxide equivalent for one gram of the sample (mg KOH/g). The reaction ends with the formation of carboxylic acid groups which are neutralised by an equimolar amount of potassium hydroxide or sodium hydroxide. Figure 2.4 shows the schematic of this reaction.

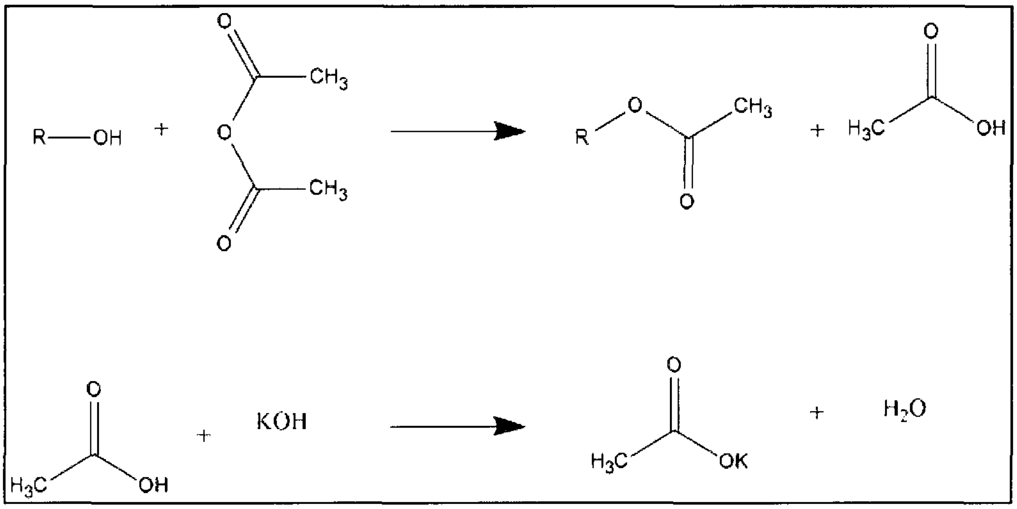


Figure 2.4: Acetylation reaction

As we can see in Figure 2.4, for one mole of the terminal hydroxyl group, one mole of KOH is used (56100 mg of KOH). According to equation (1) it is possible to evaluate the OH number as follows:

$$OH\ number = 56.1 * c\frac{B-A}{E} \qquad (1)$$

Where:

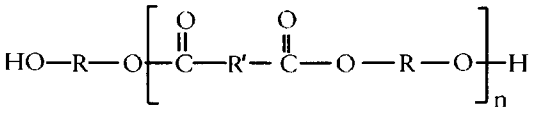
A = titre for the sample in mL
B = titre for the blank sample in mL
E = weight of the sample in g
c = concentration of KOH in mol/mL (M)

Other methods to validate the OH number are spectroscopy techniques, FTIR, NMR and NIR [26]. The hydroxyl concentration of the polyol can be measured through a comparison between the IR absorption band of THF-associated hydroxyl groups of the polyol around 3500 cm^{-1} with a calibration curve based on OH/THF-associated absorption and the concentration of primary alcohols.

2.3.2 Chemistry of polyols

The first studies on polyester polyols were done in the 1930s by Carothers at Dupont, who gave a satisfactory foundation to well describe polycondensation reactions for later studies [27]. Several years later, Flory at Cornell University developed a systematic kinetics mechanism.

Polyester polyols used for polyurethane formulation are either low or high molecular weight polymers, with the characteristic ester group in the repeating unit and they are hydroxyl-terminated (Figure 2.5).



$$HO-R-O\left[-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C}-O-R-O-\right]_n-H$$

Figure 2.5: General Polyester chain

This kind of polymer can be produced in the following ways (Figure 2.6)

1. Step-growth polycondensation reaction between carboxylic acids (or their derivatives like chloride, esters or anhydrides) and diols (or polyols)
2. Ester interchange or alcoholysis.

The focus of this research is on the first method.

The kinetics schematic of polycondensation reactions is not simple, mainly because of the consecutive reactions in which both degree of polymerization and average molecular weight of the polymer increase as the reaction proceeds. Furthermore, the esterification reaction is thermodynamically reversible and, potentially, all the polyesters can degrade in the presence of water.

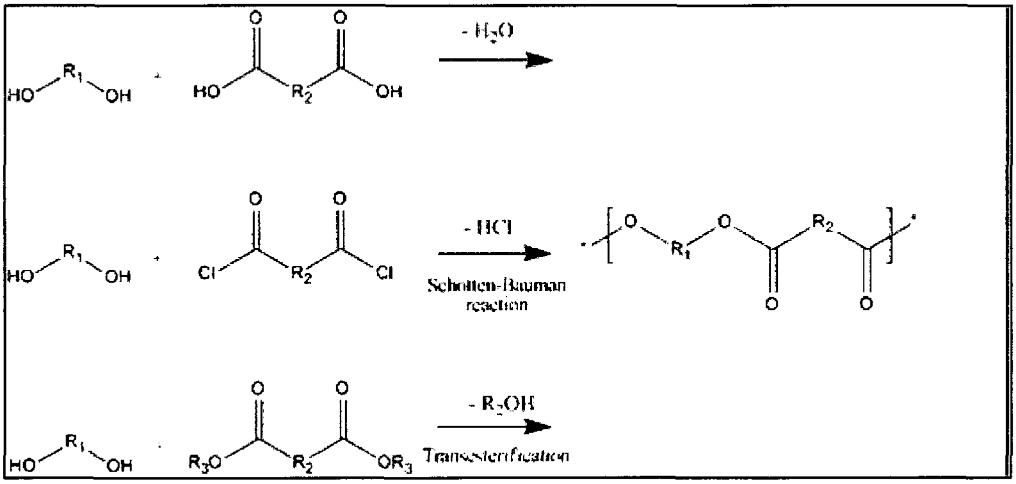


Figure 2.6: The scheme of polycondensation reaction

According to equation (2), it is possible to find a correlation between the degree of polymerization (x_n) and the number average molecular weight of the polymer (M_n):

$$M_n = x_n M_o \tag{2}$$

Where M_o is the molecular weight of the repeating unit.

The average degree of polymerization is defined as follows:

$$x_n = \frac{N_0}{N} \qquad (3)$$

Where N_o is the total number of molecules originally present and N is the total number of the molecules in the system after polymerization. The average degree of polymerization is also related to the conversion of the reaction (p):

$$X_n = \frac{N_O}{N} = \frac{C_O}{C} = \frac{1}{1-p} \qquad (4)$$

As shown by the equations above, degree of polymerization and conversion are strictly related. To control the molecular weight, the conversion has to be controlled and vice versa. This kind of reaction is reversible and the equilibrium constant (K_c) has to be large enough to produce high molar mass polyester.

$$..-C(O)OH + HO^- \overset{Kc}{\Leftrightarrow} ... - C(O)O - \cdots + H_2O \qquad (5)$$

$$K_c = \frac{[...-C(O)O-\cdots][H_2O]}{[..-C(O)OH][OH]} \qquad (6)$$

However, in most of the polycondensation reactions, the value of K_c is not very large. As a consequence, it is necessary to remove the by-product (water) from the reaction mixture to achieve a reasonable degree of polymerization, X_n. In the literature there is a correlation between X_n and Kc (equation 7):

$$X_n = K_c^{0.5} + 1 \qquad (7)$$

Most of the reactions possess a K_c value equal to about 10, which consequently results in a degree of polymerization around 4. By contrast, the value of K_c is pretty high in case of reaction in which acid chlorides, acid anhydrides or activated carboxylic acids are used.

Polyesterification reactions can be acid-catalyzed and they proceed by S_N2 mechanism, which is an addition-elimination mechanism, according to the following scheme:

Step 1: Fast Equilibrium

$$R-(C=O)OH + H^+ \underset{K1}{\Leftrightarrow} R-(C=OH\oplus)OH \tag{8}$$

Step 2: Nucleophilic attack

$$R'-OH + R-(C=OH\oplus)OH \underset{k2}{\rightarrow} R-C(OH)_2-(OH\oplus)-R' \tag{9}$$

Step 3: Loss of water

$$R-C(OH)_2-(OH\oplus)-R' \underset{k3}{\rightarrow} R-(C=OH\oplus)-O-R' + H_2O \tag{10}$$

Step 4: Regeneration of catalyst

The determining step is the alcohol addition to the protonated acid, and the rate of polyesterification is:

$$R_p = \frac{-d[COOH]}{dt} = k_2[R(C=OH^+)OH][R`OH] \tag{11}$$

Appling the equilibrium assumption we have:

$$R_p = \frac{-d[COOH]}{dt} = k_2K_{eq}[R(C=O)OH][R`OH][H^+] \tag{12}$$

In order to have a good yield, at least two important prerequisites must be respected:

1. The equilibrium constant of condensation (K_c) has to be large enough
2. Stoichiometry 1:1 must be strictly obeyed

Since the acid acts as the catalyst, its concentration should be constant. Furthermore, at the stoichiometric condition, i.e., [RCOOH] = [OH], the rate expression becomes:

$$\frac{-d[COOH]}{dt} = k_{exp}[COOH]^2 \tag{13}$$

Instead of using a carboxylic acid, it is also possible to carry the reaction with a diacid chloride, using a tertiary amine, such as triethylamine or pyridine as the catalyst. The reaction between a diol and a diacid chloride has the advantage of being faster than the direct polycondensation between a diol and a dicarboxylic acid.

$$\mathrm{R-OH} + \mathrm{R'C(O)Cl} + \mathrm{Nu} \rightarrow \mathrm{R'C(O)OR} + \mathrm{NuH^{+}Cl^{-}} \tag{14}$$

Concerning the reaction conditions, polycondensation can be conducted in inert solvents such as toluene, xylene or chlorobenzene, using an acid catalyst in mild conditions. These solvents are hydrophobic and able to form an azeotrope with water which is the by-product and it can be easily removed. It is an excellent alternative to prepare polyesters that cannot tolerate high temperature reaction or when the target is to prepare polymers with a molecular weight above 30000 g/mol [25].

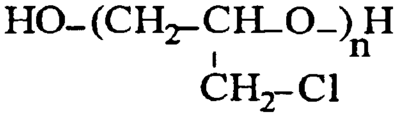
Kricheldorf and co-workers conducted a remarkable research work comparing basic methods (transesterification reaction, acid catalyzed reaction, and pyridine catalyzed reaction) to produce polyesters in order to find out the best synthetic method to produce a co-polyester with a high yield [28]. They succeeded to produce an aliphatic polyester using the pyridine catalyzed polycondensation method, through a reaction between butyne-1,4 Diol and several aliphatic dicarboxilic acids dichlorides at room temperature. In this way, the activated acid could react with an alcohol in relatively mild conditions based on the Schotten- Baumann mechanism and pyridine acts as a catalyst. However, this type of reaction has disadvantages; first of all, dicarboxylic acids dichlorides are very expensive. Also, the reaction needs very dry and purified solvents and large amount of salt is formed as by-product.

2.3.3 Raw materials for the synthesis

2.3.3.1 Polyepichlohydrin

In a polymerization reaction, a thorough knowledge of the microstructure of the reactants is necessary. For this reason, a brief literature review has been conducted on polyepichlorohydrin (PECH).

PECH (Figure 2.7) has excellent properties, especially in terms of resistance to high temperature, oil, fuel, and ozone. It can be used in certain applications such as fuel hoses, emission tubing, air ducts, and diaphragms.



$$HO-(CH_2-\underset{\displaystyle CH_2-Cl}{CH}-O-)_n H$$

Figure 2.7: Polyepichlorohydrin (PECH)

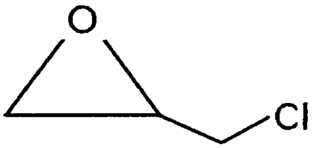


Figure 2.8: Epichlorohydrin (ECH)

PECH can be prepared via a ring opening polymerization of epichlorohydrin (ECH) (Figure 2.8) by varying the initiators and the co-initiators. This monomer is asymmetric: the attack can proceed either at the head or at the tail. Depending on the type of ring opening reaction occurring in the propagation step, different links can form in the polymer chain: head-to-head, head-to-tail and tail-to-tail.

The polymerization of ECH takes place according to a cationic mechanism using Lewis acid like BF_3 etherate, $SnCl_4$, $SbCl_5$ or $FeCl_3$. Water/aluminium alkyl, trialkyl oxonium salts can be used as initiators [29]. In the most common mechanism, at the beginning, there is an interaction between a protic compound, like water, alcohol or a diol and the Lewis acid, in this case BF_3 etherate (Figure 2.9). After this step, the activated monomer can react with the diol molecule producing a hydroxyl terminated macro-monomers which in turn reacts with the activated monomer yielding PECH with hydroxyl end groups.

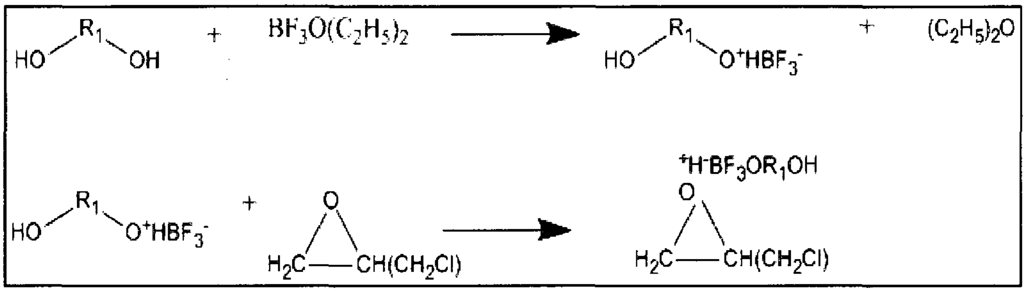


Figure 2.9: Protonation of the monomer during ring opening polymerization[30]

PECH can also be produced by a reaction between the activated chain end and ECH [30] as drawn in figure 2.10. The chain reaction terminates by reaction with a molecule of diol or water to give the hydroxyl terminated polymer.

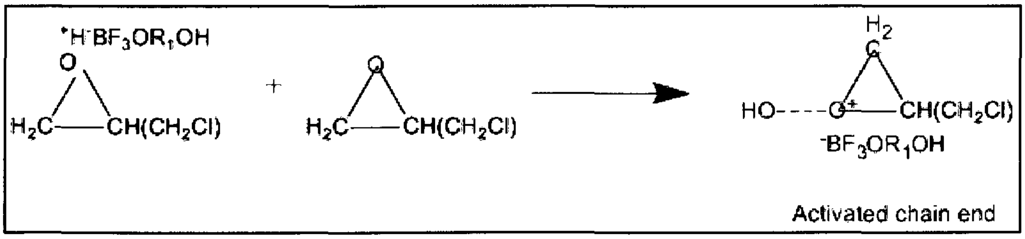


Figure 2.10: Activated chain mechanism[30]

The two mechanisms described above are complementary and they may occur simultaneously. Varying reaction conditions and starting material, it is possible to end up with products with different properties.

Polyepichlorohydrin (PECH) has been used as precursors for Glycidyl Azide Polymer (GAP), i.e. an energetic polymer, by substitution of the chlorine atoms of PECH with azide groups of sodium azide [31]. Subsequently, GAP can be cross-linked in the presence of an isocyanate giving an extended polymeric network [32].

2.3.3.2 Sebacic acid

Sebacic acid (SA) (molecular formula $C_{10}H_{18}O_4$) is a white crystal powder widely used in the production of nylon, alkyl resins, plasticizers and lubricants (Figure 2.11). It has a melting point of 131-134 °C, a boiling point of 294.4 °C (100 mmHg) and a flash point of 220 °C. This acid is obtained from the caustic fusion of oil in China, which is the second castor oil producer after India. As an intermediate product of oxidization of long-chain aliphatic acid, Sebacic acid (SA) has some impurities [33]. Nevertheless, it is preferred to short chain aliphatic acids for the preparation of polyesters, because it does not allow intra-molecular condensation.

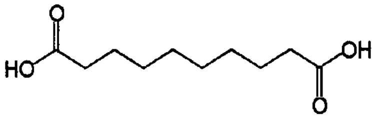


Figure 2.11: Sebacic acid

Recently, the Food and Drug Administration (FDA) of the United States approved some SA-based polymers in biomedical applications. Biodegradable polyesters have been synthesized from sebacic acid, glycol and glycerol with promising in vivo biodegradation performance and mechanical properties [34, 35].

2.3.3.3 Sebacoyl chloride

Sebacoyl chloride (or sebacoyl dichloride, SC) is a di-acyl chloride, with molecular formula $C_{10}H_{16}Cl_2O_2$. (Figure 2.12)

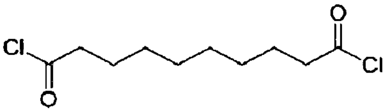


Figure 2.12: Sebacoyl chloride

Sebacoyl chloride is usually prepared through a direct reaction between sebacic acid with excess thionyl chloride; the evaporation of the excess thionyl chloride yields the sebacoyl [36]. In Table 2.1 a quick comparison between SA and SC is presented.

The choice of a dichloride dicarboxilic acid instead of a simple dicarboxilic acid can be advantageous. It is known that a polycondensation reaction between a diacid and an alcohol belongs to the group of nucleophilic substitution reaction, in which an "electron rich" nucleophile attacks the positive or partially positive charge of an atom attached to a group or atom called the leaving group (OH group). Using sebacoyl chloride the Cl^- terminal group is more nucleophilic and the reaction is more favoured.

Table 2.1: Comparison between SA and SC

	SA	SC
Formula	$COOH(CH_2)_8COOH$.	$ClOC(CH_2)_8COCl$.
MW	202.25 g/mol	239.14 g/mol
Density	1.209 g/cm^3	1.121 g/mL @ 20 °C.
Physical State	White leaflets	Liquid
Tb	295 °C	168 °C

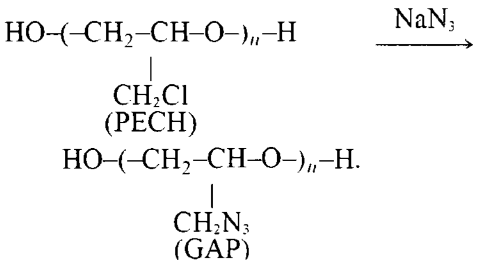
2.3.4 Energetic polyol

Originally, energetic polymers for solid propellants were born in order to replace inert hydroxyl terminated polymers. In the last decades, several attempts have been done to produce an energetic polymer with acceptable thermal stability, higher energy and environmental friendly combustion products [37]. More and more efforts have been done in the development of new energetic binders, i.e. Poly 3-nitratomethyl-3-methyloxetane (Poly (NIMMO)) , synthesized by selective nitration of OH groups of 3-hydroxymethyl-3-methyl-oxetane using N_2O_5, and Poly Glycidyl nitrate (Poly(GLYN)), synthesized by selective nitration of OH groups of glycidol using N_2O_5 [38].

GAP represents one of the most important energetic, thermally stable, insensitive hydroxyl terminated polymer, which presents low vulnerability to external stimuli (LOVA) [31]. The impact of the azide group on a polymeric chain in terms of heat capacity can be detected by differential scanning calorimetry (DSC) measurements [39]. Concerning the overall reaction, the Shell mechanism (already tested for (ECH)) was used to produce an energetic monomer for the first time [31].

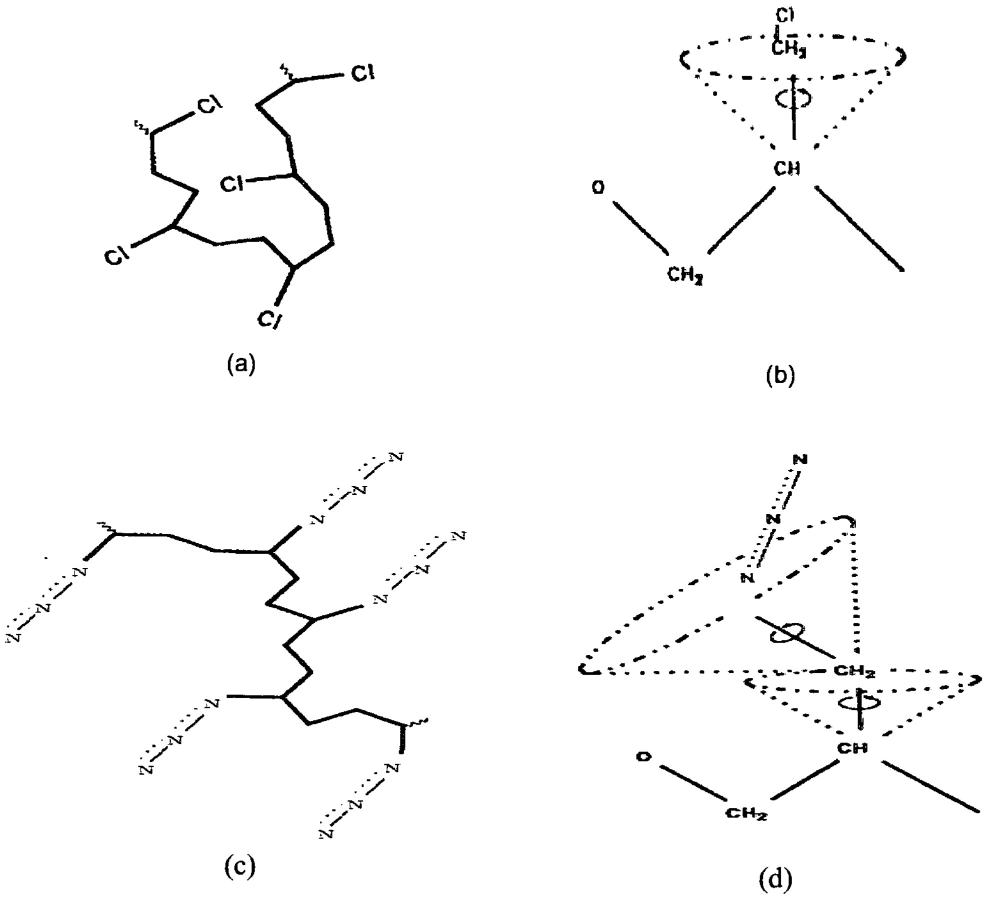
$$\begin{aligned} CH_2 - CHCH_2 - O - Cl &\xrightarrow{\overset{NaN_3}{HOAc}} CH_2 - CHCH_2 - Cl - OH \\ &\xrightarrow{OH^-} N_3CHCH_2 - O - CH_2 \end{aligned} \tag{15}$$

However, the resulting energetic monomer has a low reactivity. Accordingly, to solve the reactivity problem, following the Frankel method, PECH was polymerized using glycerol as initiator and was then successfully converted to GAP through the nucleophilic substitution of Cl with NaN_3 in DMSO (Figure 2.13) [14]. In general, GAP-diol is insensitive to detonation with unique combustion characteristics. The heat released during the combustion doesn't come from oxidation reaction, but from the decomposition of $C-N_3$ into C-N and N_2.



$$\underset{\text{(PECH)}}{\mathrm{HO{-}(-CH_2{-}\underset{\substack{|\\ CH_2Cl}}{CH}{-}O-)_{\mathit{n}}{-}H}} \xrightarrow{NaN_3} \underset{\text{(GAP)}}{\mathrm{HO{-}(-CH_2{-}\underset{\substack{|\\ CH_2N_3}}{CH}{-}O-)_{\mathit{n}}{-}H.}}$$

Figure 2.13: Synthesis of GAP



(a) (b)

(c) (d)

Figure 2.14: Molecular chain and structure of PECH (a,b) and GAP (c,d)[40]

Concerning the mechanical properties of GAP, looking at Figure 2.14, one could notice the major effects of the addition of an azido group on the molecular mobility. By replacing the Cl atom with N_3, first, the steric hindrance opposed by the N_3 reduces the flexibility of the polymeric chains (Figure.2.14a and 2.14c). Secondly, the presence of the azide groups increases the free volume available for molecular motions, which increases the degree of freedom [40].

2.4 SYNTHESIS OF POLYURETHANE ELASTOMERS

2.4.1 Raw materials for the synthesis

The synthesis of polyurethane elastomers needs at least two reagents: a polyol and a diisocyanate. In order to create a well cross-linked network, it is better to include a tri-functional alcohol, such as Polycaprolactone triol whose biodegradable properties are well known.

2.4.1.1 Polycaprolactone triol

Polycaprolactone triol (PCL) is a linear low molecular weight aliphatic polyester with moderate water solubility, prepared by ring-opening polymerization of ε-caprolactone (Figure 2.15). PCL is a processable semicrystalline polyester and it is soluble in lots of organic solvents. It has a relatively low melting point (55-60 °C) and a glass transition temperature (T_g) of -60 °C. However, one of its distinguishing features is its tendency to form miscible blends with other polymers. The functionality of PCL is three, which helps the network formation in the polyurethane formulations (the functionality should be more than 2 in order to have a cross-linked network).

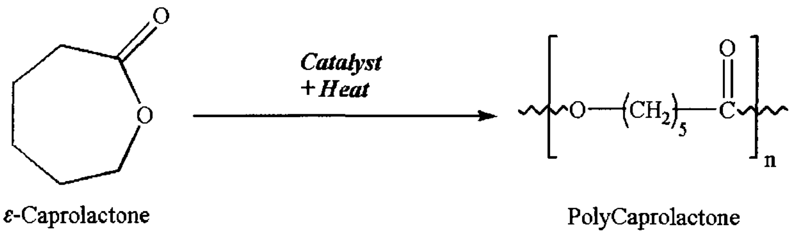


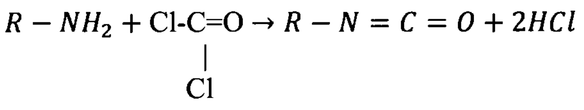
Figure 2.15: Synthesis of Polycaprolactone

Biodegradation of PCL takes place through hydrolytic degradation of the ester bonds. According to the literature, the kinetics of biodegradation of PCL is slower compared to other bio-polyesters, like poly-lactide (2-3 years) [3].

Polycaprolactone also shows biocompatibility properties; indeed, it has been used as a basic material for scaffold, matrix for long-term drug delivery and wound-covering matrix for tissue engineering [41].

2.4.1.2 Diisocyanate: L-lysine diisocyanate

The diisocyanate is an organic compound characterized by the functional group N=C=O. Its synthesis is based on the reaction between an amine, either aliphatic or aromatic, and a phosgene, as shown below (Equation 16), where R represents a given aliphatic or aromatic group.



$$R - NH_2 + \underset{\displaystyle \text{Cl}}{\text{Cl-}\underset{|}{\text{C}}\text{=O}} \rightarrow R - N = C = O + 2HCl \qquad (16)$$

The three commonly used diisocyanates for polyurethane formulations are:

1. Aromatic diisocyanates such as toluene diisocyanate (TDI).
2. 4,4-diphenylmethane diisocyanate (MDI)

3. 1,5-napthalene diisocyanate (NDI).

Aromatic diisocyanates are more reactive and they provide higher tensile strength and elongation than aliphatic ones, but aliphatic diisocyanates can enhance the biodegradability of the polyurethane, releasing non-toxic products during degradation. Moreover, aromatic diisocyanates tend to become yellowish to dark brown as they are cured, while aliphatic diisocyanates remain colourless.

Lysine-derived polyisocyanates, such as lysine methyl ester diisocyanate (LDI) in Figure 2.16 and lysine triisocyanate (LTI) are synthesized by phosgenation of amine-terminated lysine esters. These polyisocyanates present the advantage of low vapour pressure (i.e., 0.00075 mmHg at 25 °C for LTI) relative to aliphatic polyisocyanates (e.g., HDI) [5]. L-lysine is a natural amino acid, with two primary amine and one carboxyl group. It can be dissolved in water: this characteristic is likely to facilitate *in vivo* biodegradation.

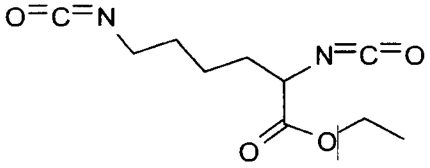


Figure 2.16: L-Lysine diisocyanate

Biodegradable aliphatic thermoplastic polyurethane based on poly(ε-caprolactone) and L-lysine diisocyanate have been synthesized with excellent low-temperature and mechanical properties [42].

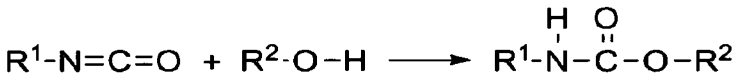
2.4.2 Chemistry of polyurethane

The kinetics of the reaction that leads to cross-linked polyurethanes is affected by the reactivity of diisocyanate, temperature, time, viscosity, ratio of reactants and the amount of catalyst and solvent. The polyurethane reaction is known since the early nineteenth century, but only at the laboratory scale. The entire formulation, now well used in different applications, has been developed during the past 30 years.

Polyurethane can be represented as a combination of three groups:

$$P - [D(CD)_m - P]_n$$

where P, D and C represent the polyol, the diisocyanate and the chain extender (if it is used in the formulation), respectively. An addition reaction between a diisocyanate and a polyol produces polyurethane through a step-growth polymerization mechanism (Figure 2.17).

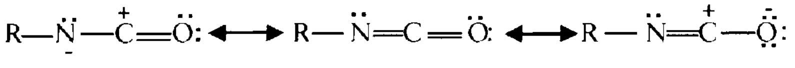


$$R^1\text{-}N=C=O + R^2\text{-}O\text{-}H \longrightarrow R^1\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R^2$$

Figure 2.17: A basic polyurethane polymerization reaction

During the curing or cross-linking process (temperature and condition can vary according to the final desired product), a three dimensional chemically cross-linked network is formed. The extent or degree of curing is expressed through the cross-link density. The extent of cross-links reflects itself in the final properties of the binder, ranging from very long, linear chain of flexible elastomers and foams to rigid, heavily cross linked polymers.

The chemistry involved on the reaction depends on the reactivity of the molecules. To begin with, the isocyanate group is very reactive: this can be explained just looking at the resonance structure in Figure 2.18.



$$R-\underset{-}{\ddot{N}}-\overset{+}{C}=\ddot{O}: \longleftrightarrow R-\ddot{N}=C=\ddot{O}: \longleftrightarrow R-\ddot{N}=\overset{+}{C}-\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:$$

Figure 2.18: Polyurethane resonance structure[43]

As shown in the figure above, the carbon atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen, has positive charge density, yielding towards nucleophilic agents such as polyols or water. Aromatic diisocyanates have higher resonance stability, ensuring higher reactivity than aliphatic diisocyanates.

Catalysts play an important role in the polyurethane production since they establish a balance in the reaction between diisocyanate and polyol. The reaction can be complicated by multiple side reactions.

Neither the polyurethane chemistry nor the processing and moulding conditions are simple. As a consequence, a good catalyst is required. Indeed, the catalyst should be able to favour different reactions in order to produce a product with the desired final properties. Basically, it is possible to distinguish two different types of catalysts:

1. *Organometallic catalysts*: they can accelerate the polyurethane reaction and the formation of urethane linkages, because they promote a faster curing process. The most used organometallic catalysts are dibutyltin dilaurate (Figure 2.19) and stannous octoate

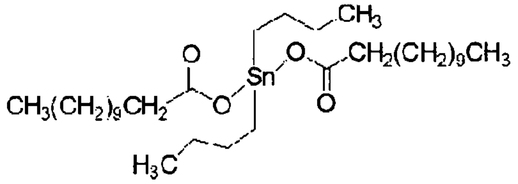


Figure 2.19: Dibutyltin dilaurate

2. *Amines catalysts*: they can promote cross-linking and also assist in controlling the cellular structure of foams. The general formula of a quaternary ammonium catalyst is presented in Figure 2.20. R_n represents a typical linear or branched saturated hydrocarbon group, with a number of carbon atoms ranging from 1 to 12; n is a number between 0 to 3: if n=0, any one of R_1 to R_6 can link together forming a heterocycle, if $n \neq 0$, they can connect together. A is a generic carbonate group and X is between 1 to 2 [44].

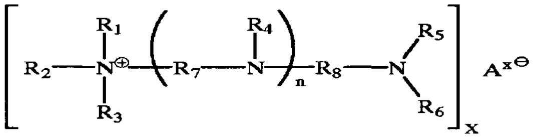


Figure 2.20: General formula of an amine catalyst

The organometallic catalysts are commonly used for isocyanate–hydroxyl reactions, while tertiary amines are the ones used for both the isocyanate–hydroxyl and the isocyanate–water reactions. Organometallic catalysts perform pretty well in the polyurethane elastomer production [45]. They act as Lewis acids and they are able to interact with basic sites in the isocyanate and polyol compounds, forming an intermediate complex. However, the steric hindrance of the metallic atom can be a barrier to the formation of the mentioned complex. As the temperature increases, the catalyst starts acting, allowing the formation of the complex intermediate and enhancing the reaction rate.

We can clearly distinguish two complementary mechanisms:

1. The polyol attacks the complex catalyst-diisocyanate in order to propagate the polymer and regenerate the catalyst.
2. The polyol reacts with the organometallic catalyst by the presence of an activated complex. In this way, it is able to interact with isocyanate to give a carbamate, which further reacts with additional polyol propagating the polymer and regenerating the catalytic species.

Dibutyltin dilaurate (DBTL) catalyzes propagation reactions very well (the reaction between isocyanate-hydroxyl) by activating hydroxyl group instead of water [46]. However, it is known that, if not used in the right proportions, DBTL can cause problems such as producing grains and unacceptable surface. The main problem of the curing is the likely gassing reaction. It can be associated to a side reaction between diisocyanate and the initial humidity present in the reactants, producing carbon dioxide.

2.4.3 Mechanical properties of polyurethane elastomers

The mechanical properties of a polymer can be characterized by its strain-stress curve [47]. Looking at Figure 2.21, it is possible to notice that a rigid plastic can withstand high values of stress, but it will not elongate too much before breaking. These kind of materials are strong (high modulus), but not tough. Flexible plastics do resist deformation to some extent, but it takes more time to break them. Fibers are basically stiffer rather than being tough.

Elastomers have a completely different mechanical behaviour in comparison to any other polymeric material. Indeed, elastomers have very low modulus and stand a very high and reversible elongation. In addition to what mentioned for elastomers, polyurethane elastomers have high elongation at break, high tensile strength and high tensile modulus. This combination of mechanical properties endows the material with toughness; a distinctive feature of polyurethane elastomers.

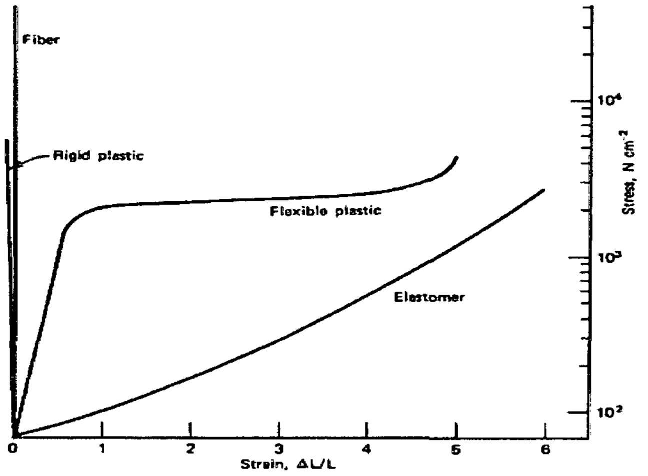


Figure 2.21: Stress-strain curve for elastomer, flexible and rigid plastic and fiber [47]

The temperature can play an important role in the mechanical response of a specific material to the stress. This is the underlying reason why the polymeric chains can move more or less easily, as temperature increases. Polyurethane forms a very complex network, in which polymer chains are interconnected by chemical and physical bonds. Its mechanical properties depend on degree of cristallinity, degree of cross-linking and glass transition temperature (T_g).

At very low temperatures, below T_g, no movement is possible. If a stress is applied, the elastic deformation of a polyurethane network depends on the elastic deformation of the polymeric chains themselves and on the local movements of the functional groups. According to Hooke's law (equation 17), the ε deformation is proportional to the stress σ:

$$\sigma = \epsilon E \tag{17}$$

As temperature increases, well above T_g, the polymeric chains can easily move [47]. This is why elastomer polyurethanes undergo a considerable and reversible elongation under a low external stress. In such a situation, the stress is proportional to the rate of deformation, because the elastic component begins to be less important than the viscous component (equation 18)

$$\sigma = \dot{\epsilon}\eta \tag{18}$$

If the temperature at which the material is used is close to the T_g, the elastic component and the viscous one can be in competition. In this case, it demonstrates a viscoelastic behaviour [48] and the elastic and dissipative components of the deformation, respectively, represented by storage modulus (*G'*) and loss modulus (*G"*), become determining. In addition, their ratio *tan*(δ) = *G"/G'* can show which component is dominant.

With regards to viscoelasticity, dynamic mechanical analysis (DMA) is a thermo-analytical technique able to detect the viscoelastic behaviour of a specific material; in particular the stiffness as function of temperature and time. The measurements can be done in different stress configurations, such as tension, shear, compression, torsion and flexure. It is possible to detect *G'*, *G''*, *tan*(δ) and T_g (which is an important property of an elastomer, representing the lower application temperature limit where the elastomer becomes stiff and loses its elastomeric properties). T_g can be evaluated in several ways:

- Peak of *tan*(δ) curve,
- Peak of *G''* curve,
- Half height of *G'* curve,
- Onset of *G'* curve.

The value of measured T_g would vary as much as 25 °C depending on the selected method [49]. For this reason, it is important to specify how T_g was originally evaluated.

In general, it is expected that the mechanical properties of a polyurethane elastomer fall after degradation. This has already been demonstrated in the case of polylactide losing its properties following degradation [50].

2.5 DEFINITION OF BIODEGRABLE MATERIALS

The social concern for the environment has pushed the propellant industry to progressively produce green materials. First, it is necessary to clarify the difference between degradable and biodegradable plastics due to the existing confusions on these concepts.

Gopferich tried to organize the ideas regarding this topic. Based on his definition, a material is degradable when it degrades during its application or at least right after. According to this definition, a non-degradable polymer will not degrade during its application and even after being used by the customers [51].

All compostable plastics are therefore also biodegradable, but not vice versa. According to the American Society for Testing & Materials, it is possible to consider a plastic as compostable only if it is able to break down into carbon dioxide, water and biomass at the same degradation rate. It should look like compost, but not produce toxic by-products [52]. Degradable plastics are not compostable, as they only degrade by chemical or physical attack and, even if there is a biological attack, it could be too slow to be significant.

The literature does not provide a universal definition of the term "biodegradation". In the biomedical field, this term implies hydrolysis of the organic material. In sustainable development theories, it means that plastics should be able to decompose into smaller products by micro-organism attack [53]. Besides that, each country has its own standards to measure biodegradability. These standards require a 60% to 90% weight loss within 60 to 180 days after being put in a standard composting environment.

As a general remark, biodegradable polymer should satisfy some requirements:

- In its own life, it must preserve its functionality during the usage,
- The polymer has to be transformed into metabolic products, like CO_2, H_2O, CH_4,
- The whole process should not have any toxic effects on the environment.

Several mechanisms need to be considered in the biodegradation process [54], as the biodegradability is influenced by:

- Chemical structure (presence of functional groups),
- Physical structure (cristallinity, orientation...).

Among these factors, since the biodegradation process starts in the amorphous regions and after develops into the crystalline ones, cristallinity is a decisive parameter. On the other hand, the key environmental parameters to take in account in a biodegradation process are:

- Presence of micro organisms,
- Availability of oxygen,
- Amount of free water,

- Temperature,
- Chemical properties of the environment (pH, humidity..),

In the literature it is possible to find different experimental procedure to measure the biodegradation of polymers. But the main three aspects to look at are the substrates of the materials, the micro organisms involved and the reaction products [55].

2.5.1 Mechanisms of biodegradation

It is possible to distinguish two different mechanisms:

- Non-Biological degradation: Polyesters, polyanydrides, polyamides, polycarbonates, polyurethanes, polyureas, polyacetals, polycarbonates can all undergo hydrolysis. In contrast to the enzymatic degradation where the polymer is degraded from the surface to the center, the polymer is degraded throughout its cross-section during hydrolysis. The degradation of PLA is one example for non-biological degradation.
- Biological degradation: It is a combination of different mechanisms. Enzymes or by-products secreted by micro organisms themselves can attack the polymers. But even the microorganisms can metabolize polymers enhancing the mechanical, chemical or enzyme aging [56].

It is important to distinguish between the degradation and the erosion of the polymers [51]. Erosion corresponds to only the loss of material due to the effective loss of monomer and oligomers leaving from the specimen. This happens during the first step process of degradation, where several small pores are formed on the surface from which monomers and oligomers can escape [51]. Acknowledging the usefulness of this distinction, in this research, the erosion phenomenon is considered as a part of degradation process.

The question to be answered is "How does biodegradation process work?" Basically ester, ether, amide or urethane bonds are hydrolyzed by a primary attack catalyzed by enzymes (Figure 2.23). In this first step, there is surface erosion, releasing water-soluble by-products, which are easily assimilated by microbial cells and consequently metabolized. Then the by-products are metabolized by micro-organisms.

Figure 2.22: Schematic hydrolysis attack of the polymeric chain

Figure 2.23 illustrates a simplified schematic of how the biological degradation works when polymers are not water-soluble and as a consequence, it is not possible to carry them directly inside the cell to be biochemically converted.

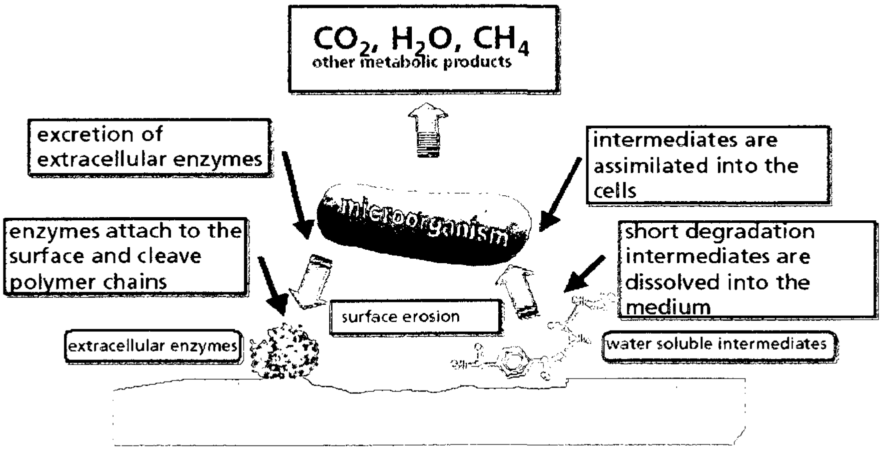


Figure 2.23: General schematic of biological degradation [54]

During the hydrolytic degradation, the molecular weight of the polymer decreases provoking an increase in the concentration of end groups (according to equation 18). Hence, in this way the hydrophilicity of polymer is enhanced [57].

$$\frac{d[COOH]}{dt} = k[COOH][H_2O]\left[\frac{Ester}{Ether}\right] \quad (18)$$

As mentioned earlier, the kinetics of degradation is influenced by the crystallinity of the material, pH, temperature and humidity. Some of these parameters involved in the biodegradation process will be discussed in more details hereafter.

2.5.1.1 The effect of the temperature

Biodegradation is itself a chemical reaction. The rate of this reaction (hydrolysis) increases with temperature, and also if the temperature is higher than the T_g of the material it will additionally enhance the reaction due to a high diffusion coefficient [58]. For example, in one case racemic polylactic acid (PLA50) has been incubated in a phosphate solution at 60 °C and at 37 °C. The weight loss and consequently the molecular weight decrease were larger at higher temperatures[58]. The combination of high elevated temperature (55-70 °C) and a good level of humidity creates the best conditions for biodegradation.

2.5.1.2 The effect of pH

Since the hydrolysis of an ester linkage is catalyzed by a base or an acid, the rate of hydrolysis reaction is faster at acidic or basic pH than at neutral pH [59]. Figure 2.24 summarizes the mechanism involved in the hydrolysis of an ester linkage by an acid or basic attack.

The most important parameter is how much water the polymer can retain which is related to the pH of the environment (soil, compost or etc.). Water absorption is favoured in the presence of a basic pH, as in that case there is an osmotic pressure towards the sample [58]. Moreover the osmotic pressure generated from basic ions diffusing inside the sample is able to neutralise the acidic pH due to the degradation of PLA [58]

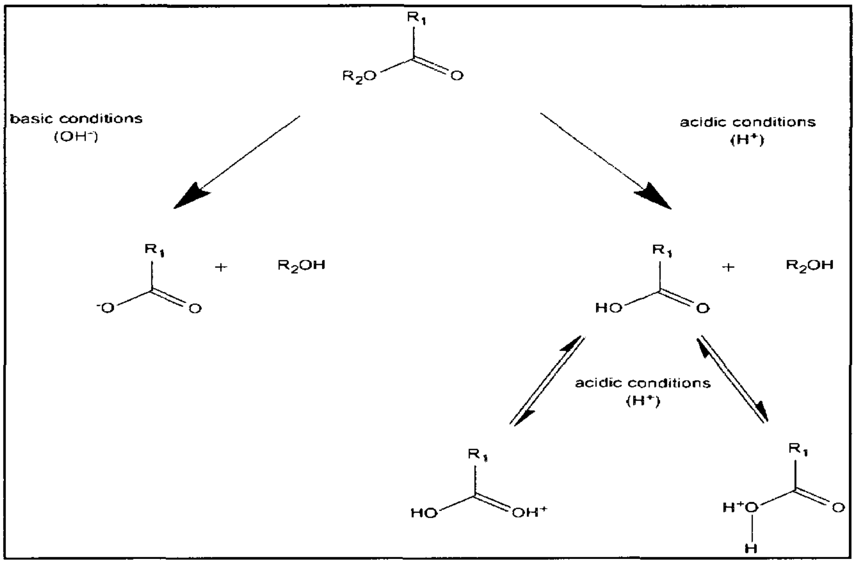


Figure 2.24: Mechanism of acid or basic catalyzed hydrolysis[58]

2.5.1.3 The effect of water uptake

As already discussed, hydrolysis reaction is the key point in the degradation of polymers. Basically, it is a bimolecular reaction in which molecules of water react with the functional groups containing labile bonds. Like other chemical reactions, the rate is determined by the concentration of the reactants.

Hydrophobic polymers cannot take too much water inside. As a result, the degradation rate will be slower. On the contrary, hydrophilic polymers are able to take a larger amount of water and the degradation rate increases.

2.5.1.4 Degradation in the compost

Composting of plastic materials can represent a valuable alternative in the waste management system, as it is a biological treatment of biodegradable materials. At the beginning, aerobic bacteria, yeasts, fungi and at the end a number of larger organisms, such as springtails, ants, nematodes and worms attack the plastic material.

The degradation of co-polyester made of PET and PCL have been widely studied and what was observed is that, Having increased the fraction of aromatic component higher than 50%, no degradation was observed in a time scale of 15 days [55]. Nevertheless, BTA co-polyester film (composed of 1,4-butanediol, adipic acid and terephthalic acid) with 51 mol% of terephthalic acid, degraded after a three-month incubation in a compost at 60 °C [60].

2.5.1.5 Degradation in the soil

The process of degradation in the soil is much slower and less conventional than the one in composting. This depends on several factors, such as temperature (it is lower in the soil than in the compost) and other environmental aspects.

There is a lack of data about degradation of plastic material in the soil. Witt et al. in a previously cited work demonstrated that a bunch of polymers could be degraded also in soil and not only in the compost [60].

2.5.2 Measuring biodegradation of polymers

In the literature several methods have been discussed in order to track the evolution of the biodegradation of polymers in the compost, soil, in vitro, etc [53]. To study the biodegradation, four processes are suggested:

- Monitoring microbial growth
- Monitoring the by-products of the degradation reaction
- Monitoring surface reduction
- Monitoring changes in surface properties

The measurements of biodegradation parameters can be based on each one of the mentioned approaches, or on a combination of them. In general, biodegradation tests can be divided into three categories: field tests, simulation tests and laboratory tests.

Field tests require the burying of the samples directly in the environment, such as soil, river, compost. However in this case, some parameters such as temperature, pH and humidity, cannot be well controlled, and the opportunity to monitor the degradation process becomes more limited. Disintegration of the materials can also take place and also the recovering of the fragments cannot be always feasible. Moreover, the tests over the fragments can be complicated by the complexity of the environment.

Simulation tests in the laboratory can be a valid approach: the samples can be buried in the compost, soil or sea-water. The degradation environment is normally very close to the natural media and all the parameters of interest (pH, humidity and temperature) can be controlled. Among these tests, soil burial test [61], controlled composting test[62], test simulating [63] can also be named.

Laboratory tests represent the most reproducible experiments, where media as well as microbial populations are well defined. In this kind of tests, polymers degrade more than they normally do in natural conditions. It could be considered as a disadvantage, since only general conclusions can be achieved.

Chapter 3 : EXPERIMENTAL METHODOLOGY

3.1 MATERIALS

Polyepichlorohydrin (PECH), 625 g/mol (relative to polystyrene standards), was supplied from 3M^{TM}, was used as stored for direct polycondensation and treated with activated charcoal to absorb impurities and contaminants. Sebacic acid (SA), 228 g/mol, and his dichloride, Sebacoyl chloride (SC), 234 g/mol, were purchased from Aldrich Co., Canada, and used as received. Dichloromethane and toluene were both purchased from Laboratoire Mat., Canada. The dichloromethane was dried using a molecular sieve. Triethylamine (TEA), pyridinium hydrochloride (PyH), pyridine (Py), p-toluene sulfonic acid (PTSA) and activated charcoal were purchased from Sigma Aldrich, Canada, and sulphuric acid from Laboratoire Mat., Canada. They were used as received.

For the polyurethane formulation, polycaprolactone triol (PCL), 300 g/mol, was purchased from Sigma Aldrich, Canada. Dibutyl tin dilaurate (DBTL), 631.56 g/mol, was also purchased from Sigma Aldrich, Canada, and used as 0.01 M, 0.1 M, and 1 M solution in dichloromethane. L-lysine diisocyanate, 226.23 g/mol, was purchased from Shanghai Infine Chemicals Co., Ltd., China.

The stabilized compost used as a substrate for the biodegradation tests, was purchased from a composting company (Fafard, Saint-Bonaventure, Canada). It contained composted manure, sphagnum peat moss, shellfish flour and seaweed, and had the following characteristics:

- pH = 6.89
- water retention = 4.29 %
- initial humidity = 1.62 %.

These parameters have been evaluated according to specific protocols [64, 65]. Before being used, the compost was homogenized using a mortar, cleaned from all inert material (rocks, metals and wood) and finally sieved.

3.2 POLYESTERIFICATION REACTION

The preparation of aliphatic polyester is not an easy reaction due to the low thermal and hydrolytic stability of this kind of polymers [66].Co- poly (ester/ether)s of poly epichlorohydrin (PECH) and sebacic acid (SA) were prepared in two different ways:

- by direct polycondensation between a di-alcohol and dicarboxilic acid
- by polycondensation between a di-alcohol and a di-acyl dicarboxylic acids.

The first method is based on a direct polycondensation reaction between the dicarboxylic acid and the diol, in solution at high temperature; the second one is a pyridine-catalyzed polycondensation between the diol and the dichloride of the carboxylic acid.

These two synthetic methods will be compared and the most efficient one will be used for the copolymer production at large scale.

3.2.1 Purification of polyepichlorohydrin

PECH was dried overnight in the oven then weighed and dissolved in THF HPLC grade under agitation on a hot plate. The charcoal was added to the mixture at high temperature. The solution was boiled for 5 minutes. The system was then cooled down to room temperature and the obtained black solution was filtered. Finally the solvent was evaporated.

Activated charcoal is carbon which has been treated with oxygen; the obtained charcoal is highly porous allowing the charcoal to have a surface area of 300-2,000 m^2/g; liquids or gases are allowed to pass through the charcoal by tines holes and interact with the exposed carbon. The carbon is able to absorb a wide range of impurities and contaminants, including chlorine and pigments.

3.2.2 Direct polycondensation

With this technique, the dicarboxilic acid and the diol are polycondensated under normal pressure by using a hydrophobic catalyst in a specifically designed reactor equipped with Dean Stark apparatus (Fig.3.1). The glassware, used in combination with a reflux condenser and a batch reactor, is able to remove the water produced during the chemical reaction performed at reflux temperature (boiling point of the solvent).

Looking at figure 3.1, during the reaction in the flask, vapours containing the reaction solvent travel out of reaction flask up to the condenser (5), and then go into the distilling trap (8). Here, the non-miscible liquids are separated into layers. When the lighter phase reaches the level of the side-arm of the apparatus it can flow back to the reactor, while the denser phase remains in the trap. The trap is at full capacity when the condensate liquids reach the level of the side-arm and the lighter phase starts to flow back into the reactor as well. In this way, water, which is a by-product of the reaction, is captured in the organic solvent, avoiding any possible contact with the polyester.

A 500 mL three necked-flask equipped with a mechanical stirrer and a Dean-Stark water trap was charged with polyepichlorohydrin (PECH) and sebacic acid (SA) in equimolar ratio dissolved in toluene. The reaction vessel was placed in an oil bath preheated in a range of temperature varying from 100 to 160 °C. The reaction mixture was stirred for a period of time between 8 and 24h. Different catalysts have been tested. Table 1 presents a summary of these experiments.

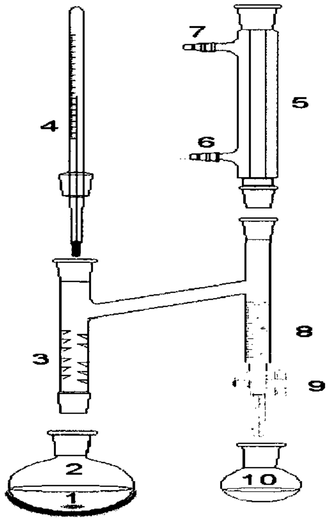


Figure 3.1: Dean Stark apparatus [67], [1]

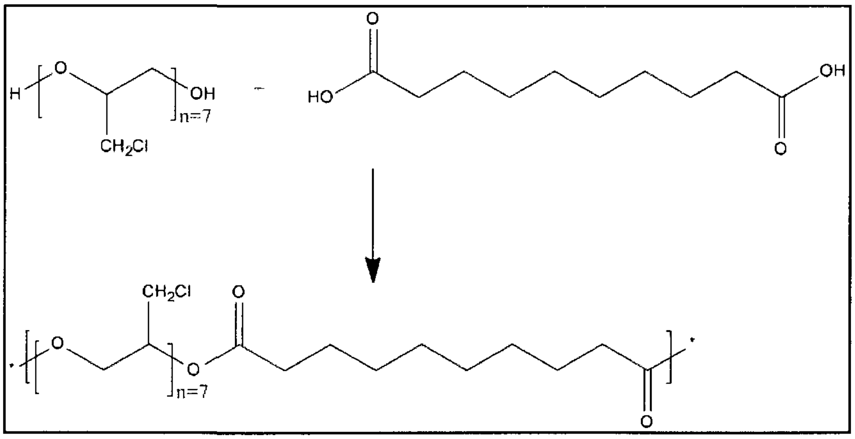


Figure 3.2: Polycondensation reaction between SA and PECH

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[1] *(1:Stirrer bar/anti-bumping granules, 2: Flask, 3: Fractionating column, 4: Thermometer, 5: Condenser, 6: Cooling water in, 7: Cooling water out, 8: Burrette 9: Tap, 10: Collection vessel*

Table 3.1: Reaction conditions of Direct Polycondensation between SA and PECH

Ex	SA/PECH	T (°C)	Time	Catalyst
1	1/1	118 °C	8 h	PyH
2	1/1	145 °C	8 h	H_2SO_4
3	1/1	145 °C	24h	PTSA*
4	1/1	145 °C	24 h	H_2SO_4

The reaction mixtures were cooled down and washed with a saturated solution of NaCl in water and extracted with toluene. They were then dried using Na_2SO_4 and filtered. The solvent was evaporated off in rotary evaporator equipment and dried over night in an oven under vacuum at 80 °C. Table 3.1 presents a summary of these experiments.

3.2.3 Polycondensation with diacid dichlorides

PECH and Sebacoyl Chloride (SC) in equimolar ratio were dissolved in dichloromethane into a three-necked glass flask, equipped with gas-inlet and gas-outlet tubes and a mechanical stirrer, and cooled -5 °C. Pyridine (240 mmol) was added drop-wise under cooling. After complete addition of the pyridine, the reaction mixture was stirred at room temperature for 24 and 48h and afterwards poured into cold methanol. The precipitated polyester was washed several times with water and NaCl saturated solution, dried over Na_2SO_4 and filtered. The solvent was evaporated off in a rotary evaporator equipment and dried over night in an oven under vacuum at 80 °C.

In figure 3.3 the reaction set up is shown.

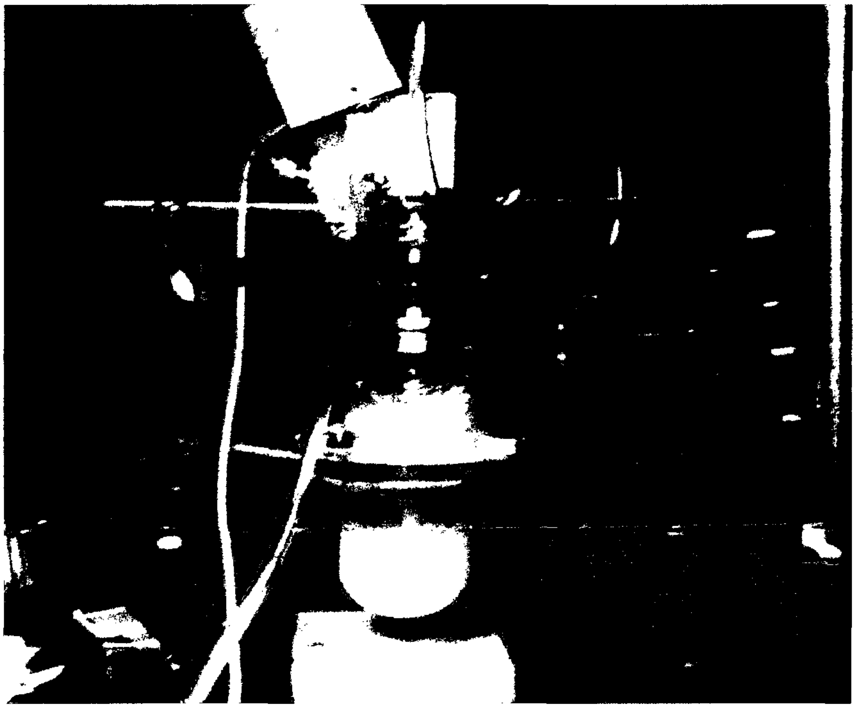

Figure 3.3: Direct polycondensation apparatus

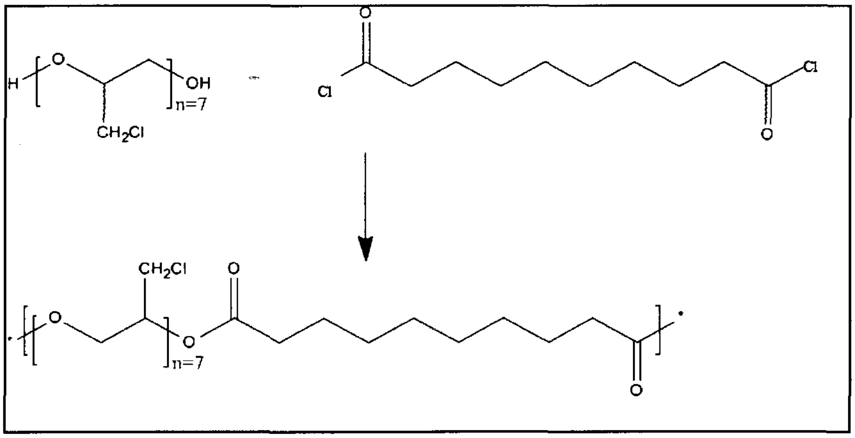

Figure 3.4: Polycondensation reaction between SC and PECH

3.2.4 Azidation of the copolymer

Forty grams of a low molecular weight copolymer, synthesized according to the procedure described in the previous section, were dissolved in 500 mL of DMSO and put in a 1L glass vessel BUCHI reactor (BUCHI laboratory autoclave BEP 280) equipped with nitrogen inlet and outlet (Figure 3.5). The jacketed reactor is heated by an external oil bath circulator and mixing is provided by a top mounted magnetic drive impeller. After 15 minutes an excess of NaN_3, dissolved as well in DMSO, was added and the temperature was slowly increased until 85 °C and the reaction was continued for 24h. The resulting reaction mixture was washed with water, and the organic phase was extracted using methylene chloride. The organic phase was dried over sodium sulphate to remove all traces of water, filtered and finally the solvent was evaporated under vacuum

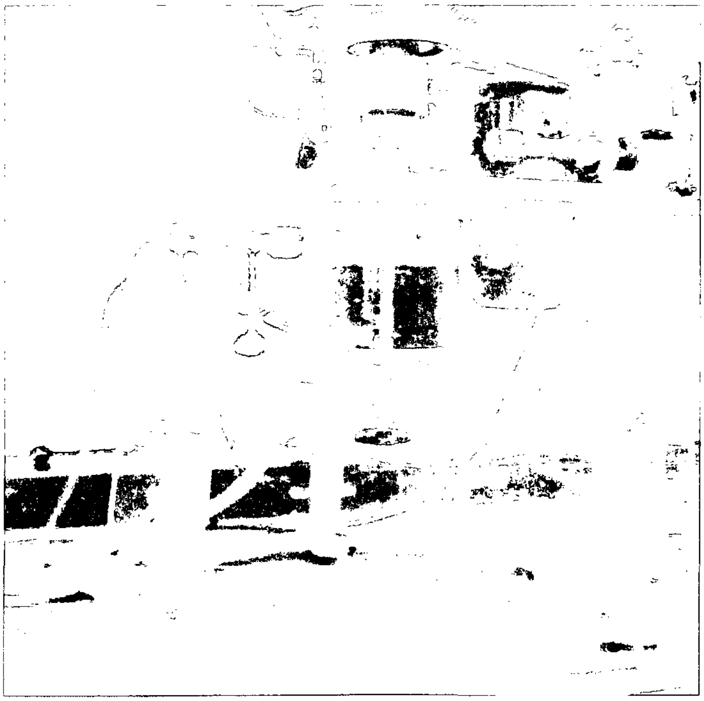

Figure 3.5: Azidation reaction in the BUCHI reactor

3.3 PREPOLYMER CHARACTERIZATION

The H-NMR and ^{13}C-NMR spectra were recorded on Bruker Avance DRX 500 MHz NMR spectrometer using 5 mm (o.d.) sample tubes. $CDCl_3$ containing TMS served as the solvent. Chemical shifts in deuterated chloroform ($CDCl_3$) were reported downfield from TMS (T=0) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CDCl_3$ (77.00 ppm) as an internal reference.

Gel permeation chromatography (GPC) was performed using a system equipped with a refractive index (RI detector Waters 2414). A combination of two columns HSP gel^{TM} HR MB-M (6.0 x 150 mm) was used in tetrahydrofuran (THF) (HPLC grade) as the mobile phase at a flow rate of 0.5 mL/min. Commercial polystyrene standards were used for calibration. Sample concentrations were approximately 1.8 mg/mL in THF, with an injection volume of 1 μL. For the copolymer synthesized in this project, no monodisperse standards are available and the molecular weight is given in terms of a polystyrene equivalent molecular weight.

Fourier-Transform infrared spectroscopy (FTIR) was performed using a FTIR Instrument (BioRad instrument, model 3000 Excalibur). Absorbance measurements were carried out using calibrated 0.5 mm KBr and BaF_2 cells. The spectrometer was operated during a scan time of 32 min on the full frequency range, with a resolution of 4 cm^{-1}. For these experiments the co- poly (ester/ether) was dried overnight in the oven at 60 °C under vacuum for two days and the solvent as well dried with molecular sieve. In this way THF and the samples were dried and oxygen-freed [68].

The hydroxyl number has been evaluated through acetylation reaction. First, 15 g of anhydride acetic were dissolved in 35 of pyridine. About 2 g of the co-polymers have been dissolved with gentle warming in pyridine. After cooling, the same amount of the acetylating solution is added. Samples of pyridine and acetylating solution were prepared as blank values. The samples have been dried at 110 °C in the oven for 1 h. After cooling, a few drops of Phenolphthalein solution are added to each sample which is titrated with 1 M NaOH solution until the color changes suddenly to violet. The hydroxyl number indicates how many grams of NaOH are equivalent to the free hydroxyl group present in 1 g of the substance.

The results of this titration method were compared with FTIR analysis. In the latter, the hydroxyl concentration or OH equivalent weight was evaluated from the comparison between the FTIR absorption bands of THF-associated hydroxyl groups of the co-poly (ester/ether) near 3500 cm^{-1}. The calibration curve was obtained using the OH/THF associated absorption of polyepichlorohydrin as a reference plotted against the concentration of PECH. The OH number was evaluated in such conditions that all the OH groups were associated to the solvent, and the presence of free or self-associated OH was negligible.

Differential scanning calorimetry (DSC) tests were performed with TA Instruments (Q1000) at scan rate 5 °C/min, varying the temperature from 30 to 300 °C.

3.4 POLYURETHANE FORMULATIONS

Two polyurethane networks with elastomeric and glassy mechanical properties have been synthesized; one from LDI, the copolymer of PECH and SC and (PCL) and another from LDI, the energetic copolymer and PCL.

All the reactants must be dried prior to use. The copolymer and PCL were dried overnight in a vacuum oven at 60 °C to eliminate all the residual water which can react with the diisocyanate and giving off carbon dioxide gas. The bubbles can escape or be trapped inside the polyurethane network, compromising the mechanical properties. The water amount was checked by Karl Fisher experiments, using a Mettler Toledo C20D Coulometric Karl Fischer.

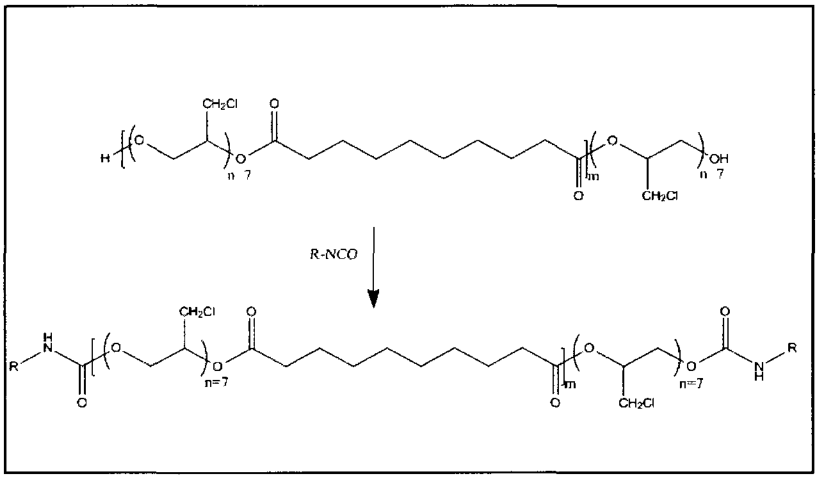

Figure 3.6: Polyurethane reaction

In the first step, the energetic or non energetic copolymer has been mixed with the PCL-triol (0.26% mol) component to form a reactive liquid mixture by adding DBTL in methylene chloride solution (0.01 M, 0.1 M or 1 M, 0.015 % mol catalyst). The reaction mixture is then put in the oven at 60 °C under vacuum for 1h. Then, LDI, according to a molar ratio of [NCO]/[OH]=1.33, was added by using a syringe.

The desired ratio satisfied the following equation:

$$\frac{NCO}{OH} = \frac{W_{LDI}/EW_{LDI}}{W_{polyol}/EW_{polyol}} \tag{19}$$

The reaction mixtures were casted in an open mould to form a solid material at 60 °C under vacuum for a couple of hours, and then left to be cured at ambient pressure at 75 °C for 24h. The excess of the diisocyanate is due to the need for the compensation of diisocyanate consumption during the reaction which can compromise the network formations.

The elastomers have been characterized before composting in order to obtain water uptake, chemical properties (NIR) and mechanical properties (DMA).

Table 3.2: Polyurethane formulations

Binder	NCO/OH	PCL	Catalyst	Conditions
LMW	1.33	0.26%(w/w)	DBTL (0.01M) 0.15%	Degassing at 60 °C Curing at 75°C for 48h
HMW	1.33	0.26%(w/w)	DBTL (0.01M, 0.1M,1M, pure catalyst) 0.15%	Degassing at 60-65-70 °C Curing at 85 °C for 48h
ENERGETIC	1.33	0.26%(w/w)	DBTL (1M) 0.15%	Degassing at 60 °C Curing at 75 °C for 24 h

3.5 POLYURETHANE CHARACTERIZATION

3.5.1 Water uptake

The degradation rate of a polymer depends on the amount of water it can absorb. During hydrolysis, there is an interaction between water and the functional group of the investigated material. The rate of reaction depends on the concentration of both reactants [51]. A hydrophobic polymer doesn't take up a large amount of water, resulting in a slower degradation rate. On the other hand, a hydrophilic polymer has the tendency to absorb water and the degradation rate increases.

The equilibrium water uptake is defined as the fraction of the gain in weight of a small sample disc and is calculated as follows:

$$\boldsymbol{Water\ uptake} = \frac{(M_2 - M_1)}{M_1} * 100\% \qquad (19)$$

M_1 is the initial weight of the sample and M_2 is its weight after 24 h in deionized water at room temperature.

3.5.2 DMA analysis

Dynamic Mechanical Analysis (DMA) was used to determine the viscoelastic relaxation transition temperatures of the elastomers. The elastic modulus (or storage modulus, G'), the viscous modulus (or loss modulus, G") and the loss tangent (Tan δ) were measured as functions of temperature and time.

61 x 13 x 3 mm^3 rectangular samples of were used and the measurements were performed with a dynamic thermo-analyzer (TA Instruments DMA-2980) using a dual cantilever geometry in the linear viscoelastic regime at a frequency of 1 Hz, under a force of 0.01 N and an oscillation amplitude of 25 μm over a temperature range of -50 to 20 °C. The scanning rate was varied between 2 and 5 °C/min

Sweep frequency tests were implemented according the following procedure:

- Cooling down until -50 °C
- Isothermal conditions at -50 °C for 5 minutes
- Data acquisition
- Heating at 5 °C/min until -40 °C
- Heating at 2 °C/min until -20 °C
- Heating at 3 °C/min until 20 °C

Tan (δ) is given by the ratio of G'' over G', and is an indicator of the relative degree of damping of the elastomers: it shows how much energy the elastomers loose because of rearrangements and internal friction after the appliance of stress.

3.6 COMPOSTING OF THE ELASTOMERS

According to the ASTM D 5988 method, a substance known to biodegrade (starch or cellulose) also has to be tested in order to verify the soil activity. The biodegradation of elastomers in compost is a relatively new field of research and is based on a procedure developed for polylactide, a well known biodegradable polyester. In Appendix 1, the protocol followed for PLA is available based on standard protocols ASTM D 5988-03 and ASTM D5338-98(2003)[69]. Some modifications have been made to it according to previous results [70] and due to the different nature of the materials involved in this work. In a previous study on polyurethane binder based on polycaprolactone diol and hexamethylene diisocyanate (HDI) it was observed that degradation does not take place in an abiotic environment, except for a change of color [70]. In this work, it has been assumed that biodegradation doesn't occur without any bacterial flora and/or in dry conditions.

3.6.1 Preparation and characterisation of the compost

The biodegradation procedure required a preliminary work to prepare the complete set up where the samples were subsequently stored. The procedure established by A. Harbec for polylactide [69], and reviewed by Maes [70], has been followed.

The compost has been homogenised: 1) all of the inert materials (rocks, metals and wood) were removed, 2) the density was made uniformed using a mortar and 3) sieving and mixing of the compost were performed. The composite on was in agreement with the limits concerning the concentration in metals and metalloids established by Quebec Gouvernament. Three parameters have been checked at the beginning: pH, water retention and humidity. In the next sections all the procedures are presented and in annexe 3 all the results are presented.

3.6.1.1 Evaluation of the pH of the compost

The pH has to be between 6 and 8 in order to guarantee the adequate environmental conditions for biodegradation. If the pH of the compost is lower than 6, the microbial flora can be atypical, while a pH over 8 can lead to the retention of the CO_2 formed during the biodegradation process. Estrella has developed a protocol for for measuring the pH in compost [64]

3.6.1.2 Water retention

The maximum water retention has to be determined in order to be able to apply the operating conditions at 60% of the water retention capacity. Leduc has developed a protocol regarding this procedure [65]. The water retention has been calculated as followed:

$$CRCss = \frac{(P2-P1)-(P3-P1)}{(P3-P1)} \tag{20}$$

Where:

p_1: Weight aluminum cupel
p_2: Weightwater saturated compost+ cupel
p_3: Weight dry compost+ cupel

3.6.1.3 Initial humidity

Another important parameter to measure is the initial humidity of the compost, in order to know the initial water content. The water content has been calculated according to the equation 25:

$$\frac{(weight_{cup+humid\ compost} - weight_{cup+dry\ compost})}{(weight_{cup+dry\ compost} - weight_{cup})} = \frac{g_{water}}{g_{dry\ compost}} \tag{21}$$

3.6.1.4 Preparation of the box and identification of the material

Three boxes have been prepared to host the samples prepared according to the procedure described in paragraph 3.4. Rectangular samples have been placed in the three boxes filled with compost. The boxes were subsequently incubated for periods of time ranging from 10 to 25 days. The water content was regularly checked and maintained at 60% humidity. The temperature was set at 55 °C, which is an average temperature evaluated from the literature [71, 72] (aerobic conditions, pH between 6 and 8 and 60% humidity).

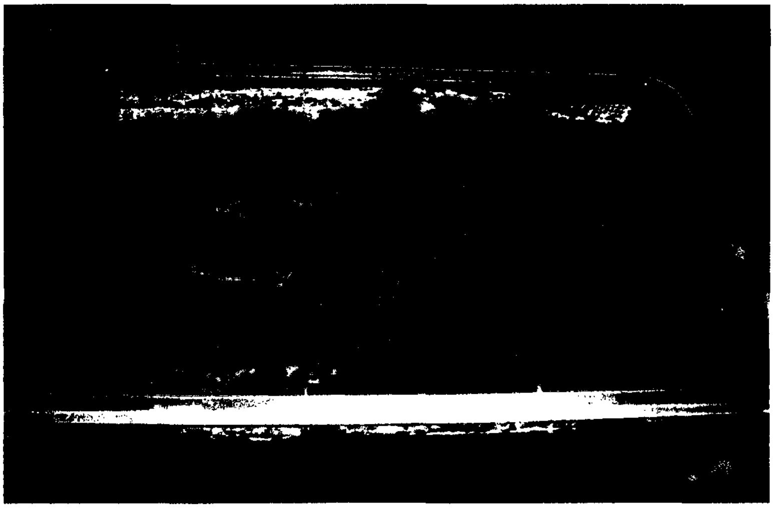

Figure 3.7: Box used for composting

Systematic sampling was performed every 10 days to check the evolution of the biodegradation. It has been evaluated by checking:

- The evolution of morphological properties (PAS FTIR analysis)
- The evolution of the weight and of the crosslinking density (Soxhlet extraction)

3.6.2 Evaluations of the biodegradation of the compost

The biodegradation of the elastomers and the impact of the composting on the polyurethane networks have been evaluated by using *soxlet extractions*.

3.6.2.1 Soxlet extraction

Soxhlet extraction is a useful technique to measure the solubilit of a given material in a solvent [73, 74]. This technique can also be used to detect the degradation of a cross-linked polyurethane elastomer [75]. The polymer is extracted by repeated washing using an organic solvent under reflux in special glassware (figure 3.8).
Every ten days Soxhlet extractions were performed to measure the soluble fraction of polyurethane. A 2g sample of the degraded cross-linked polyurethane was extracted with 200 mL of methylene chloride for 24 h. The set up is shown in figure 3.8. The remaining insoluble solid was dried under vacuum for several hours in the oven under vacuum at 40 °C before weighing.
The evolution of the degradation (conversion) has been monitored by measuring the increase of the soluble part of the polyurethane [75]:

$$\alpha = \frac{(W_0 - W)}{W_0} \tag{23}$$

where W_o is the initial weight of insoluble elastomer and W is the actual weight of insoluble elastomer.

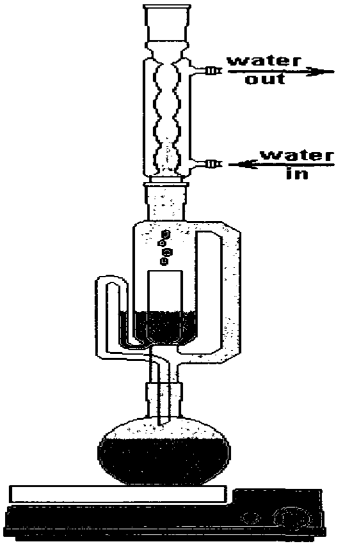

Figure 3.8: Soxhlet glassware

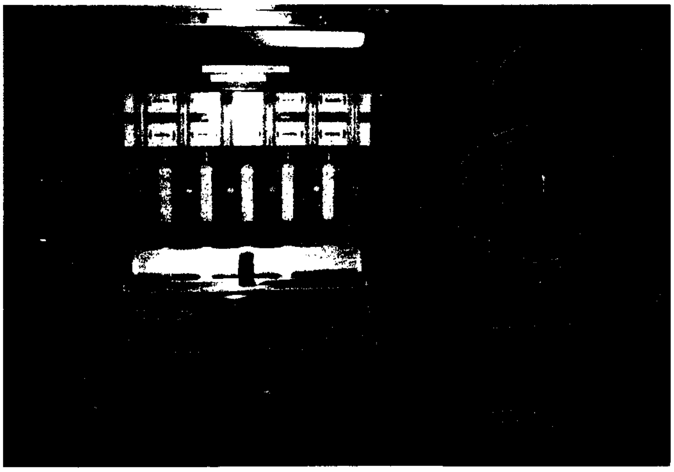

Figure 3.9: Soxhlet apparatus

3.6.2.2 FTIR PAS

Polymer degradation is often accompanied by significant changes in the chemistry and morphology of the polymer itself. Vibrational spectroscopy is a very sensitive tool to monitor these kinds of changes. Since the degraded samples either cannot transmit light or do not possess suitable surfaces for reflection, it's not always possible to obtain the absorbance or reflectance spectra of these materials.

Vibrational spectroscopy has proven to be a very useful technique for surface investigation of materials, especially for identifying chemical bonds and structures [76]. This type of IR analysis is based on the Fourier transform of the time dependent signal that arises from the penetration of thermal waves in the sample, i.e. the *photoacoustic effect*. According to this principle, an acoustic signal is generated by the sample when it is exposed to a modulated light source.

The sample, placed in a closed chamber in a helium gas atmosphere, is exposed to a modulated light source (Figure 3.10). When the sample absorbs the incident light a modulated temperature fluctuation is produced. Heat generated within the bulk of the sample is conducted to the surface so that the temperature of the layer next to the surface varies at the same frequency as the incident light. The resulting pressure modulation is an acoustic signal and it is detected by a sensitive microphone coupled to the chamber.

Each functional group present in the sample absorbs at a particular infrared frequency, generating an acoustic signal at the particular audio frequency corresponding to the incident infrared frequency.

FTIR measurements were performed using a Digilab FTS6000 FTIR spectrometer equipped with a Photoacoustic cell (MTEC Model 300 Detector; from the company MTEC Photoacoustics, Inc.) filled with Helium gas. In general, the signal to noise ratio was high enough for all the measurements, and all the samples were run in the same conditions at room temperature. Each sample was scanned 64 times with a resolution setting of 8 cm^{-1} using the rapid scan mode at the lowest mirror frequency (2.5 KHz) to maximize the signal and probe the deepest layers possible into the samples

Since water vapours and moisture can evolve from some the samples inside the PAS cell, artefact bands can be observed on the spectra. Perfect drying of the samples is then required.

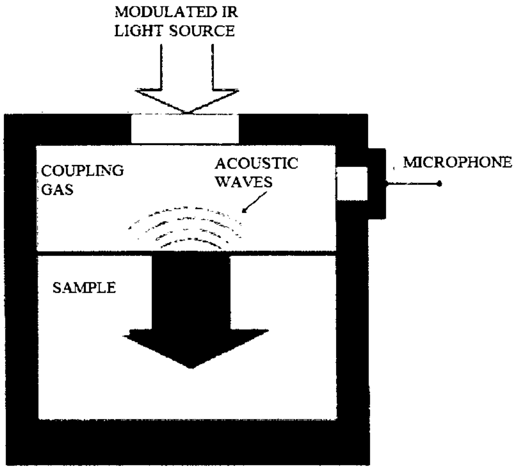

Figure 3.10: Photoacoustic cell

Chapter 4 : EARLY DEVELOPMENT OF A BIODEGRADABLE ENERGETIC POLYMER

4.1 ARTICLE PRESENTATION

Despite having been available for several decades, the production and use of plastic materials continue to increase steadily. Their applications can vary from biomedical to military domains. But nowadays a social concern is emerging along with a greater awareness for the environmental impact of plastic products.

In the propellant industry, polymeric matrices are progressively used in the manufacturing of solid rocket propellants as binders which hold together the fuel and oxidizing compounds of the propellant; however, the introduction of new pyrotechnic systems requires structured and progressive safety assessments. Over the last 40 years, several attempts have been done to synthesize a new polymer for the production of energetic solid propellants, but yet some problems remain in the formulations: for example chemical incompatibilities with other ingredients, and instabilities of the energetic groups in the polymeric chains. Also, the cost of these raw materials is significant and research is still undertaken in order to improve the mechanical properties. Most applications of biodegradable polymeric materials are restricted to biomedical and pharmaceutical fields, but nowadays the environmental issue is starting to be incorporated in military-related activities.

The main objective of this work is the development of a biodegradable and energetic co-poly (ether/ester-urethane) network, which is able to release only non-toxic degradation products, in order to be used as a propellant or gas generator. Degradable co-poly (ether/ester) polyurethanes have been developed with the aim of producing a biodegradable dual-use (civilian and military) material suitable for different applications. The choice of thermoset polyurethane elastomers for this work is motivated in part by the fact that they can exhibit good mechanical properties over a large range of temperature, because of their microstructure that consists of alternating short sequences of soft and hard segments.

The results show the effectiveness of the synthesis of a co-poly (ether/ester-urethane) suitable for the formulation of polyurethane networks. The biodegradation analysis shows that the introduction of an azide group has a strong impact on the mechanical properties and on the biodegradation behaviour of the energetic polyurethane elastomers.

4.2 EARLY DEVELOPMENT OF A BIODEGRADABLE ENERGETIC ELASTOMER

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4.2.1 Abstract

The expected depletion of oil resources and a greater awareness for the environmental impact of plastic products have created a strong interest towards energetic polymers that are not only biodegradable but also obtainable from renewable resources. In this work a co-poly(ester/ether) was synthesized from polyepichlorohydrin (PECH) and sebacoyl chloride (SC) using pyridine as a Lewis-base catalyst. The chlorinated polymer was azidified with NaN_3 in dimethyl sulfoxide solutions. The success of the reaction was confirmed by H-NMR, ^{13}C-NMR and FTIR spectroscopy. Two types of polyurethane networks were synthesized from the non energetic and the energetic copolymer, adding polycaprolactone triol (PCL) and using L-lysine diisocyanate (LDI) as a non toxic curing agent. The two resulting polyurethanes were soft thermoset elastomers. The polyurethanes were chemically and mechanically characterized and their biodegradability was evaluated in compost at 55 °C. The non energetic and the energetic polyurethanes showed a glass transition temperature of -14 °C, and -23 °C, respectively. The weight loss of the polyurethanes during the composting experiments was monitored. It increases almost linearly with time for both materials. After 20 days, the non energetic samples lost about 50% of their mass due to the biodegradation mechanism. Instead, the energetic elastomers lost only about 25% of their initial mass after 25 days. The experimental results revealed that the azide pendant group in the soft segment is the main factor that controls the physical, mechanical, and degradation properties of these polyurethane networks.

Keywords: energetic polymer, thermoset elastomers, biodegradability, polycondensation, processability

4.2.2 Introduction

Over the last few decades, plastics have become the materials of choice for the fabrication of an increasingly large number of products found in a spectrum of applications that ranges from biomedical to military uses [1-3]. However, the expected depletion of oil resources and a greater awareness for the environmental impact of plastic products have created a strong interest towards polymers that are not only biodegradable but also obtainable from renewable resources. Various natural and synthetic biodegradable elastomers have been developed by means of a cross-linked network in order to satisfy specific mechanical and physical requirements and to improve the product properties [4].

The current trend towards the development of biodegradable materials was recently extended to less traditional areas, such as energetic materials. Since a large fraction of the ordnances used by a country's armed forces are often fired on its own homeland for training purposes, the interest of employing propellants and explosives that are less harmful for the environment becomes evident. In this perspective, biodegradable polymers are an interesting option and more so due to recent advances in their production at the industrial scale. Among them, aliphatic polyester like poly(ε-caprolactone), poly(L-lactide) are well known for their biodegradability [5], but they show relatively weak physical and mechanical properties.

In order to scale up the reaction, aliphatic synthetic co-poly (ester/ethers) for polyurethane formulations are studied.

Contemporary plastic bonded energetic materials often rely on a polyurethane binder to ensure the structural integrity of formulations that may contain up to 80% in solids. Biodegradable polyurethanes based on lysine derivatives have been reported in the literature to decompose into non-toxic products [6]. L-Lysine diisocyanates (LDI) are synthesized by phosgenation of amine-terminated lysine esters and they have a lower vapour pressure than other aliphatic diisocyanates (e.g., *hexamethylene diisocyanate*, HDI) [7]. Considering the inhalation toxicity of many diisocyanates; the low vapour pressure of LDI is a key advantage for its handling and processing. However, the production of biodegradable elastomeric polyurethane networks from lysine diisocyanate has so far mainly only been investigated for biomedical applications [8].

In contemporary energetic materials formulations, perchlorate based oxidisers that decompose to chloric acid during combustion, tend to be replaced by *greener* but less powerful oxidisers such as ammonium nitrate. In order to compensate the energy loss from the change in the oxidiser, the polymeric binder found in these materials can be substituted by novel energetic polymers. These so-called energetic binders carry the double advantage of improved performance and lower vulnerability (LOVA). The energy released during their thermal decomposition is due to the presence of an azide, amino or nitro group on the side chain. In the propellant industry, there is a progressive substitution of inert binders such as hydroxyl-terminated polybutadiene (HTPB) by energetic polymers such as glycidyl azide polymer (GAP).

In fact, GAP materials are at the core of the development of most of these novel energetic binder systems. A biodegradable energetic binder could be either thermoplastic or thermoset elastomers. The latter offers the advantage of a lower viscosity and a lower processing temperature.

Therefore a polyester polyurethane thermoset elastomer could be an attractive material for the preparation of composite solid propellants in which the elastomer is an intimately mixed rubbery phase, and it can be used as a binder for other materials such as ammonium perchlorate or other oxidizers, aluminum or other metallic fuels. Azido plasticizers can also be used to add energy to the binders due to the presence of N_3 group providing 85 kcal/mol of energy to the system.

The principal chemical precursor for GAP is polyepichlorohydrin (PECH). The Cl atom in its repeating units can easily be exchanged with a N_3 by S_N2 reaction (bimolecular nucleophilic substitution) following the Frankel method [9]. However, other halogenated oligomers such as bromine containing polyether can also be employed [10]. In general, the GAP polymer is cured by the reaction of its hydroxyl groups with diisocyanate curing agents such as toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) or tri-isocyanate to yield cross-linked polyurethane network [11].

One drawback of polyepichlorohydrin-based energetic materials is that they are not biodegradable. In order to increase the biodegrability of polyepichlorohydrin-based energetic materials, a possible solution could be the insertion of some specific chemical linkages, such as ester bonds which are known to promote biodegrability. This type of polymer can be produced by a step-growth polycondensation reaction between carboxylic acids (or derivatives such as chloride, esters or anhydrides) and diols (or polyols) or by ester interchange or alcoholysis. The polycondensation reaction itself proceeds by a slow increase in the molecular weight of the polymer. In order to increase the yield of the polymerization several methods can be applied: using non-stoichiometric conditions with an excess of one of the reactants, removing the by-product formed during the reaction in order to shift the equilibrium towards the products, or activating the dicarboxilic acids. Carothers elaborated a standard method to prepare polyesters at a laboratory scale or in larger quantities with the acid-catalyzed direct polycondensation of a diol with a free dicarboxilic acid [12]. In acid-catalyzed reactions the acid catalyst forms a complex with the alcohol: the oxygen atom of the end group is electrophilic and able to accept the nucleophilic carbon of the dicarboxilic acid. Kricheldorf and co-workers conducted a remarkable research work to compare basic methods of producing polyesters in order to find a synthetic method leading to better yield [13]. They succeeded to produce an aliphatic polyester using a pyridine catalyzed polycondensation method between butyne-1,4-diol and several aliphatic dicarboxilic acid dichlorides at room temperature. In this way, the activated acid reacts with an alcohol in relative mild conditions according to the Schotten-Baumann mechanism where pyridine acts as a catalyst, shifting the equilibrium towards the products. Nevertheless the achievement of this reaction is rather delicate. Using a GAP precursor such as PECH, the pre-polymer polymerization would depend on the reactivity of PECH itself. To utilize the final product in a thermoset energetic materials formulation, it must be purified from any traces of HCl, and its viscosity must be low enough to allow for a cast-cure process.

The objective of this work is to design a biodegradable and energetic co-poly (ether/ester-urethane) network from PECH and SC derivatives able to release only non-toxic degradation products, and compatible with contemporary ingredients found in propellants and gas generators. The choice of thermoset polyurethane elastomers for this task was motivated by the fact that they can present excellent mechanical properties over a large range of temperature. At this early stage of development, the biodegradability of the synthesized products is evaluated using standardized composting experiments, but the bio/eco-toxicity of the decomposition products is not assessed.

4.2.3 Experimental

4.2.3.1 Materials

Polyepichlorohydrin (PECH), 625 g/mol (relative to polystyrene standards), was supplied from 3M™ and was treated with activated charcoal in order to absorb impurities and contaminants prior to its use. Sebacic acid (SA), 228 g/mol, and his dichloride, sebacoyl chloride (SC), 234 g/mol, were purchased from Sigma-Aldrich Ltd., Canada, and used as received. Dichloromethane and toluene were both purchased from Laboratoire Mat., Canada, and the dichloromethane was dried using a molecular sieve. Triethylamine (TEA), pyridinium hydrochloride (PyH), pyridine (Py), *p*-toluene sulfonic acid (PTSA) and activated charcoal were purchased from Sigma-Aldrich, Canada, and sulphuric acid from Laboratoire Mat., Canada, and used as received.

For the polyurethane formulation, polycaprolactone triol (PCL), 300 g/mol, was purchased from Sigma-Aldrich, Canada, dibutyl tin dilaurate (DBTL), 631.56 g/mol, was also purchased from Sigma-Aldrich, Canada, and used as 0.01 M, 0.1 M, and 1 M solutions in dichloromethane. L-lysine diisocyanate, 226.23 g/mol, was purchased from Shanghai Infine Chemicals Co., Ltd., China. The stabilized compost used as a substrate for the biodegradation tests, was purchased from a composting company (Fafard, Saint-Bonaventure, Canada). It contained composted manure, sphagnum peat moss, shellfish flour and seaweed, and had the following characteristics: pH = 6.89, water retention = 4.29 % and initial humidity = 1.62 %. Prior to being used, the compost was homogenised, cleaned from all inert material (rocks, metals and wood), homogenized using a mortar, and finally sieved.

4.2.4 Synthesis of the co-poly (ester/ether)

A co-poly(ester/ether) of polyepichlorohydrin and aliphatic dicarboxylic acids was prepared in two different ways: by direct polycondensation between a di-alcohol and a dicarboxilic acid (Figure 4.1a) and polycondensation between a di-alcohol and a di-acyl dicarboxylic acids (Figure 4.1b).

4.2.4.1 Direct Polycondensation

A 500 mL three necked-flask equipped with a mechanical stirrer and a Dean-Stark water trap was charged with an equimolar solution of polyepichlorohydrin (PECH) and sebacic acid (SA) in toluene. The reaction vessel was placed in an oil bath preheated to a temperature that ranged 100 to 160 °C. The reaction was allowed to proceed for at least 8h but, in some instances, for up to a 24h period of time. Different catalysts were tested. At the end of the reaction, the now viscous solution was cooled down and washed with brine and extracted with toluene, then dried over Na_2SO_4 and filtered. The solvent was evaporated off in a rotary evaporator and dried overnight in an oven under vacuum at 80 °C. Table 4.1 presents a summary of these experiments.

4.2.4.2 Polycondensation with Diacid Dichlorides

Polyepichlorohydrin (PECH) and Sebacoyl Chloride (SC) in equimolar ratio were dissolved in dichloromethane into a three-necked glass flask, equipped with gas-inlet and gas-outlet tubes and a mechanical stirrer, and cooled to -5 °C. Pyridine (240 mmol) was added drop-wise under cooling conditions. After a complete addition of the pyridine, the reaction mixture was stirred at room temperature for 24h to 48h and afterwards poured into cold methanol. The precipitated polyester/polyether copolymer was washed several times with brine or water, dried over Na_2SO_4 and filtered. The solvent was evaporated off in rotary evaporator equipment and dried overnight in an oven under vacuum at 80 °C. A summary of these experimental conditions is also presented in Table 4.2.

4.2.5 Azidation of the co-poly(ester/ether)

To produce an energetic co-poly(ester/ether), 40 g of a synthesized low molecular weight co-poly(ester/ether) were dissolved in 500 mL of DMSO and put in a 1L BUCHI glass reactor (BUCHI laboratory autoclave BEP 280, Switzerland) equipped with nitrogen inlet and outlet. The jacketed reactor was heated by an external oil bath circulator and mixing was provided by a top-mounted magnetic drive impeller.

After 15 minutes an excess of NaN_3, dissolved as well in DMSO, was added and the temperature was slowly increased to 85 °C and the reaction was continued for 24h. Subsequently, the product was washed with water, and the organic phase was extracted using methylene chloride. The organic phase was dried over $MgSO_4$ to remove all traces of water, filtered and finally the solvent was evaporated under vacuum. An energetic polymer was obtained with ~ 95 % yield.

4.2.6 Characterization of the co-poly(ester/ether)

The H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance DRX 500 MHz NMR spectrometer using 5 mm (o.d.) sample tubes. CDC13, containing tetramethylsilane (TMS), as reference served as the solvent. Gel permeation chromatography (GPC) was performed using a system equipped with a refractive index (RI detector Waters 2414). A combination of two columns HSP gel™ HR MB-M (6.0 x 150 mm) was used in tetrahydrofuran (THF) (HPLC grade) as the mobile phase at a flow rate of 0.5 mL/min. Commercial polystyrene standards were used for calibration. Sample concentrations were approximately 1.8 mg/mL in THF, with an injection volume of 1 μL. Fourier-Transform infrared spectroscopy (FTIR) was performed using a FTIR Instrument (BioRad instrument, model 3000 Excalibur). Absorbance measurements were carried out using THF as solvent and calibrated 0.5 mm KBr and BaF_2 cells. The sample was scanned 32 times on the full frequency range with a resolution setting of 4 cm^{-1}. For these experiments the co- poly (ester/ether) was dried overnight in the oven at 60 °C under vacuum for two days and the solvent as well dried with molecular sieve. In this way THF and the samples were dried and oxygen-freed [14].

The number of hydroxyl groups (-OH) was evaluated according to a standard procedure which consisted of an esterification reaction of the hydroxyl end groups with acetic anhydride in pyridine, followed by a titration of the excess acid reagent by an equimolar amount of potassium hydroxide in solution (ASTM D-4662-93) [15]. The hydroxyl number is expressed as milligrams of potassium hydroxide equivalent for one gram of the sample (mg KOH/g). The results of this titration method were compared with FTIR analysis. In the latter, the hydroxyl concentration or OH equivalent weight was evaluated from the comparison between the FTIR absorption bands of THF-associated hydroxyl groups of the co-poly (ester/ether) near 3500 cm^{-1}. The calibration curve was obtained using the OH/THF associated absorption of polyepichlorohydrin as a reference plotted against the concentration of PECH. The OH number was evaluated in such conditions that all the OH groups were associated to the solvent, and the presence of free or self-associated OH was negligible. Differential scanning calorimetry (DSC) tests were performed with TA Instruments (Q1000) at scan rate 5 °C/min, varying the temperature from 30 to 300 °C.

4.2.7 Synthesis of thermoset polyurethane elastomers

The synthesis procedure for a L-lysine diisocyanate (LDI) based thermoset polyurethane was as follows: in the first step, the energetic and non energetic copolymers were mixed with PCL triol (0.26 % mol) and heated at 60 °C under vacuum to form a reactive liquid mixture in the presence of DBTL in a methylene chloride solution (0.1 or 1 M, and 0.015 % mol of catalyst). In the second step, LDI was added to achieve a molar ratio of NCO groups to the OH groups of 1.33. The desired ratio satisfied the following equation:

$$\frac{NCO}{OH} = \frac{W_{LDI}/EW_{LDI}}{W_{polyol}/EW_{polyol}} \tag{1}$$

The equivalent weight (EW) for LDI was provided by the supplier and was EW_{LDI} = 113.15 g/mol. The mixtures were casted in an open mould to form a solid material at 60 °C under vacuum for 6-12 h and then left for curing at ambient pressure and 75 °C for 24 h.

4.2.8 Characterization of the thermoset polyurethane elastomers

Rectangular samples of 61 x 13 x 3 mm were analyzed by dynamic mechanical analysis (DMA). DMA was used to determine the viscoelastic properties of the polyurethane elastomers. The measurements were performed on a dynamic thermo-analyzer (TA Instruments DMA-2980) using a dual cantilever geometry in the linear viscoelastic regime at a frequency of 1 Hz and an oscillation amplitude of 25 μm over a temperature range of -50 to 20 °C. The scanning rate was varied between 2 and 5 °C/min.

Water absorption of the samples was measured according to ASTM test method D-570. The samples were weighed and placed in a container of distilled water, and the equilibrium weight value was determined after 24h of soaking in water at room temperature. The results are expressed in percentage of water absorbed relative to the dry samples.

4.2.9 Biodegradation analysis

According to the standard protocols ASTM D 5988-03 and ASTM D5338-98(2003), the samples were put in boxes filled with compost and incubated for a period of time that varied between ten and twenty days. The water content was regularly checked in order to guarantee 60% humidity. The temperature was set at 55 °C as an average recommended temperature from the literature surveyed [16,17]. Every ten days systematic sampling and Soxhlet extraction were performed to evaluate the evolution of the soluble fraction of the polyurethane. From the extraction results, it was possible to report the extent of the degradation process using a conversion defined as:

$$\alpha = \frac{(W_0 - W)}{W_0} \tag{2}$$

where:

W_0 = initial weight of insoluble elastomer before composting

W = actual weight of insoluble elastomer after Soxhlet extraction.

The chemical composition of the degraded binder was monitored through FTIR measurements performed using a Digilab FTS6000 FTIR spectrometer equipped with a Photoacoustic cell (MTEC Model 300 Detector; from the company MTEC Photoacoustics, Inc.) filled with helium gas. In general, the signal to noise ratio was high enough for all the measurements, and all the samples were tested in the same conditions at room temperature. Each sample was scanned 64 times with a resolution setting of 8 cm^{-1} using the rapid scan mode at the lowest mirror frequency (2.5 kHz) to maximize the signal and to probe the deepest layers possible into the samples. Photoacoustic spectroscopy (PAS) was also carried out to detect alterations in the surface due to the degradation, because it directly measures infrared (IR) absorption by sensing absorption-induced heating of the sample. To obtain quantitative data, it was necessary to use an internal normalization for the peaks of interest. The aliphatic β-C-H_2 stretch band peak was chosen as an internal reference due to the stability of these chemical links, and their strong absorption in IR. The decrease of specific chemical bonds was estimated based on the average area for non degraded polyurethane and the area of the peak of interest of the degraded samples[18].

$$\%change = 100 * \frac{[A_i - A_f]}{Af} \tag{3}$$

Where A_i is the area under the peak of non degraded sample and A_f is the area under of degraded samples at different composting times.

Due to the extent of degradation, DMA analysis could not be performed on the degraded samples after only 10 days of composting.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Synthesis of the co-poly (ester/ether)

In this work, the synthesis of the co-poly (ester/ether) from polyepichlorohydrin was carried out in chemically different conditions and at various temperatures. Sebacic acid (SA) was first used along with PECH in toluene and different catalysts. During this polycondensation reaction water is produced as by-product. Hence, its removal is an essential step for the completion of the reaction. For this purpose a Dean Stark apparatus in combination with a reflux condenser. The reaction was carried out under reflux in toluene which is less dense than water, immiscible with it and forming an azeotrope. The apparatus allows the water to be separated from the condensed azeotrope, preventing it from returning to the reaction mixture. The temperature was varied from 120 to 145 °C (see Table 4.1). PyH at 5-10 %wt, H_2SO_4 at 10% or PTSA at 1% were used as catalyst. The extent of the polycondensation was evaluated by GPC measurements. As shown in Table 4.1, the direct polycondensation between PECH and SA did not yield a high molecular weight copolymer. The highest molecular weight ($M_n \approx 1500$ g/mol) was obtained using PTSA in toluene. It is known that polyesterification reactions are very sensitive to elevated temperature, and side reactions, such as hydrolysis due to the presence of residue of water, or dimerization of the chains can lead to a low yield, to low molecular weight polymers and a loss of functionality.

Another method to produce the co-poly (ester/ethers) is the reaction between dicarboxylic dichlorides using pyridine as catalyst as well as HCl acceptor. This kind of reaction still remains somewhat unattractive due to the cost of the dicarboxilic chlorides and the required dry operating conditions. However, it has the advantages of being carried out at lower temperature being of the enhanced reactivity of the chloride as compared to the acid. The GPC results presented in 4.2 clearly confirm the more complete polymerization obtained with this approach. After 24h, a copolymer of about 6000 g/mol relative to polystyrene standard was produced (polydispersity ≈ 1.5). After 48h the molecular weight reached the value of about 25000 g/mol relative to polystyrene standard. These results were obtained in perfect stoichiometric conditions of the reactants, and using an excess of pyridine (catalyst). It has been reported however that the molecular weight based on polystyrene standards can overestimate the real molecular weight by about 50-70 % [19], hence the reported values may be larger than in reality.

The OH equivalents of the synthesized polymers were evaluated with FTIR and also using the acetylation/titration technique. An equivalent weight of 1990 g/equiv was evaluated for the low molecular weight copolymer using the FTIR technique while the titration technique gave a value of 2000 g/equiv. Therefore, within the limits of experimental error both techniques provided similar values, confirming their reliability.

The polycondensation of PECH with SC proved to be easy to control and polymers of higher molecular weight were also produced. However, they were not transformed to energetic polymers in light of their high viscosity that rendered them not practical for the preparation of polyurethane elastomers using a cast-cured process. In a following step, only the 6000 g/mol copolymer was azidified to give an oily yellow product with a molecular weight of about 6500 g/mol relative to polystyrene standards and an equivalent weight of about 2230 g/eq. The energetic copolymer showed monomodal distribution in GPC analysis (polydispersity $\approx$ 1.8). During the azidation reaction, the molecular weight could drop due to the degradation of the polymer backbone itself [20]. However in this work, our GPC results confirmed that both the ether and ester links were conserved, showing a slight increase of the molecular weight due to the substitution of the Cl atom (35 Da) by the the N_3 group (42 Da) on each repeating unit.

The success of the reaction was confirmed by ^{13}C-NMR, H-NMR and FTIR. Figure 4.2 shows the comparison of H-NMR for the non-energetic and energetic copolymers. Comparing the H-NMR spectra of the non-energetic copolymer (Figure 4.2a) and of the energetic copolymer (Figure 4.2b), it is possible to notice the changes in the polymeric chains. The non-energetic copolymer showed peaks between 3.5 and 3.8 ppm due to the presence of $-CH_2Cl$, $-O-CH_2$ and $-O-CH$. On the other hand, the presence of resonance signals around 3.4 ppm corresponding to $-CH_2N_3$ protons of the energetic copolymer has confirmed the conversion of $-CH_2Cl$ into $-CH_2N_3$.

The ^{13}C-NMR spectra of the non-energetic (Figure 4.3a) and energetic copolymers (Figure 4.3b) Figure 4.3 confirm the information provided by the H-NMR spectra. The peaks observed between 65 and 80 ppm in both spectra correspond to methylene carbons along both copolymer chains, either attached to hydroxyl or ether oxygen. The dual chloro-methyl peaks of the PECH units of the non-energetic copolymer are found between 43 and 46 ppm. The energetic copolymer showed the azidomethyl carbon resonance peak at 54 ppm along with a quasi total absence of resonance signals at 43–46 ppm corresponding to chloro-methyl protons.

Moreover, FTIR spectra of the copolymers also reveal the completion of the azidation reaction, since the energetic copolymer showed the appearance of the $-C-N_3$ characteristic peak at 2100 cm^{-1}, proving the conversion of $-C-Cl$ into $-C-N_3$ (Figure 4.4). For both copolymers, the broad band close to 3500 cm^{-1} is attributed to the hydroxyl groups in the polymeric chains.

Differential scanning calorimetry (DSC) experiments were carried out on the energetic copolymer and on the non-energetic one to better understand the structure-property relationships and thermal stability of these copolymers. As shown in Figure 4.5, no endothermic peak is found for either products and hence they are supposed to be completely amorphous. The DSC traces show only a single exothermic peak. The single exothermic peak at 176 °C in the energetic copolymer is associated with the decomposition temperature, for a heat flow of 7000 mW/g. This is mainly attributed to the elimination of nitrogen due to the cleavage of the azide bonds from the pendant azide group. In the literature, a decomposition temperature (T_{mcd}) of about 220-250 °C has been reported for GAP [21,22]. The addition of N_3 on the polymer chains has the expected effect on the thermal stability of the copolymer itself, but the alternating pattern of ether/ester groups on the polymeric backbone has lowered the temperature of decomposition. It is assumed that the linear moieties increase the mobility of the polymeric main chain during the decomposition of the azide pendant groups, reducing the decomposition temperature.

4.3.2 Synthesis of thermoset polyurethane elastomers

Several methods have been investigated for the synthesis of the thermoset polyurethane elastomers starting from the copolymers described in the previous section.

Two co-poly (ester/ethers-urethane) networks were formed based on the low molecular weight non energetic copolymer (NE) and the energetic copolymer (E). In

Table 4.3 the reaction conditions are summarized. The most effective method for both copolymers was the two-stage method. Prior to the addition of the diisocyanate (LDI), which provides the hard segment of the elastomeric network and also enhances the biodegradability of the material itself, the polyol and the PCL were carefully hand mixed with a solution of DBTL catalyst. Both polyurethane formulations were cured for 24h. The reaction time and the temperature reflected the appropriate conditions to prepare polyurethane with complete consumption of the polyols and the diisocyanates.

Dynamic mechanical analysis (DMA) gave further insight on the mechanical properties and viscoelastic behaviour of the two elastomers. Figure 4.6 shows the storage modulus and *tan*(δ) as a function of temperature. Both *tan*(δ) curves display broad peaks which are attributed to the glass transition of the co-poly(ester/ether) soft blocks of the elastomers. According to the literature[23], the glass transition temperature T_g values can be evaluated at the peak of the *tan*(δ) curve as a function of temperature. According to this criteria, the T_g of the polyurethanes are nearly 10 °C apart, with -23 °C) and -14 °C for the (E) and (NE) elastomers, respectively.

Also shown in Figure 4.6 is the storage modulus, presented in a semi-logarithmic plot to clarify the transition region. The storage modulus *G'* represents the elastic and non-dissipative component of the elastomers, hence is related to the energy stored in the samples. At low temperature, below -34 °C, the (E) polyurethane presents a storage modulus of about 3300 MPa, as compared to 1800 MPa for the (NE) polyurethane. At these low temperatures, i.e. below the glass transition temperature, the storage modulus is mainly affected by the polymer structure[23], e.g. by the molecular weight and chemical structure of the pre-polymer, with larger molecular weight resulting in larger storage modulus. Consequently the (E) polyurethane presents a higher modulus at low temperature, due to the moderately higher molecular weight of the energetic pre-polymer (6500 g/mol) as opposed to the non-energetic one (6000 g/mol). Starting from approximately -41 °C and -31 °C for the (E) and (NE) elastomers, respectively, the storage modulus decreases progressively with temperature due to the increase in thermal energy and molecular chain motions.

The decrease of the storage modulus in the glass transition region occurs at lower temperature and more sharply for the energetic elastomer than for the non-energetic one. Taking into account the correspondence between time and temperature, the kinetics of relaxation affects the temperature range necessary for the rearrangement of the molecules[24]. Thus, these different behaviours can be explained based on molecular hindrance of the two polymeric chains. The energetic polymer backbone differs from the non-energetic one, where the former carries three nitrogen atoms at each repeating unit instead of only a chlorine atom in the latter case. As a result, for the (E) elastomer only a small portion of the total volume is occupied by the backbone of the polymeric chain, easing molecular motion and resulting in a faster relaxation process, or considerable relaxation over a lower temperature range. In addition, since these are cross-linked materials, the storage modulus should eventually approach a rubbery plateau at elevated temperatures. At room temperature (20 °C) the storage modulus is quite small, 0.26 Pa for the (E) elastomer and 0.45 Pa for the (NE) one, indicating that these materials do not have tremendous mechanical properties. In addition the rubbery plateau is not completed reached at room temperature as the *G'* curves are still decreasing slightly.

In Figure 4.7 the loss modulus *G"* of both polyurethanes is presented. The loss modulus, related to the energy dissipation, shows a peak at -32 °C for the (E) elastomer, and at -21 °C for the (NE) elastomer. The glass transition temperature T_g, can also be evaluated from the peak of the loss modulus curve as a function of temperature. These values are reported in Table 4.4, along with the ones corresponding to the maximum peak of *tan*(δ). There is approximately a 10 °C difference between the T_g values evaluated from both methods, with the ones from the loss modulus being lower.. These lower values seem more representative of the elastic modulus behaviour in Figure 4.6. Nevertheless, the T_gs reported in Table 4.4 are in the neighbourhood of the glass transition temperature of PECH-based elastomers (-20 to- 25 °C) [20]. The addition of ester bonds to PECH reduces the flexibility of the polymeric chains and consequently slightly increases the T_g of the non-energetic polyurethane. In a polymer with non-symmetrical chains, an additional restriction to rotation is imposed by steric effects, increasing T_g as seen for the (NE) elastomer[23]. In addition to the effects related to the polymeric backbone, the presence, polarity, size and flexibility of pendant groups can also affect the viscoelastic properties of the materials. Generally, polar pendant groups such as CH_2-Cl tend to increase the T_g rather than non-polar ones such as CH_2-N_3. Thus, although the further substitution of a Cl atom by a larger size azide group on the polymeric backbone increases the steric hindrance and reduces the flexibility of the polymeric chain, at the same time it results in an increase of the free volume required for molecular motions[25]. Consequently, the created additional free volume and the non-polar nature of the azide groups can possibly explain the lower T_g values of the energetic elastomer (Table 4.4).

Finally, the (E) elastomer is observed to be less viscous and less elastic at room temperature (Figures 4.7 and 4.6, respectively). This can be interpreted in terms of neighbouring molecules and their effects on *G'* and *G"*, i.e. lower local frictional forces between short and long segments of the polymeric chains [24]. This explanation is valid for low molecular weight materials, which is the case here if we consider the pre-polymers. However the effect of cross-linking may discard this simple interpretation.

4.3.3 Biodegradation in the compost of the energetic and non-energetic polyurethane binders

In Figure 4.8, the evolution of the degradation of the (E) polyurethane is shown. It is seen from the pictures that even after only ten days in the compost, the degradation process was already in progress. At this point, the elastomers retained their original shape but were no longer transparent. The degradation was initiated at the surface of the samples, as expected. After 25 days, the bacterial attack became stronger, penetrating deeper inside the samples and creating holes all through them. The surface roughness increased and the samples lost their original shape and dimensions. The degradation of the (NE) polyurethanes is depicted in Figure 4.9 for comparison purposes. In this case, after10 days, the degradation is already more advanced; showing signs of hydrolytic and bacterial attack the surface of the samples; and causing a colour change from transparent amber yellow to white opaque. After 15 days, the samples were more and more degraded and a width reduced of about 50% was observed. The samples extracted after 20 days showed a severe degradation and they lost their original shape.

Comparing Figures 4.8 and 4.9, it is possible to notice how the degradation proceeded in each material: slower for the energetic polyurethanes, and faster for the non energetic ones. The degradation mechanism depends on the chemical structure and configuration of the polymeric chains. One can therefore affirm that the energetic co-poly(ester/ether) segments are more stable and resistant to degradation than the non-energetic ones. Figure 4.10 shows the weight loss of both polyurethane binders versus degradation time at 55 °C. The weight loss increases almost linearly with time for both materials, but it is more pronounced for the non-energetic binder: after 20 days the samples lost about 50% of the mass due to the biodegradation mechanism. Instead, the energetic elastomers lost only about 25% of their initial mass after 25 days.

The network integrity of the degraded samples was evaluated by Soxhlet extraction in dichloromethane and FTIR-PAS analysis. From the Soxhlet extraction results (Figure 4.11), it appears that the solubility of the polyurethane networks in the solvent increases with time in the compost. After 10 days, both polyurethanes binders show a conversion (Equation 2) larger than 0.7, which slowly continues to increase with time. Accordingly, the spontaneous cleavage of the polyurethane network during the composting process resulted in low molecular weight by-products soluble in organic solvents.

FTIR spectroscopy has already been used extensively to investigate chemical changes in degraded polymers[26-28]. FTIR-PAS spectroscopy was used to investigate the structural difference in the degraded samples as compared to the non-degraded ones. Figures 4.12 and 4.13 present the FTIR-PAS spectra of non-energetic and energetic binders respectively. According to the literature[26], N-H stretching is detected near 3300 cm^{-1}, the carbonyl urethane stretching near 1730 cm^{-1} and 1700 cm^{-1}, the N-H bending and C-N stretching near 1535 cm^{-1}, the C-N stretching near 1222 cm^{-1}, and the ester absorbance near 1110 cm^{-1}. For this study, two more peaks were detected: $C-N_3$ antisymmetric stretching near 2100 cm^{-1} and CH_2-Cl near 750 cm^{-1}. At the first glance, it is possible to notice in both Figures 4.12 and 4.13 the decrease in the magnitude of the absorption bands relative to the mentioned functional groups with the composting time.

Generally speaking, the absorbance in a FTIR-PAS spectra depends on the heat transport properties in the sample. Given the significant changes in the polyurethane binders during the composting experiments it is not possible to compare the spectra from samples taken at different times on an absolute basis. Nevertheless, it was desired to highlight, if any, the differences in in the degradation process of each type of polymer. Therefore, the absorbance intensity for the few peaks of interest was normalized by the intensity of the peak corresponding to aliphatic antisymmetric $\beta-CH_2$ stretching (2940 and 2943 cm^{-1}), which was used as an internal reference seen as more stable than other links in the polymer molecules. Figures 4.14 presents the evolution in the ratio of the normalized area of the CH_2-N_3 or CH_2-Cl peak to carbonyl C=O signal at different stages of degradation. As can be observed, because of the limited set of data, it is difficult to make definitive conclusions but clearly, the degradation process proceed differently for each type of elastomers. For (NE) elastomers, the ratio remains more or less constant while it decreases for the energetic elastomer. Considering that the weight loss over time is more pronounced in the (NE) polyurethanes, this would indicate that in the latter case, the fraction in polyether segments in the network decreases more rapidly than the polyester parts.

Ester bonds play a fundamental role during the degradation process since they can undergo hydrolytic scission more easily than other chemical bonds. The urethane and urea linkages are less sensitive to hydrolysis than the ester bonds [29]. An initially homogeneous sample undergoes hydrolysis, with consequent cleavage of the ester bonds confirmed by a decrease in the mass. On the FTIR spectra shown in Figures 4.12 and 4.13, a very broad absorbance band develops in the 3300-3000 cm^{-1} area during the first half of the composting experiment. This can probably be associated to the presence of carboxylic acid groups resulting from hydrolytic chain scissions. The velocity of the hydrolysis is determined by the 'concentration' of reaction partners, water and labile bonds [30]. From water uptake tests (NE) elastomers resulted to be more hydrophilic (7.1%) than the (E) elastomers (2.3%) and after 10 days the absorption peaks of ester bonds substantially decreased. This is in accordance with the larger weight loss occurred to non energetic binders. The inherent more hydrolytic resistance of the energetic polyurethane must be attributed to the presence of the azide group in the backbone chains. The final hydrolysis products of the polyesters will be degraded by microorganisms to smaller end products after they are released in a natural environment. But at this stage of the work no eco-toxicity tests were conducted.

In summary FTIR-PAS spectra have shown that the combination of the hydrolytic and bacterial attack in the compost was more efficient in the case of non-energetic binders.

4.4 CONCLUSIONS

This work aimed to produce an energetic biodegradable polyurethane elastomer. The first step was devoted to the production of a low molecular weight pre-polymer. The synthesized azide polyol was suitable for being modified by an azidation reaction and being included in polyurethane elastomer formulation. Co-poly(ester/ethers) of polyepichlorohydrin (PECH) and sebacic acid (SA) were prepared by two standard polycondensation methods in order to evaluate the appropriate operation conditions. First, direct polycondensation of PECH with SA was conducted in toluene using a Dean Stark apparatus. Even if different reaction conditions and catalysts were tried, a copolymer of satisfactory molecular weight was not produced. On the other hand, pyridine-promoted polycondensation of PECH with SC resulted in producing copolymers of higher molecular weight (6000 to 25000 g/mol, relative to polystyrene standard). Biodegradable cross-linked energetic and non-energetic polyurethanes (binders) were prepared from PCL and copolymers of PECH and SC as soft segments, and LDI as hard segments. The cross-linked elastomers showed good biodegradability in the compost. The rate of weight loss was significantly higher for the non-energetic binders with respect to energetic ones. This was due to the presence of the chlorine group in the molecular chains on non-energetic binder. The ether/ester bonds of the energetic polyurethane were found to be less susceptible to hydrolysis; probably because the azide group affecting the steric hindrance reduced the possibility of cleavage of the molecular chains. These biodegradable binders with elastomeric properties may be used in military applications where more environmentally acceptable products are sought. Future work includes the optimization of the mechanical properties of these novel materials.

4.5 ACKNOWLEDGMENTS

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Table 4.1: Polycondensation of PECH and SA

Ex	SA/PECH	T (°C)	Time	Catalyst	Solvent	M_n (g/mol)	Polydispersity
1	1/1	165	48 h	PyH 10% wt	Toluene	650	1.28
2	1/1	118	8 h	PyH 5% wt	Toluene	680	1.3
3	1/1	145	24 h	H_2SO_4 10% wt	Toluene	1068	1.25
4	1/1	145	8 h	H_2SO_4 10% wt	Toluene	1452	1.21
5	1/1	145	24h	PTSA 1% wt	Toluen	1572	1.22

Table 4.2: Polycondensation of PECH and SC

Ex	SC/PECH	T (°C)	Time	Catalyst	Solvent	M_n (g/mol)	Polydispersity
1	1/1	25	24 h	Py	CH_2Cl_2	5857	1.50
2	1/1	25	48h	Pyridine	CH_2Cl_2	25000	1.41

Table 4.3: Polyurethane formulation

Polyurethane network	NCO/OH	PCL	Catalyst	Conditions
NE	1.33	0.26% (w/w)	DBTL (0.01M) 0.15%	Degassing at 60 °C Curing at 75 °C for 48h
E	1.33	0.26% (w/w)	DBTL (1M) 0.15%	Degassing at 60 °C Curing at 75 °C for 24 h

Table 4.4: Comparison of the polyurethane networks

Polyurethane network	**Tg (°C)** (peak *tan*(δ))	**Tg (°C)** (peak *G"*)
NE	-14	-32
E	-23	-21

NE = non energetic
E = energetic

Table 4.5: Proposed assignments of FTIR PAS absorbance peaks for NE and E polyurethane

NE elastomers	**E elastomers**	**Assignments**
3370 cm^{-1}	3381 cm^{-1}	N-H stretching (hydrogen bonded to carbonyl)
2943 cm^{-1}	2940 cm^{-1}	aliphatic antisymmetric β-CH_2 stretching
2869 cm^{-1}	2862 cm^{-1}	aliphatic antisymmetric α-CH_2 stretching + symmetric /βCH_2 stretching
	2100 cm^{-1}	C-N_3 stretching
1753 cm^{-1}	1764 cm^{-1}	non-hydrogen bonded urethane C=O stretching
1476 cm^{-1}	1463 cm^{-1}	aliphatic CH_2 bending
1243 cm^{-1}	1242 cm^{-1}	CH_2 wagging
1133 cm^{-1}	1132 cm^{-1}	aliphatic asymmetric C-O-C stretching (ether)
1056 cm^{-1}	1103 cm^{-1}	urethane C-O-C stretch and aliphatic symmetric C-O-C ester stretching
756 cm^{-1}		C-Cl_2 stretching

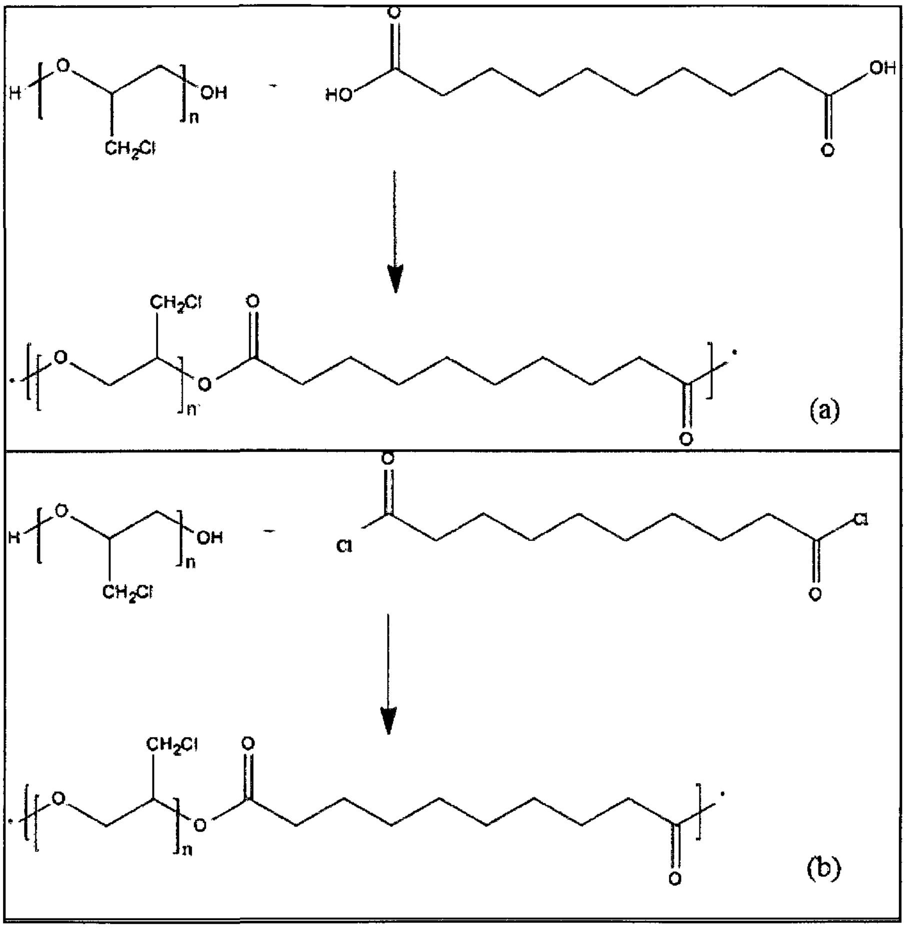


Figure 4.1: Polycondensation between PECH and SA (a) and PECH and SC (b)

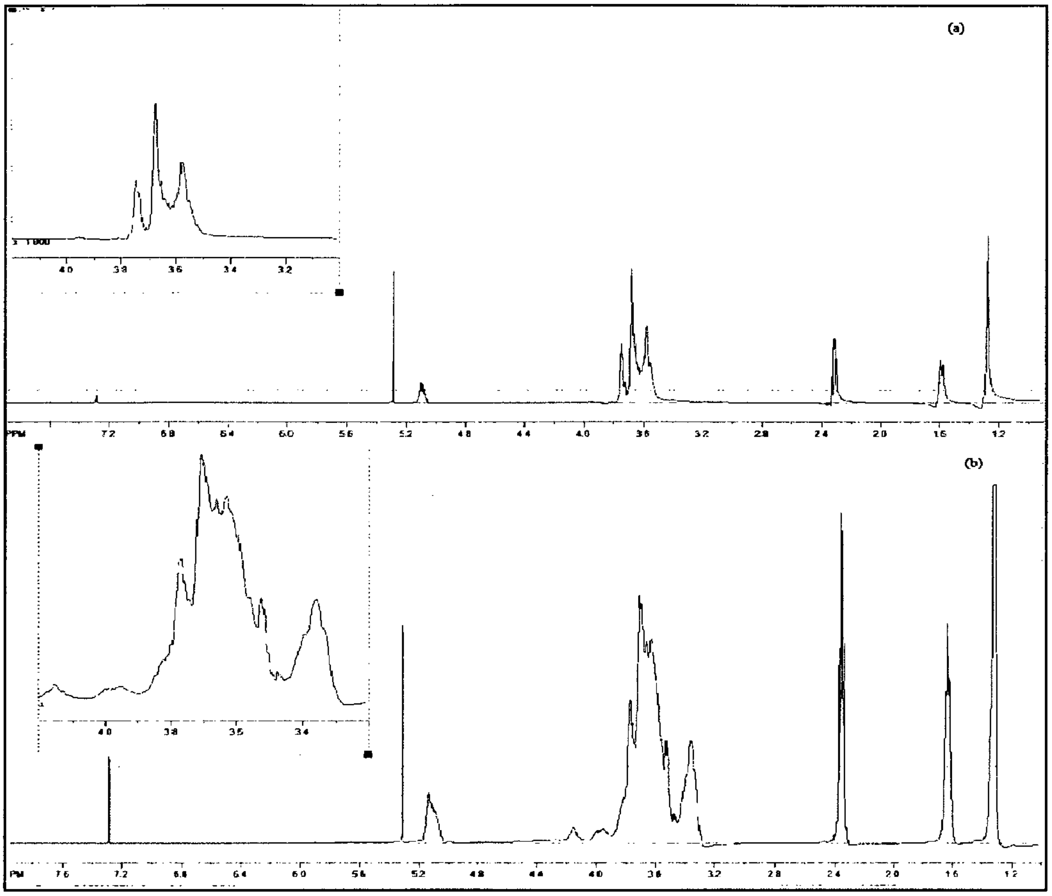


Figure 4.2: Comparison of H-NMR of the copolymer (a) and the energetic copolymer (b)

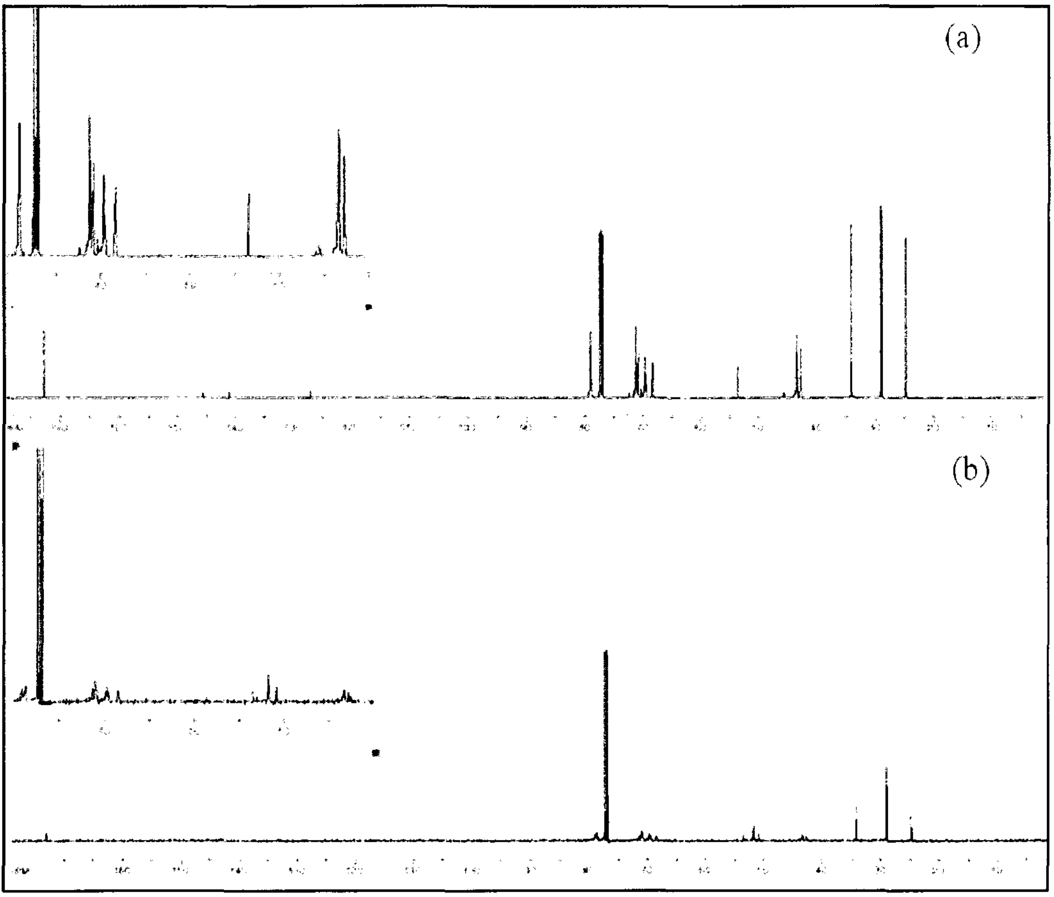


Figure 4.3: Comparison of C-NMR of the copolymer (a) and the energetic copolymer (b)

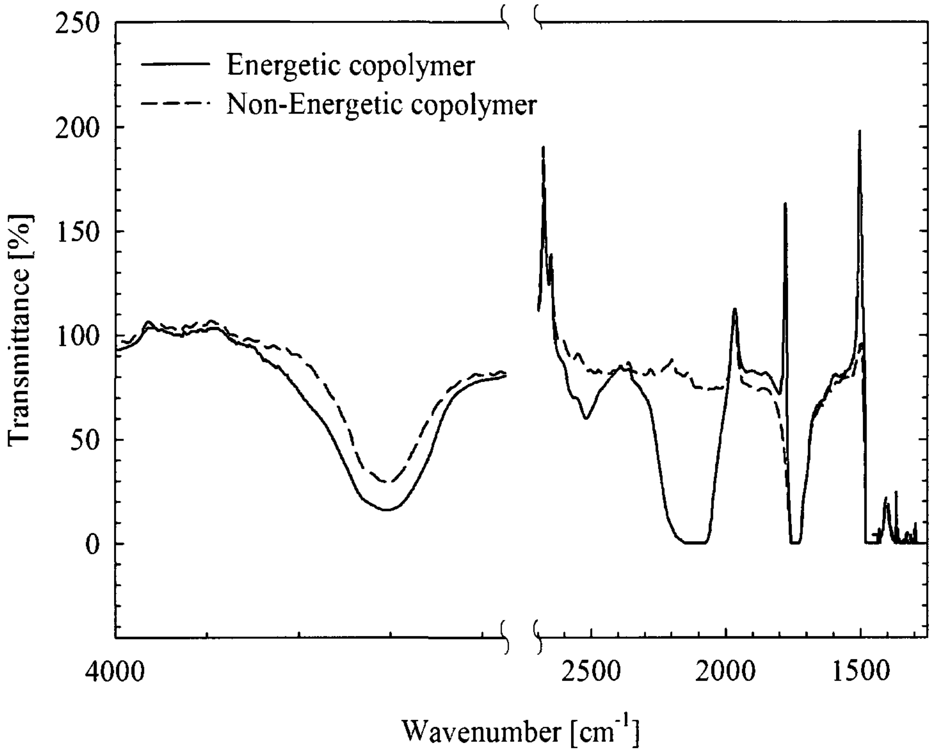


Figure 4.4: FT IR of the copolymer and of the energetic copolymer

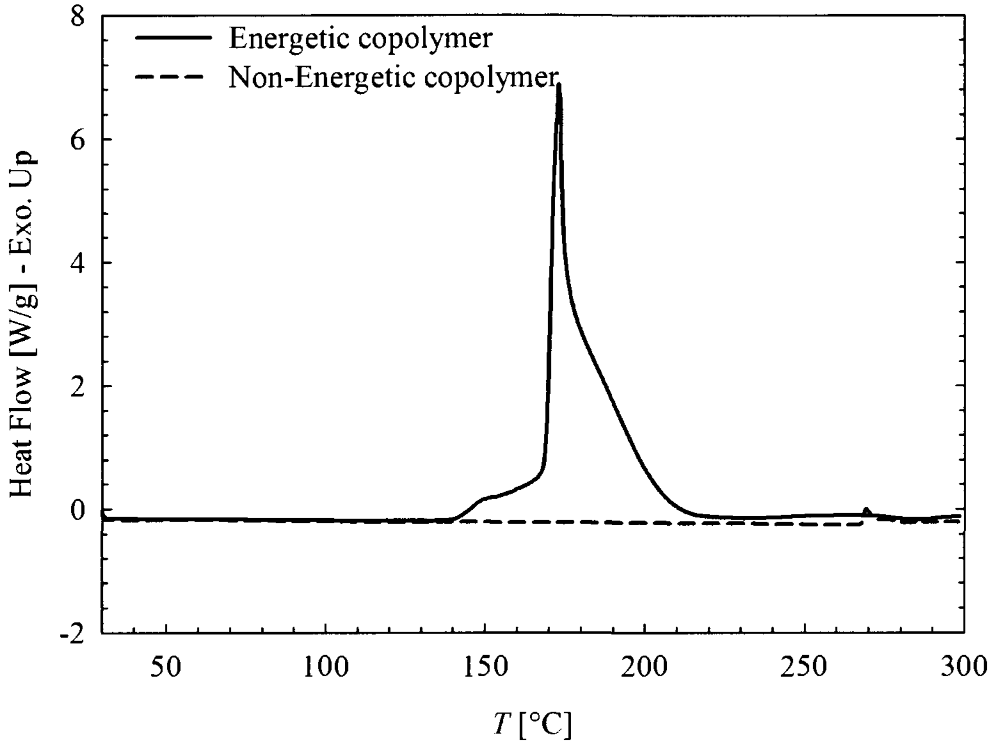


Figure 4.5: Comparison of DSC curves of energetic copolymer and non energetic copolymer

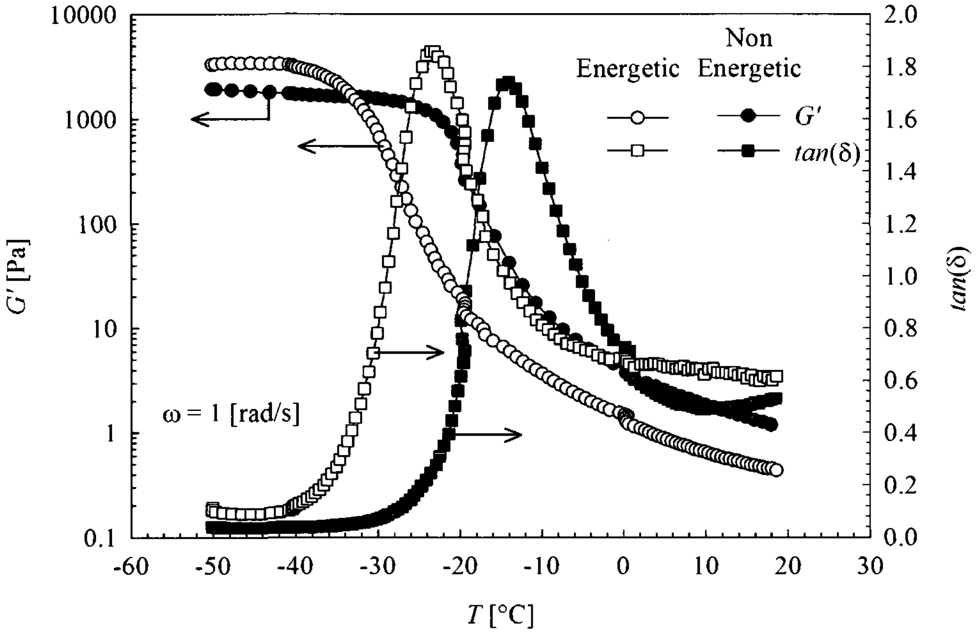


Figure 4.6: DMA of the elastomers: storage modulus and tan(δ) vs temperature

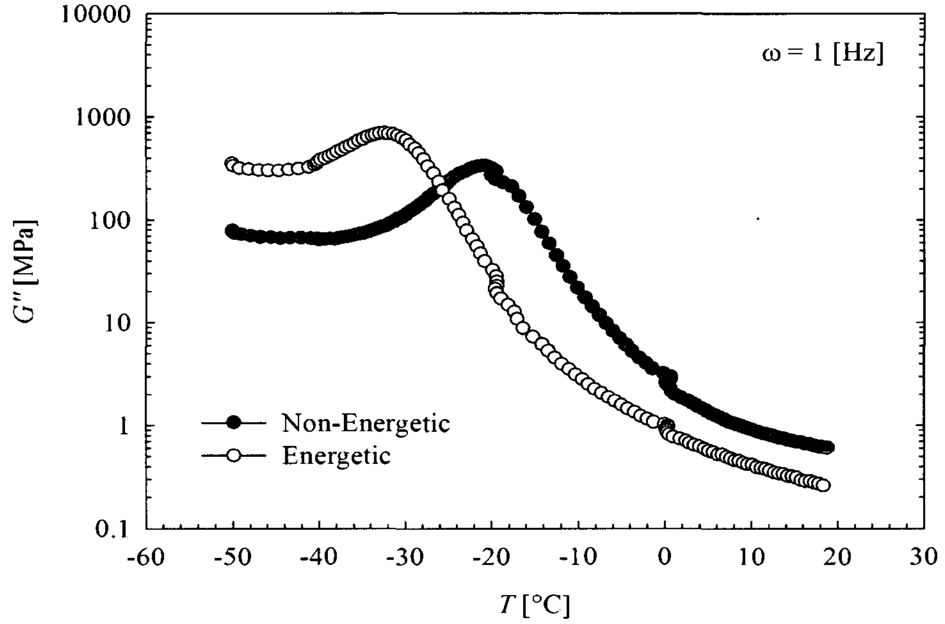


Figure 4.7: DMA of the elastomers: loss modulus vs temperature

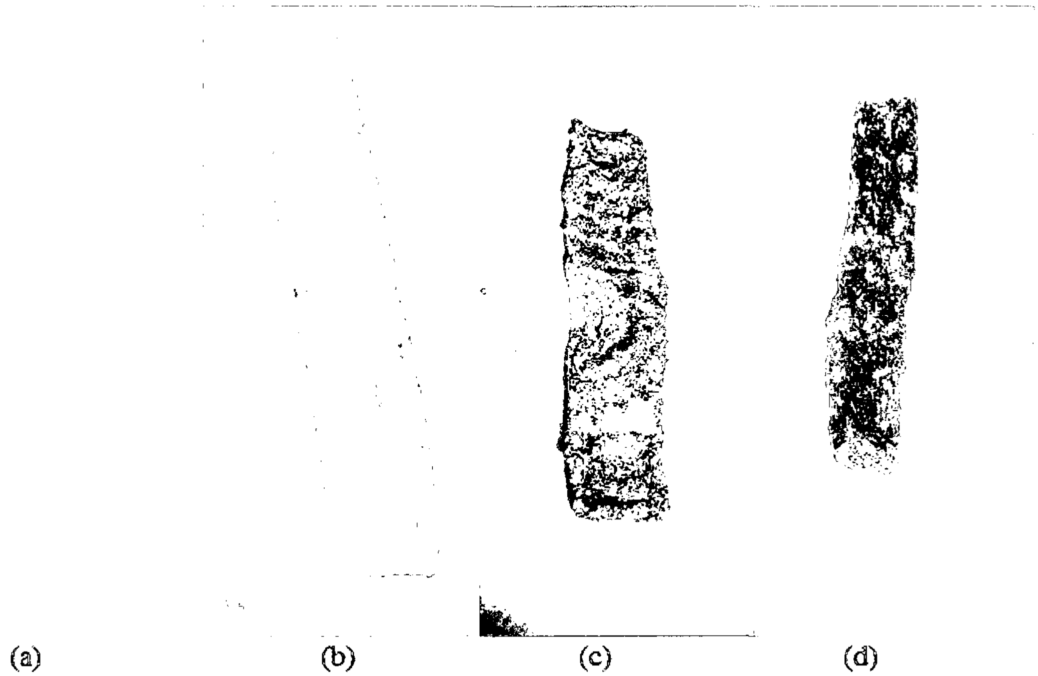
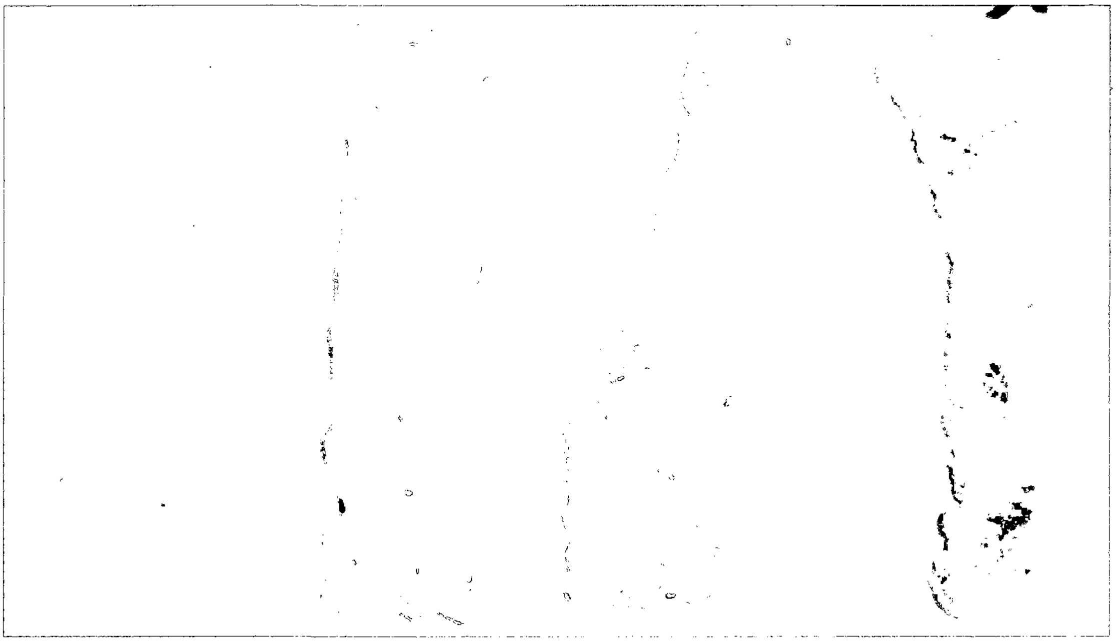


Figure 4.8: Evolution of the degradation of the E elastomers at different time; (a) t=0, (b) t=10, (c) t=20, (d) t=25



(a) (b) (c) (d)

Figure 4.9: Evolution of the degradation of the NE elastomers at different time; (a) t=0, (b) t=10, (c) t=15, (d) t=20

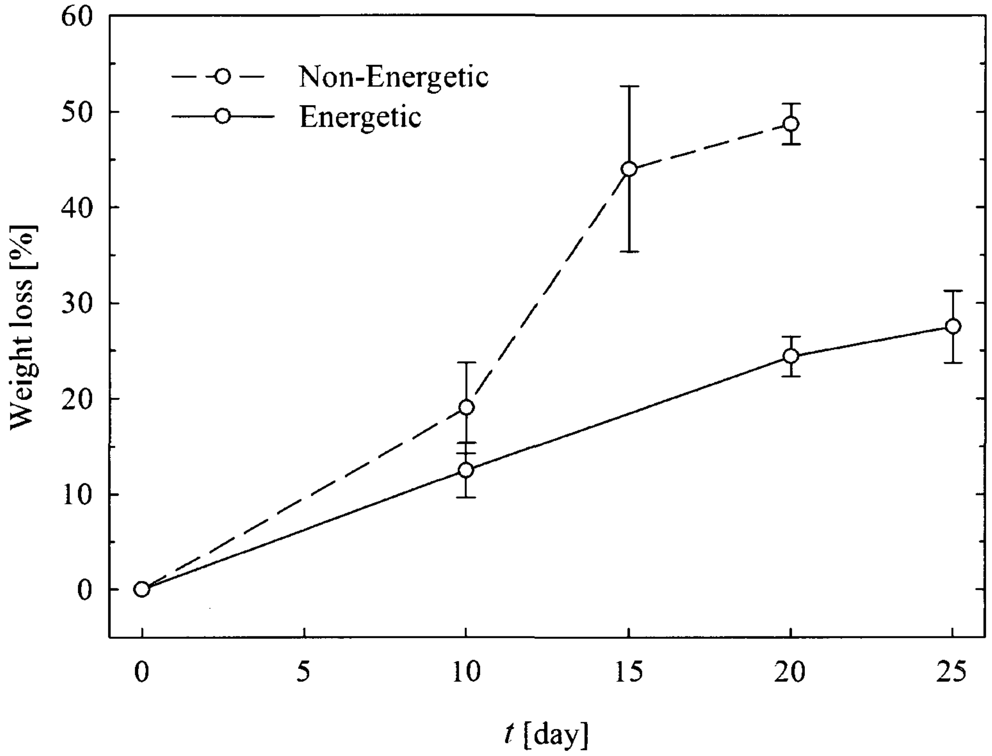


Figure 4.10: Weight loss of the E and NE elastomers

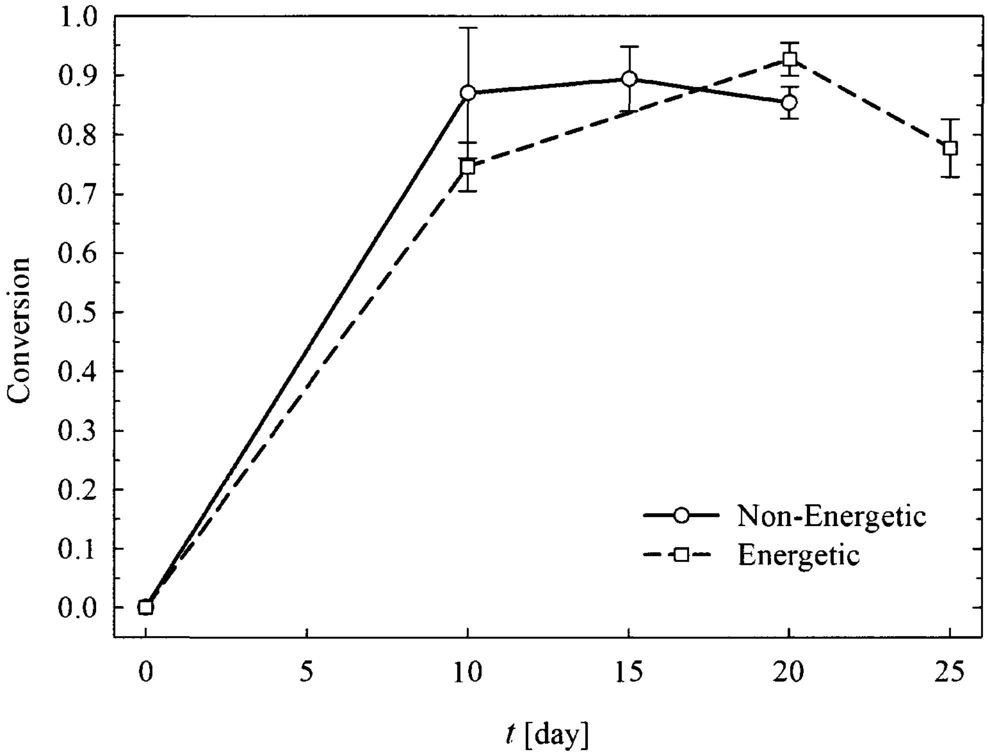


Figure 4.11: Soxhlet extraction results

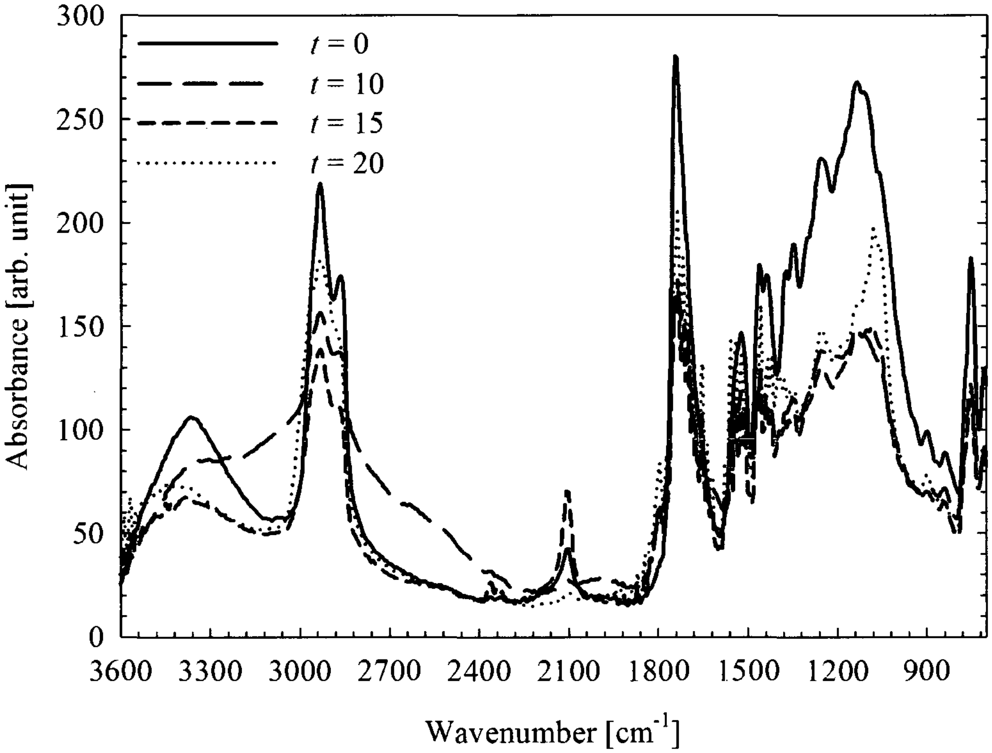


Figure 4.12: FTIR PAS of NE elastomers

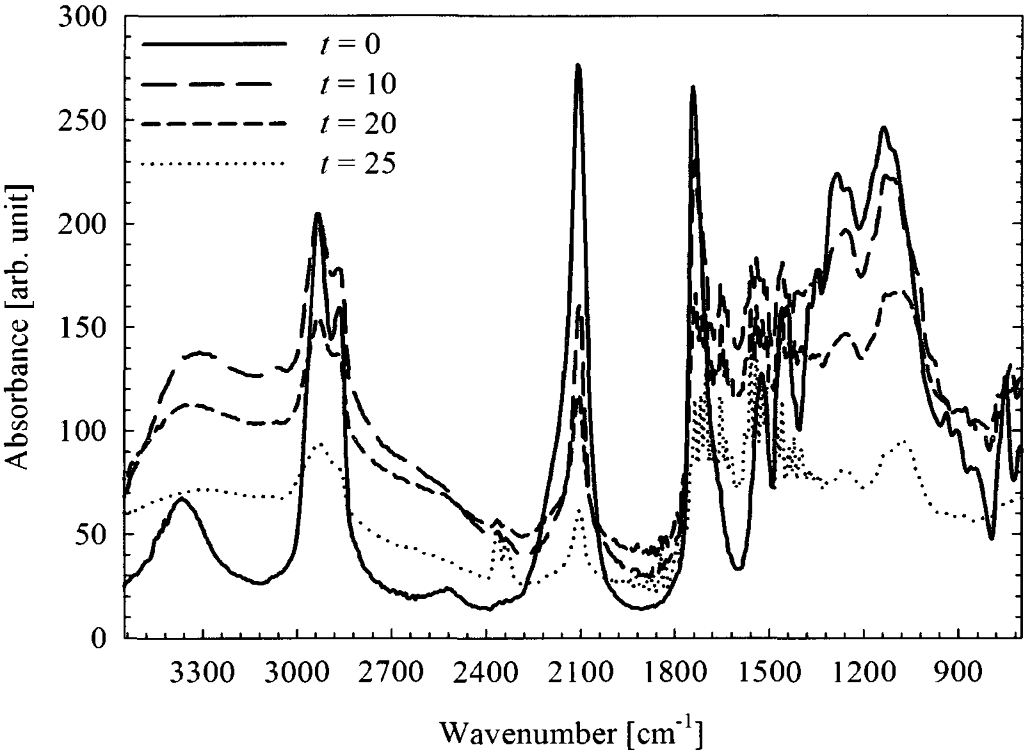


Figure 4.13: FTIR PAS of E elastomers

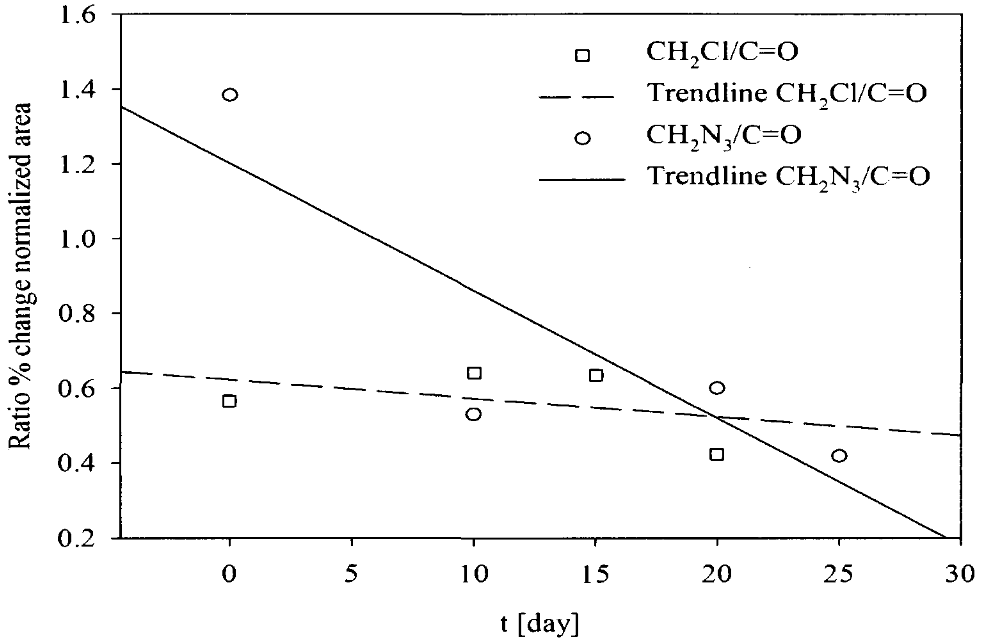


Figure 4.14: Comparison degradation rate E and NE elastomers

Chapter 5 : GENERAL DISCUSSION

5.1 DEVELOPMENT OF BIODEGRABLE ENERGETIC ELASTOMERS

According to Insensitive Munitions (IM) criteria, munitions and weapons should be designed to withstand unplanned stimuli, such as heat, blast and fragment. Moreover the materials used in their formulations should be consistent with Safety and Interoperability. In order to respect these requirements, energetic binders (polymers and plasticisers) have been used since the last two decades in cast-cured polymer in which oxidisers and fuels are bonded for rocket propellants.

In parallel, the demand for green plastic is growing; in 2013 in the US, the demand for green plastic is estimated to be $45 billion, including biodegradable plastic and packaging made from post consumer waste. The progress in green plastic development is driven by the prominence of environmental issues as a result of elevated raw material and fuel costs in the past several years. There is a fervent activity among product manufacturers to make their products more environmentally friendly. And also military and civil industries started to adapt themselves to the present situation.

For these reasons, the main objective of this project was the design of a biodegradable and energetic co-poly(ether/ester-urethane) network, which is able to degrade in the environment, in order to be used as propellant or a gas generator. The first step was the synthesis of hydroxyl-terminated polymer by the reaction between PECH and SC. Then azide group ($-N_3$) have been introduced in the polymeric chain to produce an energetic polymer according to the Frankel method [14]. After that, polyurethane networks have been formulated by a reaction between the hydroxyl-terminated polymer, a biodegradable diisocyanate, L-Lysine diisocyanate (LDI) and polycaprolactone (PCL) using dibutyl tin dilaurate (DBTL) as catalyst. Biodegradability was verified via a twenty-five days long experimental study of decomposition in the compost.

5.1.1 Synthesis of the co-poly(ester/ether)

Polyesterification reactions are the most important reaction in organic chemistry and a lot of methods have been explored and developed. It is well known that the direct polyesterification of dicarboxilic acid and alcohol is not a simple process and there are several efforts to improve the reaction conditions. To increase the yield of the polymerization there are several possibilities:

- Working by using non-stoichiometric conditions using an excess of one of the reactants;
- Removing the alcohol formed during the reaction or the water in order to shift the equilibrium of the reaction towards the products;
- Activating the dicarboxilic acids;
- Conducting the reaction at high temperature.

The use of stoichiometric condition or high reaction temperature is especially not advantageous since the alcohol can undergo side reactions, involving the production of low molecular weight polymers.

It was an object of this work to provide a process for the production of a co-poly(ester/ether) where PECH is condensed with a bifunctional dicarboxylic acid wherein a relatively short reaction time is necessary and neither large excess of PECH nor high temperature are used.

The synthesis of the co-poly(ester/ether) from PECH and SA was carried under chemically different conditions, at various temperatures and different catalysts were used. In several experiments PTSA, pyH, and H_2S have been used as transesterification catalyst and the temperature was varied from 120 to 145 °C. The removal of water resulted to be necessary to conduct the reaction to completion and this was done using a Dean Stark apparatus in combination with a reflux condenser. Toluene was used as solvent since it is less dense than water, immiscible with it, forming an azeotrope. The apparatus allows water to be separated from the condensed azeotrope preventing it from returning to the reaction mixture.

The direct polycondensation between PECH and SA did not yield any high molecular weight copolymer. The highest molecular weight ($M_n \approx 1500$ g/mol) was obtained using PTSA in toluene. These results can be explained analysing the mechanism of the reaction. During the polycondensation between a diacid and a diol, the acid proton of the catalyst forms a complex with the diol, which is able to attack the diacid. The terminal carbon of the COOH group becomes more electrophilic, and hence more susceptible to the attack of the alcohol itself. An intermediate is formed and only the removing a molecule of water can end up the reaction. However, polyesterification reactions are very sensitive to high temperature, side reactions can take place, leading to a low yield, low molecular weight polymers and loss of functionality.

Another method to produce co-poly (ester/ethers) is the reaction between dicarboxylic dichlorides using pyridine as catalyst. This kind of reaction still remains less feasible for the cost of the dicarboxilic acids and the dry conditions requested, but the results were satisfactory. After 24 h a copolymer (LMW) of about 6000 g/mol relative to polystyrene standard has been produced. After 48 h the molecular weight reached the value of about 25000 g/mol relative to polystyrene standard (HMW). In Figure 5.1 GPC curves of both copolymers are shown. These results have been obtained in perfect stoichiometric condition, using an excess of pyridine.

The equivalent molecular weights of the two copolymers have been evaluated by acetylation reaction followed by titration and FT IR technique. For the low molecular weight copolymer the equivalent weight was estimated around 2000 g/equiv, instead for the high molecular weight around 8200 g/equiv. FT IR methods was not consistent for high molecular weight copolymer, due to the low concentration of OH groups. In case of high molecular weight copolymer, the hydrogen bonding tends to shift and broaden the OH stretching absorption around 3500 $cm^{-1;}$ no single peak is detected (Figure 5.2).

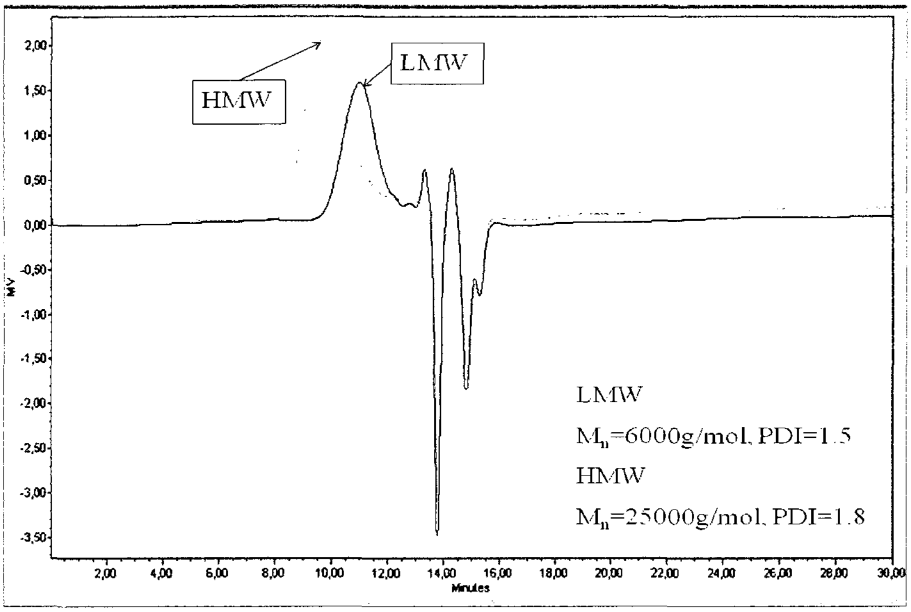


Figure 5.1: GPC curves of non energetic copolymer

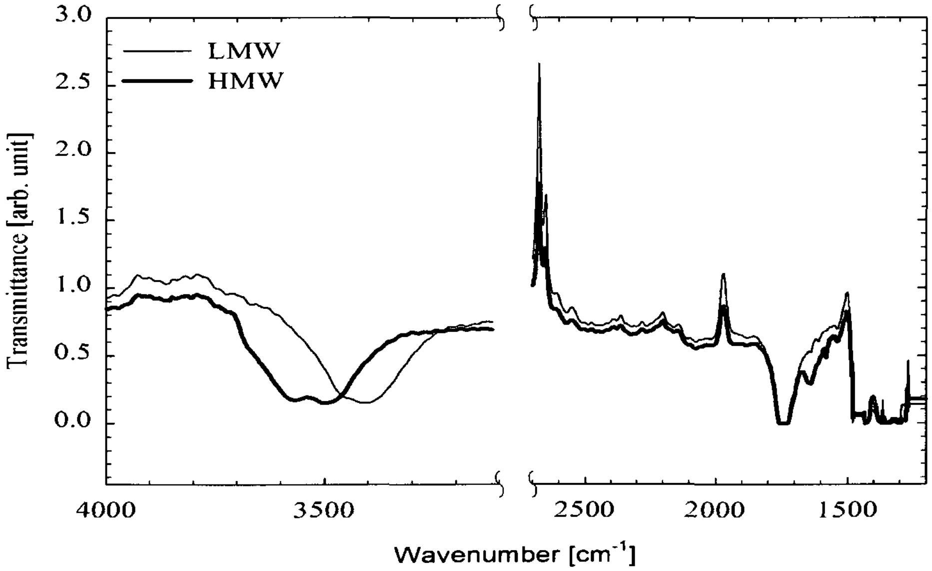


Figure 5.2: FTIR of LMW and HMW copolymers

The copolymer produced by the reaction between PECH and SC was then azided by the nucleophilic reaction with NaN_3 in DMSO. In the propellant industry the suggested absolute molecular weight of the polymer which undergoes the azidation reaction should be between 2000 g/mol and 3000 g/mol, because otherwise the viscosity would be too high to be controlled in the following polyurethane reaction [77]. The azidation of 40g of the low molecular weight polymer yields an oily yellow product with a molecular weight of about 6500 g/mol relative to polystyrene standards and an equivalent weight of about 2230 g/equiv (see Figure 5.3).
The success of the reaction was confirmed by C-NMR, H-NMR and FTIR. All these analysis confirmed the substitution of Cl group with N_3 on the polymeric chains.

In H-NMR spectrum of the non-energetic copolymer there are peaks between 3.5 and 3.8 ppm due to the presence of $-CH_2Cl$, $-O-CH_2$ and -O-CH. On the other hand, in the H-NMR spectrum of the energetic copolymer, the presence of resonance signals around 3.4 ppm, corresponding to $-CH_2N_3$ protons of the energetic copolymer, has confirmed the conversion of $-CH_2Cl$ into $-CH_2N_3$. The ^{13}C-NMR spectra confirm the information provided by the H-NMR spectra. The peaks observed between 65 and 80 ppm in both copolymer correspond to methylene carbons along both copolymer chains, either attached to hydroxyl or ether oxygen. The dual chloro-methyl peaks of the PECH units of the non-energetic copolymer are found between 43 and 46 ppm. The energetic copolymer showed the azidomethyl carbon resonance peak at 54 ppm along with a quasi total absence of resonance signals at 43–46 ppm corresponding to chloro-methyl protons.

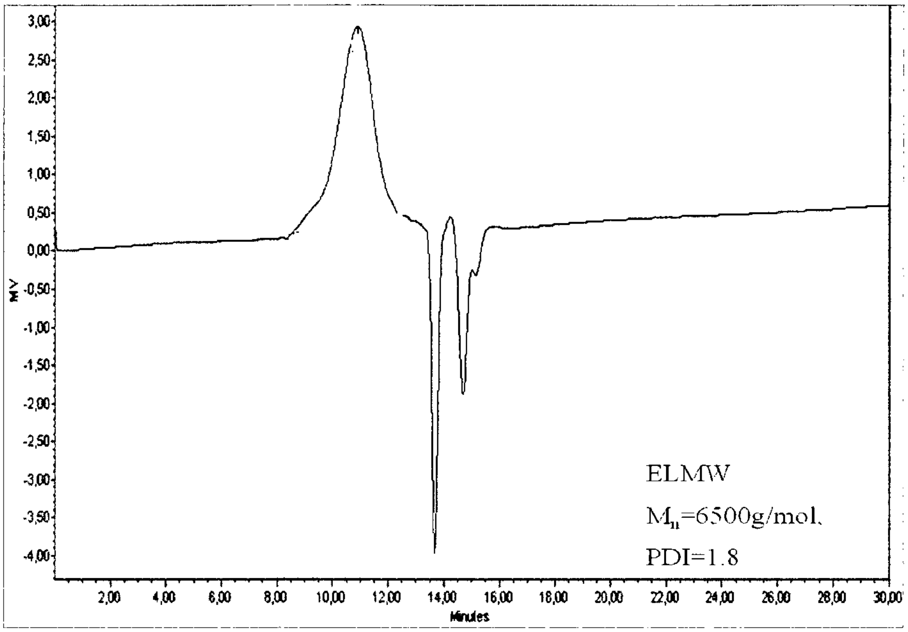


Figure 5.3 GPC curve of energetic copolymer

In FTIR spectra it was possible to detect the appearance of the $-C-N_3$ characteristic peak at 2100 cm^{-1} and the quasi disappearance of the -C-Cl peak at 750 cm^{-1}, proving the conversion of -C-Cl into $-C-N_3$.

Differential scanning calorimetry (DSC) experiments have been carried out on the energetic co-polymer and on the non energetic. This thermal analysis is an important tool in order to understand better the structure- property relationship and thermal stability of the copolymers. The heat flow, associated with the increase of the temperature, gives information's about decomposition temperature of the two systems.

The single exothermic peak at 176 °C in the energetic copolymer is associated with the decomposition temperature, for a heat flow of 7000 mW/g. This is mainly attributed to the elimination of nitrogen due to the cleavage of the azide bonds from the pendant azide group. In the literature, a decomposition temperature (T_{mcd}) of about 220-250 °C has been reported for GAP [78, 79].

Kubota has suggested a model for the decomposition of azide polymers [78]:

$$R - CH_2 - N_2 = N \dashrightarrow R - C \equiv N + N_2 + H_2$$

Subsequently, the nitrile $R - C \equiv N$ can decompose to carbonaceous by-products.

The addition of N_3 on the polymer chains has the expected effect on the thermal stability of the copolymer itself, but the alternating pattern of ether/ester groups on the polymeric backbone has lowered the temperature of decomposition. It is assumed that the linear moieties increase the mobility of the polymeric main chain during the decomposition of the azide pendant groups, reducing the decomposition temperature.

5.1.2 Synthesis of polyurethane elastomer and biodegradation analysis

Several methods have been investigated for the synthesis of thermoset polyurethane elastomer starting from the co-polymers produced.

Before formulating energetic binder, non energetic ones have been prepared using the two copolymers as polyols. Basically the reaction was performed in two steps: first, the mixture of polyol, catalyst (di-butyl dilaurate, dissolved in methylene chloride) and polycaprolactone triol (used to increase the functionality of the alcohol) was degassed at 60 °C, given enough time to form a reactive mixture. Then the diisocyanate (LDI), which is demanded to provide the hard segment, was added and again degassed for a certain amount of time at 60 °C. The temperature was raised to let the binder cure for 24h. L-lysine diisocyanate has been used as curing agent because of its well known biodegradability. The polyurethane formulations with the low molecular weight polyol have been satisfactory. However, high molecular weight copolymers showed some problems due to degassing and degradation of the material during the curing, and as a result they didn't allow the production of a good binder at the laboratory scale.

The formulation of energetic binders was realized following the same two stages method. For both elastomers the reaction time and the temperature reflect the appropriate conditions to prepare polyurethane with complete consumption of the polyols and the diisocyanates.

Dynamic mechanical analysis (DMA) gave further insight on the mechanical properties and viscoelastic behaviour of the two elastomers, detecting storage and loss modulus and *tan*(δ). Both *tan*(δ) curves display broad peaks, between -35 °C and -4 °C for (E) elastomer and between -20 °C and 1 °C for (NE) elastomer which is attributed to the glass transition region of the co-poly(ester/ether) soft block of the elastomers. According to the literature [80], T_g values can be evaluated at the peak of the *tan*(δ) curve as a function of temperature. According to this criteria, the T_g of the polyurethanes are nearly 10 °C apart, with -23 °C) and -14 °C for the (E) and (NE) elastomers, respectively. At these low temperatures below -34 °C, the (E) polyurethane has a storage modulus of about 3300 MPa, as compared to 1800 MPa for the (NE) polyurethane. The storage modulus *G'* represents the elastic and non-dissipative component of the elastomer, i.e. the energy stored in the sample. Below the glass transition temperature, the storage modulus is mainly affected by polymer structure [80], e.g., by the molecular weight and chemical structure of the pre-polymer, with larger molecular weight resulting in larger storage modulus. Consequently the (E) polyurethane presents a higher modulus at low temperature, due to the moderately higher molecular weight of the energetic pre-polymer (6500 g/mol) as opposed to the non-energetic one (6000 g/mol). Starting from approximately -41 °C and -31 °C for the (E) and (NE) elastomers, respectively, the storage modulus decreases progressively with temperature due to the increase in thermal energy and molecular chain motions. Starting from ~ -41 °C and -31 °C for the (E) and (NE) elastomers, respectively, the storage modulus decreases progressively with temperature due to the increase in thermal energy and molecular chain motions. The decrease of the storage modulus in the glass transition region occurs at lower temperature and more sharply for the energetic elastomer than for the non-energetic one.

Taking into account the correspondence between time and temperature, the kinetics of relaxation affects the temperature range necessary for the rearrangement of the molecules[81]. Thus, these different behaviours can be explained based on molecular hindrance of the two polymeric chains. The energetic polymer backbone differs from the non-energetic one, where the former carries three nitrogen atoms at each repeating unit instead of only a chlorine atom in the latter case. As a result, for the (E) elastomer only a small portion of the total volume is occupied by the backbone of the polymeric chain, easing molecular motion and resulting in a faster relaxation process, or considerable relaxation over a lower temperature range. In addition, since these are cross-linked materials, the storage modulus should eventually approach a rubbery plateau at elevated temperatures. At room temperature (20 °C) the storage modulus is quite small, 0.26 Pa for the (E) elastomer and 0.45 Pa for the (NE) one.

The loss modulus, representing the energy dissipation, shows a peak at -32 °C for the (E) elastomer, and at -21 °C for the (NE) elastomer. T_g can be also evaluated as the peak of the loss modulus. It is possible to notice that there is about 10 degrees difference between T_g values evaluated at the peak of *tan*(δ) and at the peak of loss modulus. Nevertheless, these two values of T_g are closer to the T_g of PECH based elastomer (-20 to- 25 °C) [82]. The addition of ester bonds in PECH reduces the flexibility of the polymeric chains and consequently increases the T_g of the non energetic polyurethane. In a polymer with non-symmetrical chains, an additional restriction to rotation is imposed by steric effects increasing T_g such as the case for (NE) elastomer [80]. In addition to the effects caused by the polymeric backbone, the presence, the polarity, the size and flexibility of pendant groups also affects the viscoelastic properties of polymers. Generally, polar pendant groups such as CH_2-Cl tend to increase T_g rather than non-polar one such as CH_2-N_3. Thus although the further substitution of Cl atom by a larger size azide group on the polymeric backbone increases the steric hindrance reducing the flexibility of the polymeric chains, but at the same time increases the free volume required for molecular motions [83]. Consequently, the created additional free volume and the non-polar nature of azide groups would possibly explain the difference between the T_g values of non-energetic and energetic elastomers.

Furthermore, the (E) elastomer is less viscous at higher temperature. This could be generally interpreted by the effects of neighbouring molecules on G' and G'' in terms of local frictional forces between short segment and long segments of the polymeric chains [81].

The biodegradation ability of these binders has been evaluated through a twenty days biodegradation test. The samples were put in boxes filled with compost and incubated for a period of time that varied between ten and thirty days. The water content was regularly checked in order to guarantee 60% humidity. The temperature was set at 55 °C, as an average recommended temperature from the literature surveyed.

The weight loss increases almost linear with the time for both material, and it is more pronounced for the non NE elastomer: after 20 days in the compost the samples have lost about 50% of the mass due to the biodegradation mechanism. Instead the E elastomers, after 25 days, have lost about 25% of the initial mass.

At the beginning of the process, it is possible that the degradation occurs mostly on the elastomeric surface because of the water absorption, causing change on the colour of the samples, which have lost their transparent aspect. However the degradation mechanism depends on the chemical structure and configuration of the polymeric chains. One can affirm that the azide group results to be more stable and resistant to degradation than the chlorine group; NE elastomers can easily undergo hydrolytically and bacterial attack after only 10 days in the compost

The physical properties of the degraded samples have been evaluated by FTIR PAS analysis and soxhlet extraction in dichloromethane.

The spontaneous dissolution of the polyurethane networks in the solvent showed increase with the time in the compost. After 10 days both polyurethane show a conversion bigger than 0.7, which slowly increases with time passing. It means that spontaneous cleavage occurs randomly along the polymer chains in the compost and, with the time, the presence of low molecular weight by-products soluble in organic solvents remains stable.

Generally speaking, the absorbance in a FTIR-PAS spectra depends on the heat transport properties in the sample. Given the significant changes in the polyurethane binders during the composting experiments it is not possible to compare the spectra from samples taken at different times on an absolute basis. Therefore, the absorbance intensity for the few peaks of interest was normalized by the intensity of the peak corresponding to aliphatic antisymmetric β-CH_2 stretching (2940 and 2943 cm^{-1}). Changes (%) in the normalized area of the CH_2-N_3, CH_2-Cl, urethane C=O and C-O-C peaks respectively, at different stages of degradation, were detected.

Figure 5.5 shows the spectrum of the NE elastomers around 750 cm^{-1}. Figure 5.6 shows the spectrum of E elastomers around 2100 cm^{-1}.

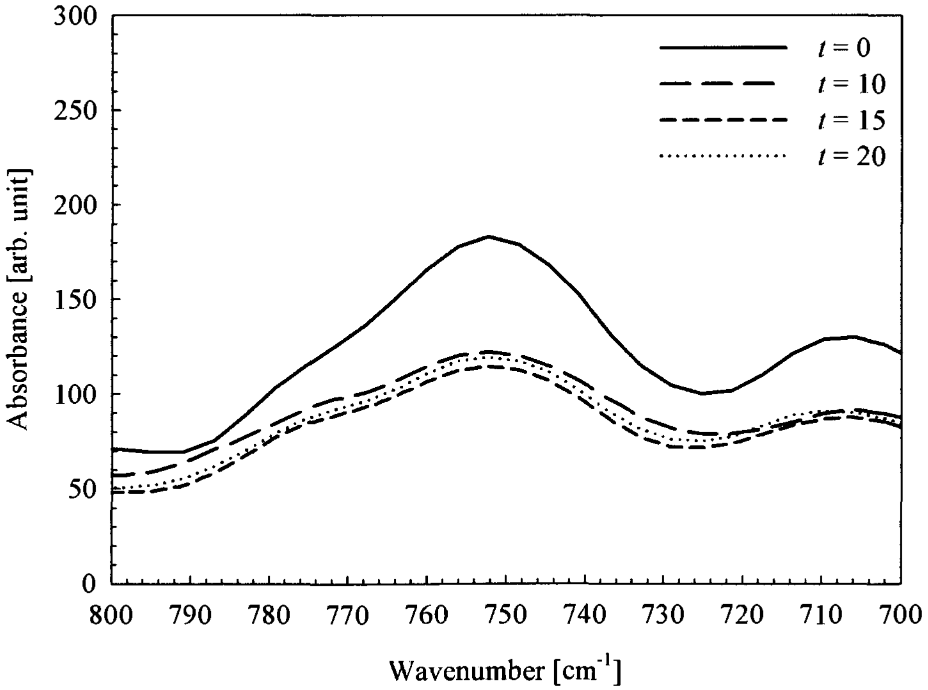


Figure 5.4: FTIR PAS of NE elastomers (zoom at 750 cm^{-1})

For (NE) elastomers, the evolution of carbonyl urethane (C=O) and CH_2-Cl peaks showed the same trend, with about 50% loss after 20 days in the compost. For the ester group, the loss is significantly higher, of about 90% after 20 days. Concerning the (E) elastomers, after 25 days in the compost the CH_2-N_3 bonds decreased of about 90%, instead of 70% for the C=O links. In summary the change of the normalized area was more accentuated for the azide group. The ester group has decreased of about 65%. Considering that the weight loss over time is more pronounced in the (NE) polyurethanes, it means that the degradation process proceeds differently in each type of materials.

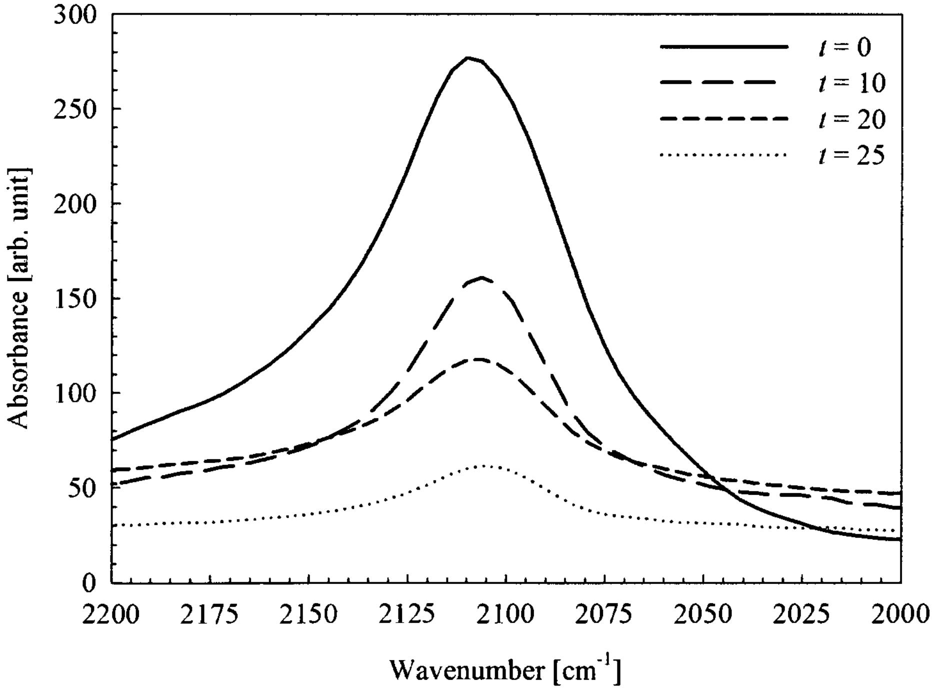


Figure 5.5: FTIR PAS of E elastomers (zoom at 2100 cm^{-1})

Ester bonds play a fundamental role during the degradation process since they can undergo hydrolytic scission more easily than other chemical bonds. The urethane and urea linkages are less sensitive to hydrolysis than the ester bonds [84]. An initially homogeneous sample undergoes hydrolysis, with consequent cleavage of the ester bonds confirmed by a decrease in the mass. The velocity of the hydrolysis is determined by the 'concentration' of reaction partners, water and labile bonds [51]. From water uptake tests (NE) elastomers resulted to be more hydrophilic (7.1%) than the (E) elastomers (2.3%) and after 10 days the absorption peaks of ester bonds substantially decreased. This is in accordance with the larger weight loss occurred to non energetic binders. The inherent more hydrolytic resistance of the energetic polyurethane must be attributed to the presence of the azide group in the backbone chains. The final hydrolysis products of the polyesters will be degraded by microorganisms to smaller end products after they are released in a natural environment. But at this stage of the work no eco-toxicity tests were conducted.

In summary FTIR-PAS spectra have shown that the combination of the hydrolytic and bacterial attack in the compost was more efficient in the case of non-energetic binders.

Chapter 6 : CONCLUSIONS AND RECOMMANDATIONS

6.1 CONCLUSIONS

The aim of this project was to produce an energetic biodegradable polyurethane elastomer to be used for military applications. Important variables in the material formulation and biodegradability tendency were glass transition temperature, storage and loss modulus (G' and G"), and weight loss after composting.

From the experimental point of view, the first goal was to find a synthetic method to produce a copolymer of polyepichlorohydrin and sebacic acid suitable for polyurethane formulations.

Two different techniques were used. The first method was the direct polycondensation between polyepichlorohydrin and sebacic acid using a *Dean Stark* apparatus. Despite different reaction conditions were tested, no high molecular weight product was obtained. However, the reaction between polyepichlorohydrin and sebacoyl chloride, using pyridine as HCl acceptor, gave the best result. The major problem was the reactivity of PECH, which was overcome using the diacid dichloride of sebacic acid. The copolymer was then azidified with NaN_3 in DMSO. Spectroscopy analysis (H-NMR, ^{13}C-NMR and FTIR) were carried out to verify the substitution of the Cl groups with N_3 groups.

Therefore thermoset elastomers with a hard segment which do not withstand hydrolysis were required. Both non-azidified and azidified copolymers were cross-linked in the presence of polycaprolactone triol (PCL) and L-lysine diisocyanate (LDI) as a non toxic coupling agent. Subsequently, the chemical and mechanical properties of the produced polyurethanes along with the water uptake and biodegradation in compost of these materials were characterized

Biodegradability was verified via a twenty five days composting study. The cross-linked elastomers showed high biodegradability in the compost. The rate of weight loss was higher for the NE elastomers (50 % for non energetic elastomers, 25% for energetic). Both materials after 10 days were so degraded that no mechanical tests could be conducted. PAS FTIR spectra were important tools for a first investigation of the rate of degradation of urethane bonds in the two systems. The hydrolysis and the bacterial attack were more intense for the non-energetic polyurethane. One can conclude that N_3 groups can act as a barrier, protecting the ester/ ether bonds, but it is a hypothesis to be verified in future works.

The research presented in this work has described the route from the first trial where two co-poly(ester/ether) containing respectively Cl and N_3 were synthesized, via the synthesis of new polyurethane elastomers based on lysine diisocyanate with biodegradability. These materials exhibit potential of being the next generation of highly elastic biodegradable thermoset elastomers for military applications.

6.2 RECOMMANDATIONS

Both the polymer synthesis and the biodegradation analysis invite to further studies and investigations. In the work presented in the article remarkable results are shown, but further experiments should be undertaken.

The synthesis of the co-poly(ester/ ether) can be optimised with respect to temperature, time and reactants. It could be also interesting to vary the chemical conditions performed to produce copolymers of different molecular weight to be used in the following steps. In the biodegradation analysis, soft segments, with different repeating units and molecular weight, could have a big impact on the final results.

Moving to the polyurethane synthesis, different formulations could be tested, varying the ratio of the diisocyanate respect to the alcohol, using glycerol instead of polycaprolactone triol, improving the mechanical properties of the final product. Mixing under vacuum can overcome problems of spontaneous gassing during the reaction. Even a small amount of bubbles inside the polyurethane network, which can create voids in the cured solid, can have big impact on the final formulations: uncontrolled burn rates, reduced density and available energy. The reaction kinetics could also be studied by DSC analysis.

Moreover, many aspects of the degradation of the polyurethane are not fully understood. Since the investigation of the biodegradation was one goal of this research, the results obtained so far should be expanded in future work.

It is also well known that the degree of cross-links of a thermoset elastomer play a major role in determining whether it has good mechanical properties or not and this parameter can be related to the degree of degradation in the compost. Swelling analysis can be carried out on degraded samples in order to find out if the matrix of the elastomer has been attacked by degradation.

The evolution of the molecular weight between cross-links with the composting time could also studied be by swelling experiments and solvent extraction.

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ANNEXE 1: Protocole expérimental pour la dégradation du PLA

PROTOCOLE EXPÉRIMENTAL	
Protocole # :	Nombres de pages: 39 **Date:** mai 2006 **Dernière modification:** août 2006
Auteurs: Andréanne Harbec Lucie Jean, associée de recherche Charles Dubois, *Ph.D.*	
Titre: Montage expérimental dans le but éventuel de caractériser la dégradabilité d'échantillons de poly(L-lactide) dans le temps à l'aide de l'analyse dynamique mécanique (DMA) en torsion.	
Mots-clés: poly(L-lactide), PLA, PLLA, dégradabilité, compost, DMA, flexion	

1. OBJECTIFS

Développer un montage où des échantillons de poly(L-lactide) (PLLA) seront enfouis à l'intérieur de compost organique et soumis à des conditions opératoires fixées pour une période de temps variable. Ces échantillons permettront éventuellement de caractériser l'évolution de la dégradabilité dans le temps par la mesure de propriétés mécaniques en torsion, soit par l'analyse dynamique mécanique (DMA). Les expérimentations s'effectueront en triplicatas.

2. CONDITIONS OPÉRATOIRES

1. Température : 57 °C
2. Conditions aérobes
3. Durée de l'expérience : 11 jours
4. Milieu environnemental : compost
    - pH : entre 6 et 8
    - Humidité : 60% de la capacité de rétention
    - Composition : Les concentrations en métaux et métalloïdes ne doivent pas dépasser les teneurs de fond de la *Politique de protection des sols et de réhabilitation des terrains contaminés : Annexe 2 : Les critères génériques pour les sols et pour les eaux souterraines*, Tableau 2 : Teneurs de fond (critères A) pour les métaux et métalloïdes, ministère du Développement durable, Environnement et Parcs du Québec, 2005 (voir annexe).

3. MATÉRIEL ET SUBSTANCES

Pour la partie 4.1 Caractérisation du compost

Substances :

- ✓ Eau distillée
- ✓ Échantillon de compost (minimum de 103 g)

Appareils :

- ✓ Balance de précision (± 0.01g et 0.0001g)
- ✓ Dessiccateur (HR < 10-15%)
- ✓ Four 105 °C
- ✓ Minuteur
- ✓ pH-mètre Accumet muni de l'électrode de type *ROSS® SURE-FLOWM (ORION)*
- ✓ Plaque chauffante

Instruments :

- ✓ Bécher de 100 mL
- ✓ 2 béchers de 600ml
- ✓ Chaudière
- ✓ Coupelles en aluminium (voir la section **7. RECOMMANDATIONS**)
- ✓ Entonnoir Buchner Coors No 60240
- ✓ Mortier
- ✓ Papier filtre Whatman GF/C de 47mm
- ✓ Spatules en acier inox
- ✓ Support à entonnoir
- ✓ Tamis de 4.75 mm
- ✓ Thermomètre pouvant atteindre 100 °C
- ✓ Tige de verre

Pour les parties subséquentes :

Substances :

- ✓ 70 litres de compost
- ✓ Eau déionisée (18.2 MΩ.cm)
- ✓ Éthanol (C_2H_5OH) 70% et 95%
- ✓ 100g de NatureWorks® PLA (polylactide) polymer 4042D

Appareils :

- ✓ Dessiccateur (HR < 10-15%)
- ✓ Four dépressurisé (vaccum) (45 °C)
- ✓ Hotte microbiologique
- ✓ Incubateur (57 °C)
- ✓ Mini-presse pour la mise en forme des polymères
- ✓ Plaque de mise en forme (mini-presse) ayant un moule de 6 cm de longueur x 1.2 cm de largeur (minimum) et 3 mm d'épaisseur

Instruments :

- ✓ Arrosoir à bec perforé
- ✓ 5 bacs de plastique transparents de 4 (dimension : 10 cm haut x 29 cm long x 19 cm de large) avec couvercles
- ✓ Bécher de 500 mL
- ✓ Bécher de 800 mL
- ✓ Petit brosse
- ✓ Chaudière
- ✓ Crayons marqueurs indélébiles
- ✓ Mortier
- ✓ Plats d'aluminium
- ✓ Rubans collants de couleur
- ✓ Ruban adhésif (scellant)
- ✓ Petits sacs de plastiques refermables
- ✓ Grosse spatule en inox
- ✓ Tamis de 4.75 mm
- ✓ Truelle
- ✓ 2 vaporisateurs

4. MÉTHODOLOGIE

Homogénéisation du compost

Cette étape doit être préalablement effectuée pour chaque échantillon de compost utilisé pour toute caractérisation ou avant son introduction dans le bac. Toutefois, il n'est pas requis d'effectuer cette étape pour tout le volume de compost nécessaire aux expérimentations au même moment.

1. Retirer tout matériel inerte du compost (ex. : roche, verre, métal, bois ...)
2. Uniformiser la densité du compost à l'aide d'un mortier
3. Tamiser le compost à l'aide d'un tamis de 4.75 mm

4. Mélanger le compost ;

Afin de faciliter le tamisage, tamiser tout d'abord le compost à l'aide d'un tamis d'un peu plus de 5 mm puis à reprendre le tamisage à l'aide du tamis de 4.75 mm.

4.2 Caractérisation initiale du compost

pH

À réaliser en triplicata

Le pH du compost devrait se situer entre 6 et 8. Un pH en dessous de cet intervalle peut abriter une flore microbienne atypique tandis qu'un pH situé au-dessus de 8 favorise le maintient dans le compost du CO_2 provenant de la biodégradation.

Pour les manipulations, se référer au protocole : ESTRELLA, Sandra, *Détermination du pH d'un échantillon de tourbe à l'aide d'un pH-mètre*, Protocole standard d'opération de la Chaire industrielle CRSNG en assainissement et gestion des sites, École Polytechnique de Montréal, no. A8, 2000, 4 pages.

Noter les résultats au tableau suivant :

Tableau 1 : Mesures du pH du compost

Réplicat	pH (± 0.01)
1	
2	
3	
Moyenne	

Composition du compost

La composition du compost est fournie par le fournisseur.

4.1.1 Capacité de rétention d'eau au champ

À réaliser en triplicata

La capacité de rétention d'eau au champ maximale du compost doit être déterminé afin d'appliquer les conditions opératoires fixées, soit 60% de la capacité de rétention d'eau. Pour les manipulations, se référer au protocole : LEDUC, Manon, *Capacité de rétention d'eau au champ d'un échantillon de sol*, Protocole standard d'opération de la Chaire industrielle CRSNG en assainissement et gestion des sites, École Polytechnique de Montréal, no. A23, 2002, 4 pages.

Noter les résultats au tableau suivant :

Tableau 2 : Mesures pour l'évaluation de la capacité de rétention d'eau au champ (CRCss) du compost

Données	**Réplicat**		
	1	**2**	**3**
Masse de la coupelle (P1) (± 0.0001g)			
Masse compost saturé en eau + coupelle (P2) (± 0.0001g)			
Masse compost sec + coupelle (P3) (± 0.0001g)			
CRCss (g d'eau/ g de compost sec)			

4.1.2 Humidité initiale du compost

À réaliser en triplicata

La quantité d'eau initialement contenue dans le compost est déterminée initialement.

1. Peser une coupelle d'aluminium vide et noter la masse obtenue au tableau 3 ;
2. Ajouter environ 3 grammes de compost dans la coupelle et noter la masse de l'ensemble coupelle + compost ;
3. Assécher l'échantillon pendant 16 heures (minimum) au four à 105 °C ;
4. Peser de nouveau l'ensemble coupelle + compost et noter la masse;

5. La quantité d'eau par gramme de compost est calculée à l'aide de cette relation (éq.1) :

$$\left(\text{masse}_{\text{coupelle+composte humide}} - \text{masse}_{\text{coupelle+composte sec}}\right) \Big/ \left(\text{masse}_{\text{coupelle+composte sec}} - \text{masse}_{\text{coupelle}}\right) [=] \frac{g\ d'eau}{g\ de\ compost\ \text{sec}} \quad (1)$$

Tableau 3: Caractérisation de l'humidité initiale

Données	**Réplicat**		
	1	**2**	**3**
Masse coupelle (± 0.0001g) (P4)			
Masse coupelle + compost humide (± 0.0001g) (P5)			
Masse coupelle + compost sec (± 0.0001g) (P6)			
Humidité initiale (g eau / g compost sec) (P7) = (P5-P6)/(P6-P4)			
Masse compost sec / masse compost humide (P8) = (P6-P4) / (P5-P4)			

Note : Prévoir l'assèchement au four de cet échantillon de compost en même temps que celle permettant de déterminer la capacité de rétention en eau (voir la section **4.1.3 Capacité de rétention d'eau au champ)**

4.1.3 Préparation des échantillons de PLLA

Préalablement, le polylactide en pastilles doit être asséchées dans un four dépressurisé (vacuum, pression < 400 Pa) à 45 °C pendant 24 heures (minimum). Par la suite, ceux-ci doivent être mise en forme dans la plaque prévu à cet effet (voir **3. MATÉRIELS ET SUBSTANCES**). Pour les manipulations, se référer à l'article : BURLET, Jérôme, Marie-Claude Heuzey, Charles Dubois, Paula Wood-Adams, Josée Brisson, *Thermal stabilization of high molecular weight L-polylactide*, ANTEC, 2005, 5 pages.

Suite à la mise en forme des échantillons, ceux-ci doivent être taillés et asséchés dans un four dépressurisé (vacuum, pression < 400 Pa) à 45°C pendant 24 heures (minimum). La longueur des échantillons doit se situer entre 2.5 et 3 cm. La largeur et l'épaisseur doivent être les mêmes pour tous les échantillons, soient respectivement 1 cm et 3 mm. Les échantillons doivent être entreposés dans le four dépressurisé jusqu'à leur insertion dans le compost.

Préparation des bacs de compost et identification du matériel

Il y aura 3 bacs contenant les échantillons expérimentaux. À l'intérieur de ces bacs, il y aura 6 échantillons d'enfouis (18 échantillons au total). Le retrait des triplicatas s'effectuera à intervalle régulier pendant 11 jours. L'ordre du retrait des réplicats se fera selon la séquence présentée au tableau 4, car les échantillons de chaque triplicata sont dispersés à travers les deux bacs.

De plus, il y aura deux bacs contenant des témoins. Le premier bac contiendra les témoins biotiques secs tandis que le second contiendra les témoins abiotiques. À l'intérieur de ces bacs, il y aura 2 triplicatas d'enfouis, soit 6 échantillons. Au bout de 4 à 5 jours et au bout de 11 jours, un triplicata sera prélevé.

Selon la littérature, la dégradation du polylactide s'effectue en deux étapes. Tout d'abord, ce polymère est dégradé chimiquement par sa réaction avec l'eau, soit l'hydrolyse. Ensuite, la biodégradation proprement dite entre en jeu. Les oligomères de ce plastique peuvent être dégradés par les micro-organismes du milieu, qui ne peuvent s'attaquer initialement directement au polymère. Le témoin biotique sec permettra de confirmer ce fait. Quant au témoin abiotique humide, celui-ci permettra d'affirmer si la biodégradation a débuté au niveau des bacs expérimentaux.

1. Graduer chaque bac à 4 et 8 cm à partir du bas ;
2. Identifier chaque bac (expérimentaux : E, témoins biotiques secs : TS, témoins abiotique : TA)

3. Identifier l'emplacement des échantillons sur la paroi du bac. Ne pas identifier directement sur l'échantillon afin d'éviter toute perturbation au niveau de la dégradation des échantillons. Pour de plus amples informations sur la disposition des échantillons, se référer à la figure 1.
4. Peser chaque bac et noter la masse obtenue au tableau 4.

Tableau 4 : Identification du matériel pour les échantillons expérimentaux

Identification du bac (sem-type)	Identification du réplicat	Ordre du retrait	Masse de l'échantillon (± 0.0001g)	Masse totale des triplicatas du bac (± 0.0003g)	Masse du bac/ Masse du bac + couvercle (± 0.1g)
E-1	1E	1			
	2E	2			
	3E	3			
	4E	4			
	5E	5			
	6E	6			
E-2	7E	1			
	8E	2			
	9E	3			
	10E	4			
	11E	5			
	12E	6			
E-3	13E	1			
	14E	2			
	15E	3			
	16E	4			
	17E	5			
	18E	6			
TS	1S	1			
	2S	1			
	3S	1			
	4S	2			
	5S	2			
	6S	2			
TA	1A	1			
	2A	1			
	3A	1			
	4A	2			
	5A	2			
	6A	2			

4.1.4 Préparation du compost

Échantillons expérimentaux

1. Remplir de compost préalablement homogénéisé (voir section **4.1 Homogénéisation du compost**) les bacs expérimentaux environ 1 cm au-dessus du trait de 8 cm ;
2. Fermer le bac et imperméabiliser à l'aide de ruban adhésif ;

Témoins secs

Les témoins secs seront enfouis dans du compost déshumidifié. Afin de faciliter le tamisage du compost lors de cette étape, l'homogénéisation du compost doit être faite lorsque le compost a été asséché.

1. Assécher environ 20 litres au four à 105 °C pendant 16 heures dans des plats d'aluminium ;
2. Laisser refroidir les plats d'aluminium rempli de compost secs au dessiccateur (HR<10%) pendant 1 heure.
3. Procéder à l'homogénéisation du compost (voir section **4.1 Homogénéisation du compost**) et entreposer le compost dans le bac prévu à cet effet ;
4. Fermer le bac et imperméabiliser à l'aide de papier aluminium ;

Le compost ayant été asséché se durcit de façon non négligeable et ne peut donc être tamisé directement. Tout d'abord, inséré une portion de compost sec dans un grand sac de type Ziploc et refermé ce dernier. À l'aide d'un mortier, concasser les agrégats de compost puis procéder au tamisage.

Puisque que l'assèchement du compost peut se faire sur plusieurs jours étant donné la grandeur limitée du four, entreposer le compost asséché et tamisé dans le bac prévu pour les témoins secs, refermé et scellé à l'aide de paraffine.

Témoins abiotiques

Les témoins abiotiques seront enfouis dans du compost ayant été autoclavé. Bien qu'un sol ayant été traité à l'autoclave n'ait pas tendance à conserver sa stérilité à long terme, des expériences antérieures ont démontré que le compost peut demeurer stérile à court terme. Afin de s'assurer que le compost utilisé puisse en faire autant, il est recommandé de procéder à des tests préliminaires au BacLight sur un échantillon de compost ayant été stérilisé il y a une semaine. Pour les manipulations, se référer au protocole : CASTEGNIER, Françoise, Lucie Jean, *Énumération directe des bactéries viables et totales d'un échantillon d'eau ou de sol par microscopie à épifluorescence,* Protocole standard d'opération de la Chaire industrielle CRSNG en assainissement et gestion des sites, École Polytechnique de Montréal, no. 43J, 2000, 11 pages.

1. Remplir de compost homogénéisé le bac prévu pour les témoins abiotiques dépassé le trait de 8 cm (2-3 cm de plus) (voir section **4.1 Homogénéisation du compost**) ;
2. Refermer le bac et couvrir de papier d'aluminium le pourtour ;
3. Autoclaver à deux reprises le bac pendant 40 minutes en mode liquide ;
4. Laisser refroidir le bac pendant une nuit ;

4.1.5 Caractérisation de l'humidité du compost des échantillons expérimentaux et témoins

Échantillons expérimentaux

1. Transférer le contenu des trois bacs dans une chaudière ;
2. Mélanger à l'aide d'une truelle le compost à l'intérieur de celle-ci;
3. Procéder à la caractérisation du niveau d'humidité pour les trois bacs selon la méthode détaillée à la section **4.2.4 Humidité initiale du compost**. Noter les résultats obtenus au tableau 5 ;

4. Remplir les bacs de compost au-dessus du trait de 8 cm, les refermer et les imperméabiliser à l'aide de ruban adhésif ;

Témoins abiotiques

1. Stériliser à l'autoclave pendant 20 minutes en mode instrument le matériel suivant :
    - ✓ 1 spatule
    - ✓ 3 coupelles d'aluminium
    - ✓ 1 truelle
2. Nettoyer à l'éthanol 70% la hotte microbiologique ;
3. Vaporiser l'extérieur du matériel stérilisé et du bac contenant le compost abiotique d'éthanol 70% en déposant le tout sous la hotte microbiologique ;
4. Procéder ainsi pour la balance de précision (± 0.0001 g) en prenant soin de la calibrer ;
5. Démarrer la ventilation en allumant les lumières UV pour 15 minutes ;
6. Éteindre les lumières UV et allumer les néons ;
7. Mélanger à l'aide de la truelle le contenu du bac ;
8. Peser environ exactement 3 grammes de compost dans trois coupelles d'aluminium sous la hotte ;
9. Procéder à la caractérisation du niveau d'humidité pour les deux bacs selon la méthode détaillée à la section 4.2.4 **Humidité initiale du compost**. Noter les résultats obtenus au tableau 5 ;
10. Refermer le bac et imperméabiliser à l'aide de papier aluminium ;
11. Éteindre la ventilation et les lumières de la hotte microbiologique.

Tableau 5 : Caractérisation du niveau d'humidité de départ

BAC E-1, E-2, E-3			
Données	**Réplicat**		
	1-1	**1-2**	**1-3**
Masse coupelle (± 0.0001g) (P4)			
Masse coupelle + compost humide (± 0.0001g) (P5)			
Masse coupelle + compost sec (± 0.0001g) (P6)			
Humidité initiale (g eau / g compost sec) (P7) = (P5-P6)/(P6-P4)			
Masse compost sec / masse compost humide (P8) = (P6-P4) / (P5-P4)			
BAC TA			
Données	**Réplicat**		
	A-1	**A-2**	**A-3**
Masse coupelle (± 0.0001g) (P4)			
Masse coupelle + compost humide (± 0.0001g) (P5)			
Masse coupelle + compost sec (± 0.0001g) (P6)			
Humidité initiale (g eau / g compost sec) (P7) = (P5-P6)/(P6-P4)			
Masse compost sec / masse compost humide (P8) = (P6-P4) / (P5-P4)			
BAC TS			
Données	**Réplicat**		
	A-1	**A-2**	**A-3**
Masse coupelle (± 0.0001g) (P4)			
Masse coupelle + compost humide (± 0.0001g) (P5)			
Masse coupelle + compost sec (± 0.0001g) (P6)			
Humidité initiale (g eau / g compost sec) (P7) = (P5-P6)/(P6-P4)			
Masse compost sec / masse compost humide (P8)= (P6-P4) / (P5-P4)			

4.3. Insertion des échantillons dans le compost

Bacs expérimentaux et témoins biotiques secs

1. Prélever du four le nombre requis d'échantillons pour chaque bac et peser la masse de chacun. Noter le résultat au tableau 4. Déposer les échantillons sur une feuille numérotée afin de conserver leur identification jusqu'à leur enfouissement dans le compost ;
2. Aérer le compost à l'aide d'une truelle ;
3. Abaisser le niveau du compost dans le bac à 4 cm. Se servir, par exemple, de plat de pyrex pour contenir le compost supplémentaire. Ne pas mélanger le compost entre les bacs expérimentaux et le témoin ;
4. Placer les échantillons de chaque bac sur la surface du compost disposés selon la figure 1, espacés le plus uniformément possible ;
5. Recouvrir de compost les échantillons jusqu'au trait de 8 cm en reprenant le compost contenu dans les plats correspondants ;
6. Fermer les bacs et imperméabiliser à l'aide de ruban adhésif.

Témoins abiotiques

1. Stériliser à l'autoclave pendant 20 minutes en mode instrument le matériel suivant :
   - ✓ 1 truelle
   - ✓ 3 plats de pyrex
2. Procéder de la même façon pour l'introduction des échantillons expérimentaux et témoins biotiques secs, mais sous conditions stériles, soit sous la hotte microbiologique. Pour les manipulations relatives à ce type de condition, se référer à la section **4.3.4 Caractérisation de l'humidité du compost des échantillons expérimentaux et des témoins**. Étant donné que l'eau entraîne la dégradation du PLLA, vaporiser les échantillons d'éthanol 95% au lieu de 70% ;
3. Fermer le bac et imperméabiliser à l'aide de papier d'aluminium.

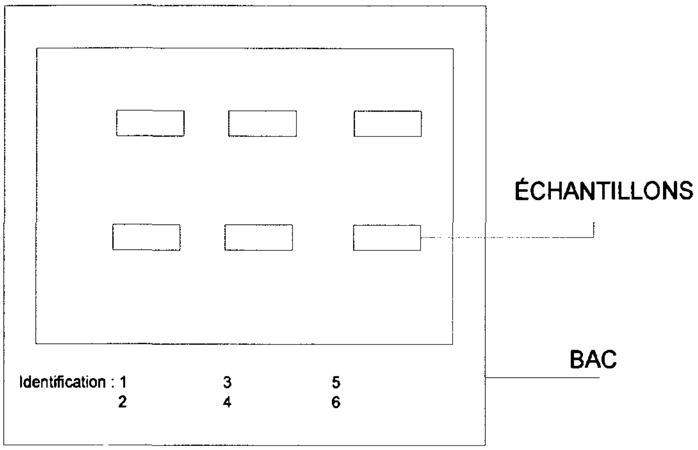

Figure 1: Disposition des échantillons (exemple du bac E-1, vu de haut)

4.5 Humidification des bacs et démarrage de l'incubation

Pour les échantillons expérimentaux et les témoins abiotiques seulement :

1. Stériliser 2 bouteilles autoclavables de 1 L remplis d'eau distillée à l'autoclave en mode liquide pendant 20 minutes ;
2. Peser la masse des bacs expérimentaux et témoins abiotiques remplis de compost (avec le couvercle) à l'aide de la balance ± 0.01 g et noter les résultats au tableau 6. Calculer par le fait même la masse de compost de chaque bac à l'aide des données du tableau 4 et 6 et noter le résultat au tableau 6 ;

3. Calculer la quantité d'eau nécessaire pour obtenir une humidité correspondant à 60% de la capacité de rétention. Cette quantité d'eau est calculée à l'aide des données du tableau 3, 5 et 6. Noter le résultat au tableau 7.

Masse d'eau à ajouter (g d'eau) =

$$(0.6 \times CRC_{ss} - P7) \times P8 \times masse\ compost dans\ le\ bac \quad (2)$$

4. Ajouter la quantité d'eau nécessaire aux bacs à l'aide de l'arrosoir en maintenant les bacs sur la balance. Pour les témoins, effectuer cette manipulation sous la hotte microbiologique. Se référer encore à la section 4.3.4. Ne pas oublier de vaporiser l'intérieur et l'extérieur de l'arrosoir ainsi que la balance à l'éthanol. Utiliser l'eau ayant été stérilisée ;
5. Refermer les bacs ;
6. Reprendre l'étape 2 avec le compost humidifié. Ceci correspondra à la masse recherchée lors des ajouts d'eau subséquents ;

Pour tous les échantillons :

7. Incuber les bacs avec leur couvercle et imperméabilisé à l'aide de papier d'aluminium dans l'incubateur à 55°C ;
8. Noter la date et l'heure du début de l'incubation au tableau 8.

Tableau 6 : Masses de compost des bacs

Bac	Masse (bac + couvercle + compost + échantillons) (± 0.01g)	Masse compost (± 0.03g)
E-1		
E-2		
TA		

Tableau 7 : Masses d'eau à ajouter aux bacs et humidité relative initialement

Bac	Masse d'eau à ajouter (± 0.01 g)	Masse d'eau ajoutée (± 0.01 g)	Masse bac + couvercle + compost humidifié (± 0.01 g)	Masse bac + compost humidifié (± 0.01 g)
S1-E				
S2-E				
TA				

4.6 Suivi des échantillons

À tous les jours, vérifier le niveau d'humidité des bacs des échantillons expérimentaux et des témoins abiotiques et ajuster le contenu en eau à l'aide d'un vaporisateur rempli d'eau distillée. Afin de vérifier la quantité d'eau à ajouter s'il y a lieu, peser l'ensemble bac + couvercle + compost sur la balance ± 0.01 g. Ouvrir le bac et ajouter l'eau manquante directement sur la balance jusqu'à l'obtention de la masse recherchée. Pour les témoins abiotiques, stériliser le vaporisateur à l'aide d'éthanol 70% et procéder aux ajouts d'eau stérile sous la hotte microbiologique (se référer à la section 4.3.4). Lorsqu'il y aura prélèvement d'échantillons, l'ajout d'eau devra être effectué après le retrait. De plus, il sera nécessaire de tenir compte de la masse perdue suite à leur retrait pour l'ajustement de l'eau (voir section **4.6 Prélèvements des échantillons)**.

4.7 Prélèvements et nettoyage des échantillons

Pour les échantillons expérimentaux, prélever les triplicatas du compost de manière échelonné sur 11 jours. Pour les témoins, prélever le premier triplicata au bout d'une environ 5 jours et le second au bout de 11 jours.

1. Identifier pour chaque échantillon à retirer 3 béchers à leur numéro d'identification ;

Pour les échantillons expérimentaux et les témoins biotiques secs :

2. Prélever les échantillons à retirer à l'aide de spatules. Minimiser autant que faire se peut les pertes de compost. Ne pas utiliser les mêmes spatules entre les bacs;
3. Pour chaque échantillon, mettre un bécher identifié à son numéro sur la balance de précision ± 0.0001 g et remettre celle-ci à zéro. Peser ensuite l'échantillon sale et noter la masse au tableau 8 ;
4. Égaliser le sol à l'aide des spatules et refermer le bac ;

Pour les témoins abiotiques :

5. Stériliser 2 spatules à l'autoclave pendant 20 minutes en mode instrument ;
6. Reprendre l'étape 2 à 5 en effectuant les manipulations sous la hotte microbiologiques. Se référer à la section 4.3.4 ;

Pour tous les échantillons :

7. Nettoyer avec précaution à l'eau distillée les échantillons afin d'enlever les résidus de compost et l'assécher à l'aide de papier kimwipes ;
8. Déposer l'échantillon dans un nouveau bécher propre identifié ;
9. Ajouter de l'éthanol 95% dans le bécher pour que l'échantillon soit immergé (environ 1 cm d'éthanol) ;
10. Laisser reposer sous la hotte ventilée pendant 5 minutes ;
11. Retirer les échantillons de l'éthanol et les assécher à l'air puis les déposer à nouveau dans un bécher propre identifié. Le surplus d'éthanol sera laissé sous la hotte jusqu'à son évaporation complète ;
12. Rincer à l'eau distillée les échantillons et les assécher de nouveau à l'aide de papier kimwipes ;
13. Déposer chaque échantillon sur du papier d'aluminium identifié (type plastique, nom expérimentateur, date, numéro échantillon) ;
14. Déposer le temps dans four vacuum à 25 degrés Celsius pour 24 heures en notant la date et l'heure à laquelle chaque échantillon a été mis dans le four. Suite aux 24 heures de séchage, entreposé les échantillons dans un dessicateur jusqu'à la prise de mesure ;

15. Pour l'ajustement de la quantité d'eau dans le bac, la nouvelle masse recherchée de l'ensemble bac + couvercle + compost se calcule en soustrayant la masse des échantillons sales ayant été retiré du bac à l'ancienne masse recherchée.

Notes : La durée de compostage des échantillons correspond au temps s'étant écoulé entre l'insertion des bacs dans l'incubateur lors du départ de l'expérience et le début de l'assèchement au four.

4.8 Vérification de la stérilité du compost des témoins abiotiques

Afin de s'assurer que le compost des témoins abiotiques est demeuré stérile au bout de 11 jours, il est recommandé de procéder à des tests au BacLight sur un échantillon de compost. Pour les manipulations, se référer au protocole : CASTEGNIER, Françoise, Lucie Jean, *Énumération directe des bactéries viables et totales d'un échantillon d'eau ou de sol par microscopie à épifluorescence,* Protocole standard d'opération de la Chaire industrielle CRSNG en assainissement et gestion des sites, École Polytechnique de Montréal, no. 43J, 2000, 11 pages.

5. SANTÉ ET SÉCURITÉ

- Consulter la fiche signalétique de l'éthanol et du poly(L-lactide) ;
- Le port de lunette protectrice, gants et sarrau est nécessaire lors des manipulations.
- Les manipulations avec l'éthanol doivent être faite sous une hotte ventilée ou microbiologique si nécessaire ;

6. RÉFÉRENCE(S)

- Norme ISO 846 :1997(F)

- Norme ASTM D 5988-03
- Norme ASTM D5338-98(2003)
- BURLET, Jérôme, Marie-Claude Heuzey, Charles Dubois, Paula Wood-Adams, Josée Brisson, *Thermal stabilization of high molecular weight L-polylactide,* ANTEC, 2005, 5 pages.
- CASTEGNIER, Françoise, Lucie Jean, *Énumération directe des bactéries viables et totales d'un échantillon d'eau ou de sol par microscopie à épifluorescence,* Protocole standard d'opération de la Chaire industrielle CRSNG en assainissement et gestion des sites, École Polytechnique de Montréal, no. 43J, 2000, 11 pages.
- ESTRELLA, Sandra, *Détermination du pH d'un échantillon de tourbe à l'aide d'un pH-mètre*, Protocole standard d'opération de la Chaire industrielle CRSNG en assainissement
- LEDUC, Manon, *Capacité de rétention d'eau au champ d'un échantillon de sol,* Protocole standard d'opération de la Chaire industrielle CRSNG en assainissement et gestion des sites, École Polytechnique de Montréal, no. A23, 2002, 4 pages.
- Politique de protection des sols et de réhabilitation des terrains contaminés : Annexe 2 : Les critères génériques pour les sols et pour les eaux souterraines, Tableau 2 : Teneurs de fond (critères A) pour les métaux et métalloïdes, ministère du Développement durable, Environnement et Parcs du Québec, 2005.

7. RECOMMANDATIONS

- Il est recommandé d'utiliser des coupelles d'aluminium au lieu des coupelles de plastique lors des pesées afin d'éviter la statique ;
- Il est recommandé de procéder à une période d'évaluation de la température à l'intérieur de l'incubateur, afin de déterminer si celui-ci peut maintenir une température de 55 degrés Celsius à long terme et déterminer à quelle

température l'indicateur doit être positionné réellement (dû à l'incertitude de l'incubateur) ;

- Le compost devrait avoir été préférablement produit à partir de matières organiques que l'on retrouve généralement dans les dépotoirs (ex. : herbes, feuilles mortes, etc.) afin d'être le plus représentatif du milieu à l'intérieur duquel se dégrade le PLLA. Éviter le compost de fumier.
- Les échantillons de PLLA doivent être le plus uniformes possible. Par exemple, éviter la présence de bulles d'air à l'intérieur de ceux-ci lors de l'extrusion des plaques.

ANNEXE 2: Characterization of the compost

Table 1: pH measurements of the compost

Replicate	pH (±0.01)
1	6.89
2	6.92
3	6.86
Average	6.89

Table 2: Water retention of the compost

Data	Replicate 1	 2	 3
Weight aluminum cupel (P1) (±0.0001 g)	1.032	1.030	1.0400
Weight water saturated compost+ cupel (P2) (±0.0001 g)	38.413	41.240	39.564
Weight dry compost+ cupel (P3) (±0.0001 g)	9.512	10.475	10.193
CRCss (g water/g dry compost)	4.408	4.257	40.208
Average CRCss (g water/g dry compost)	4.291		

Table 3: Initial humidity of the compost

Data	Replicate		
	1	2	3
Weight aluminum cupel (P4) (±0.0001 g)	0.775	1.036	1.011
Weight humid compost+ cupel (P5) (±0.0001 g)	7.763	9.025	8.595
Weight dry compost+ cupel (P6) (±0.0001 g)	3.285	4.15	4.024
Initial humidity (g water/ g dry compost) (P7)=(P5-P6)/(P6-P4)	1.784	1.565	1.517
Weight dry compost/ weight humid compost (P8)=(P6-P4)/(P5-P4)	0.359	0.389	0.397
Average (g water/ g dry compost) initial humidity	1.622		
Average Weight dry compost/ weight humid compost	0.382		

ANNEXE 3: LVE regions of Polyurethane networks

DMA is able to investigate the mechanical properties of the polyurethane. What happens during a DMA test, a sinusoidal deformation is applied at a specific frequency and the material response is detected. But in order to have accurate values, the material has to be deformed in the linear viscoelastic region (LVE).

LVE can be measured by a strains sweep test, fixing the frequency and varying the amplitude. Plotting storage modulus vs amplitude, it is possible to detect the end of this region when storage modulus starts to change of about 5%.

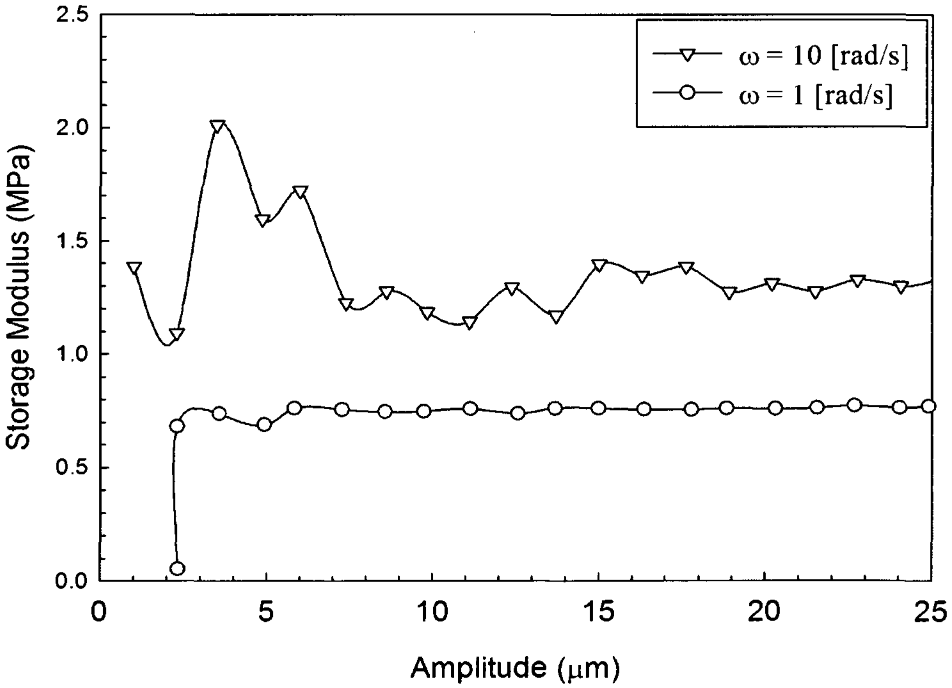

Figure 1. Strain sweep at different frequency of E elastomers

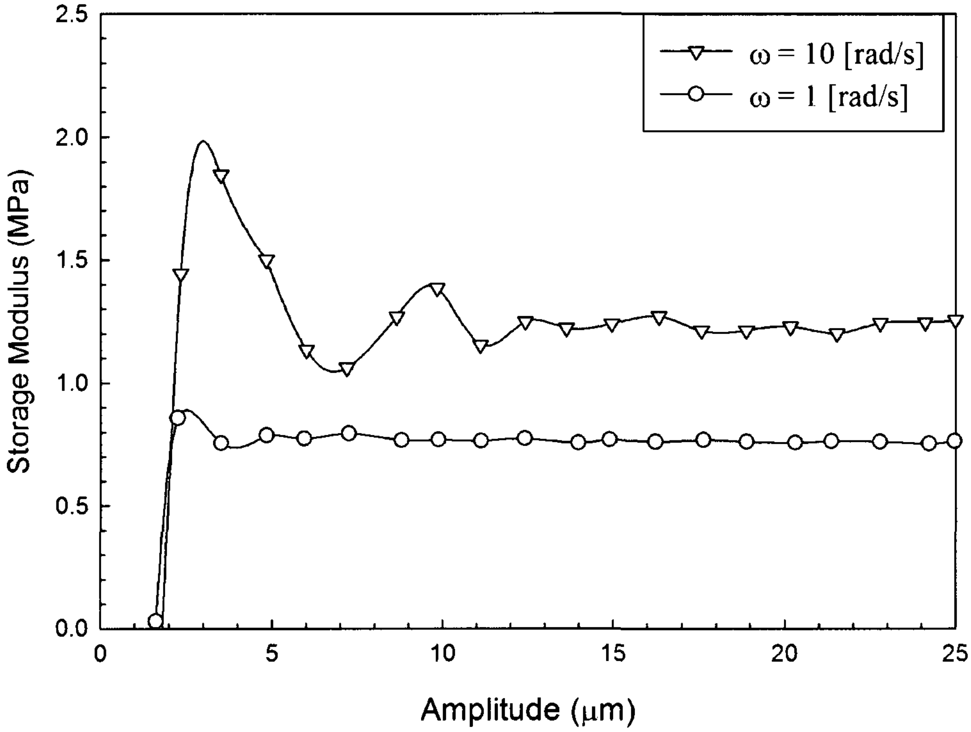

Figure 2. Strain sweep at different frequency of E elastomers

Both E and NE elastomers show linear viscoelastic behaviour between 5 and 25 μm of amplitude at 1 rad/s. Increasing the amplitude to 10 Hz, for both materials the answer is noisy at lower amplitude, showing LVE region after have reached 15 μm of amplitude.