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UNIVERSITÉ DE MONTRÉAL

RHEOLOGICAL AND MECHANICAL PROPERTIES OF PEO/BLOCK COPOLYMER BLENDS

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Ce mémoire intitulé:

RHEOLOGICAL AND MECHANICAL PROPERTIES OF

PEO/BLOCK COPOLYMER BLENDS

présenté par: FERRETTI Antonio

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. CARREAU Pierre J., Ph.D., membre et directeur de recherche

M. BERTRAND François, Ph.D., membre

to Bertrand, and his family

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RÉSUMÉ

L'oxyde de polyéthylène (PEO) a été très étudié dans ces dernières années, pour ses très intéressantes propriétés. Il est utilisé sous la forme de films, par exemples, comme électrolyte dans les batteries aux polymères, où des films très minces sont laminés en couches dans des structures 'sandwich'. Pour des procédés comme par exemple le laminage, la rhéologie en cisaillement et la rhéologie élongationelle du polymère sont très importants.

Le but de ce projet était d`améliorer la processabilité de l`oxyde de polyéthylène, sans affecter ses propriétés mécaniques ou électriques. D`un point de vue rhéologique le but principal était d`améliorer l`élasticité à l`état fondu (G'/G'').

Le PEO a été mélangé avec des petits pourcentages de copolymères tri-blocs, SBM (styrène-butadiène-méthylméthacrylate) et MAM (méthylméthacrylate-butylacrylate-méthylmétacrylate). Cinq grades de SBM et deux grades de MAM, différents pour la taille des blocs et pour le poids moléculaire ont été étudiés. Les mélanges ont été obtenus avec deux méthodes différents : en mélangeant les polymères à l`état fondu et par solution. Nous avons comparé les deux méthodes et recherché les conditions optimales pour améliorer les propriétés rhéologiques le plus possible. Un problème majeur a été que le PEO est un matériel très sensible quand il est exposé au cisaillement. La dégradation mécanique a été trouvée très dépendante de la température. On a vérifié l`effet de la technique du mélange sur le poids moléculaire du PEO avec une mesure de chromatographie par perméation de gel (GPC) et plusieurs mesures basées sur la viscosité intrinsèque. Une caractérisation rhéologique de tous les mélanges a été menée avec des tests oscillatoires à faible amplitude (SAOS). Le copolymère a un bon effet sur les propriétés rhéologiques du PEO, en augmentant plus le module élastique que la viscosité complexe, et par conséquence son élasticité. L`amélioration de l`élasticité était plus grande pour les mélanges obtenus par solution. Par la suite, une caractérisation mécanique de tous les mélanges a été complétée.

Des expériences en analyse mécanique dynamique (DMA), avec un rhéomètre en torsion et une machine de traction Instron, ont été faites. Le copolymère a aussi un bon effet sur les propriétés mécaniques du PEO. Les mélanges obtenues à l`état fondue ont montré des meilleures propriétés. La cause était probablement liée à des petites traces du solvant encore présent dans les éprouvettes obtenues par solution. Des mesures calorimétrie différentielle à balayage (DSC) ont été faites, pour vérifier si le copolymère avait quelque influence sur la cristallinité du PEO. On a conclu qu'il n'avait pas d'effet claire et que le degré de cristallinité était presque pareil. Finalement, on a fait un test pour avoir des indications sur les propriétés élongationelles. Des expériences additionnelles devraient être faites pour avoir une idée réelle de la rhéologie élongationelle des mélanges.

ABSTRACT

Polyethylene oxide (PEO) has been widely studied in these last decades for its many interesting properties. It is used as a film, for example, as an electrolyte in polymer batteries, for which very thin films are laminated in many layers in a sandwich structure. For such processes as lamination, film casting, film blowing, the shear and the elongational rheological properties of the polymer are very important.

The aim of this project was to improve the processability of polyethylene oxide, without affecting its mechanical and electrical properties. From a rheological point of view the main goal was to increase its melt elasticity (G'/G'').

Pure PEO was blended with small percentages of two block copolymers, SBM (styrene-butadiene-methylmethacrylate) and MAM (methylmethacrylate-butylacrylate-methylmetacrylate). Five grades of SBM and two grades of MAM, different in the size of the blocks and in the molecular weight, were investigated. Blends were obtained by two different methods: melt processing and solution casting technique. We compared the two methods and looked for the optimum conditions that would most improve the rheological properties. A major problem was that PEO is a very sensitive material when it is exposed to shear. Mechanical degradation was found to be very dependent on temperature. We verified the impact of the processing method on PEO's molecular weight with one measurement with gel permeation chromatography (GPC) and several measurements of the intrinsic viscosity. A rheological characterization of all the blends was carried out with small oscillatory shear tests. The copolymer had a good impact on rheological properties compared to the pure PEO as it increased its elastic modulus more then its complex viscosity, thus increasing its elasticity. The increase in elasticity was larger for blends obtained by solution. Then a mechanical characterization of all the blends was carried out. Experiments were done with dynamic mechanical analysis (DMA), a torsion rheometer, and a tensile tester. The copolymer also had a good impact on the mechanical properties compared to the pure PEO. However, blends obtained by melt processing showed better properties. This was probably caused by some small

traces of solvent still present in samples obtained by solution. A DSC (differential scanning calorimetry) scan was done on all the blends, in order to check if the copolymer had any influence on the cristallinity of pure PEO. We concluded that it did not have any clear effect, as degree of cristallinity was almost unvaried. Finally, we carried out a test to have some indications on elongational properties. However, more experiments should be conducted to clarify the extensional rheology of the blends.

CONDENSÉ EN FRANÇAIS

Propriétés rhéologiques et mécaniques des mélanges de PEO et copolymères bloc

Introduction

L`oxyde de polyéthylène (PEO) est un thermoplastique semi cristallin qui a de nombreuses propriétés très intéressantes et beaucoup d'applications, grâce à la large gamme de poids moléculaires dans laquelle il est disponible commercialement. Il est soluble dans l`eau. Les films faits avec le PEO à haut poids moléculaire sont résistants, thermo soudables et, grâce à leur degré de cristallinité élevé, résistent bien à l`humidité atmosphérique. Récemment, le PEO a aussi été utilisé comme élément conducteur dans des batteries aux polymères. Dans les batteries, de très minces couches de PEO sont assemblées dans une structure multicouche. Le procédé le plus économique à travers lequel une telle structure est créée est le laminage. Il est souhaitable d`améliorer la processabilité du PEO pur, afin que des films puissent être obtenus de façon plus économique et effective.

La processabilité d`un polymère est directement liée à sa rhéologie en cisaillement et par ses propriétés élongationelles. Dans ce projet, on a porté plus d`attention à la rhéologie en cisaillement. Quelques mesures de la viscosité élongationelle ont aussi été effectuées. On sait que, pour avoir une bonne processabilité, la viscosité en cisaillement doit être la plus faible possible. Aussi, l`élasticité à l'état fondu (liée au rapport G'/G'') devrait être la plus grande possible, comme il a été montré par Fang et al. (2003) pour des polyéthylènes dans des procédés de soufflage de films. Dans leurs expériences, la stabilité de la bulle s'améliorait si le rapport G'/G'' augmentait. Les copolymères blocs, en particulier, sont en train de devenir très populaires, pour leur capacité de s`organiser dans des nano structures très compliquées grâce aux interactions thermodynamiques entre les blocs. Pour les mélanges étudiés dans ce projet, le PEO est toujours

compatible avec un des trois blocs de copolymère, le méthacrylate de méthyle (PMMA); les autres blocs (PS, PB, PBA) sont incompatibles et créent une séparation de phase. Dans ces mélanges, il n`y a pas besoin d`un agent compatibilisant, vu qu`il est déjà incorporé dans le copolymère. Les domaines sont de l`ordre du nanomètre.

En travaillant avec le PEO, on doit considérer que c`est un matériau fragile, qui se dégrade facilement et, pour cette raison, c`est un matériau difficile à étudier. Dans la littérature, il y a beaucoup de contradictions sur les données du PEO. Il se dégrade sous l`effet de la température, autour de 225°C (Fares et al. 1994). Il est aussi très sensible à l`oxydation thermique, qui dépend beaucoup du poids moléculaire. La dégradation mécanique a été reportée lors de préparation en solution ou en masse, à l'état fondu.
On doit porter aussi une attention particulière aux conditions dans lesquelles est entreposé le PEO, vu qu'il se dégrade même à l`état solide. La vitesse de dégradation augmente avec la température. En général, dans la majorité des études, les mélanges ont été préparés par solution. On sait que, d`un point de vue industriel, il est préférable de préparer les mélanges en masse pour les coûts et les problèmes environnementaux liés à l'utilisation d'un solvant. Dans ce projet, nous avons préparé les mélanges selon les deux méthodes et avons comparé les résultats.

Méthodologie

Matériaux

Les caractéristiques des matériaux utilisés sont présentées au tableau 2.1. Les copolymères ont des poids moléculaires différents et différentes longueurs de blocs. Des quantités non négligeables des copolymères SB sont présentes dans le SBM.

Préparation des mélanges

Deux méthodes de préparation des mélanges ont été investiguées et comparées: méthodes en masse et en solution. Les mélanges obtenus en masse ont été préparés dans un mini mélangeur (Haake Minilab). Il s`agit d`une mini extrudeuse, équipée avec deux vis coniques et avec un canal de recyclage, qui nous permet de contrôler le temps de résidence du polymère dans le mélangeur. Un mélange final (PEO et 5% SBM E20) a été préparé avec une extrudeuse bi-vis en mode co-rotatif (Leistritz ZSE 18HP), à 120°C et 90 RPM. Les mélanges obtenus par solution ont été préparés dans le chloroforme. Les polymères ont été dissous et laissés pendant 24h à 61°C. Le solvant a été évaporé à température ambiante et les échantillons ont été gardés dans un four sous vide à 40°C pendant plusieurs jours.

Mesures de viscosité intrinsèque

La technique de la viscosité intrinsèque a été utilisée pour quantifier la dégradation causée par les différentes méthodes de mélanges. Le PEO a été dissous dans l`eau à différentes concentrations, et la viscosité des solutions diluées a été mesurée en utilisant un viscosimètre Cannon-Fenske à 25°C. L'équation de Mark-Sakurada ($[\eta] = K \cdot M_V{}^a$) a été utilisée pour trouver *Mv*. (a=0,78; K=0.127 mL/g, calculés pour le valeur nominale du PEO pur).

Mesures rhéologiques

Les mesures rhéologiques ont été faites en utilisant deux rhéomètres à contrainte imposée (un SR5000 de Rheometric Scientific et un CSM de Bohlin). Tous les tests ont été effectués dans une atmosphère inerte (dans l`azote). L`effet du copolymère a été quantifié avec les résultats des balayages en fréquence entre 0.01 Hz et 50 Hz. La contrainte imposée était de 400 Pa; cette valeur était dans la zone linéaire pour tous les

mélanges. Des balayages dans le temps ont été aussi effectués, pour s'assurer de la stabilité thermique des mélanges.

Viscosité élongationelle

La viscosité élongationelle a été mesurée à l`IMI (Institut des matériaux industriels, CNRC, Boucherville, QC) à l`aide d`un rhéomètre élongationel RER (Rheometrics RER 9000). Les mesures ont été effectuées à 100°C avec un taux de déformation constant. Les échantillons, qui ont été préparés avec une procédure spéciale pour enlever toutes les contraintes résiduelles, ont été immergés dans un bain d'huile chaude, et ensuite déformés en variant exponentiellement la déformation de l'échantillon dans le temps.

Tests de traction

Les courbes contrainte-déformation ont été obtenues à l'aide d'une machine Instron 4400 R (ASTM D638-02a, éprouvettes du type V). Les mesures ont été effectuées autour de 25°C et à 0.5 mm/min.

Analyse mécanique dynamique

Des mesures d`analyse mécanique dynamique en flexion ont été effectuées à l'aide d'un analyseur de *TA Instruments* (ASTM D 4092 – 01). Les propriétés en torsion ont été étudiées avec un rhéomètre ARES de *Rheometrics Scientific* (ASTM D 5279-01).

Processus du mélange

La figure 4.2 présente la viscosité complexe, les modules élastiques et visqueux du PEO, mesurés à 1 Hz, à une déformation imposée de 0.05 et une température de 150°C, en fonction du temps. Il n'y a aucun signe d'une diminution de ces fonctions du matériau. Le PEO est stable à cette température. La figure 4.3 présente la diminution de la viscosité complexe du PEO pur, en fonction de la vitesse de rotation des vis du mini mélangeur. La mesure a été faite à 100°C et 0.01 Hz. La viscosité complexe diminue quand la vitesse des vis augmente, et aussi diminue considérablement avec l'augmentation de la température. Par exemple, pour une vitesse de vis de 90 rpm, la diminution de la viscosité complexe, η^*, après 5 min est de 18% quand le mélangeur est opéré à 100°C, 23 % quand il est opéré à 120°C et de 33% à 140°C. Comme il est montré à la figure 4.4, on a comparé la diminution de la viscosité complexe quand le mélange a été préparé sous atmosphère inerte ou en présence d'air. On peut voir que, sous atmosphère inerte, la viscosité complexe tend à être stabilisée après 5 min. Dans le cas contraire, i.e. sans azote, la viscosité complexe continue à décroître rapidement.
Le tableau 4.2 montre les résultats des mesures de la viscosité intrinsèque. Elles ont été faites sur le PEO pur, le PEO pur traité en solution, le PEO pur préparé par le mini mélangeur, et le PEO pur mélangé par l'extrudeuse bi-vis. Les résultats montrent que le PEO mis en solution a la plus faible diminution du poids moléculaire (~18%), suivi par le pur PEO du mini mélangeur (~27%) et le PEO de l'extrudeuse.

La première conclusion est que le PEO pur est stable à 150°C. Ceci confirme les résultats de la littérature. Comme les copolymères ne se dégradent pas, on pourrait mélanger les polymères à 150°C sans se préoccuper de la dégradation thermique. En quantifiant la diminution de la viscosité complexe on peut avoir une idée de l'extension de la dégradation mécanique du PEO, et une plus grande diminution de la viscosité correspond à une plus grande dégradation. La forte dépendance de η^* de la vitesse des vis indique qu'il y a dégradation mécanique, favorisée par l'augmentation de la

température de mélange et par la présence de l`air. Comme largement expliqué, la dégradation du PEO ne peut pas être évitée, puisqu'elle se produit toutes les fois qu`il est exposé aux cisaillement. Au contraire, pour obtenir une meilleure dispersion des domaines du copolymère dans la matrice du PEO, il est nécessaire d`appliquer un fort cisaillement. On peut conclure le même pour la température; une haute température de mélange provoquerait une forte dégradation du PEO, mais favoriserait une meilleure solubilisation du copolymère dans la matrice dans un temps plus court. Le problème est donc de trouver les conditions optimales. Comme on a déjà dit, le paramètre le plus important qui affecte la dégradation du PEO est la température; on a essayé d'opérer le mini mélangeur à la température la plus petite possible, qui était de 120°C. Pour des températures plus faibles, le copolymère n`était pas bien solubilisé dans la matrice. Sous atmosphère inerte, la viscosité complexe devient presque stable après très peu de temps; le poids moléculaire du polymère diminue mais le taux de la diminution est faible; au contraire, quand le polymère est laissé en contact avec l`air, la viscosité complexe continue à diminuer à grande vitesse. On peut conclure que le mini mélangeur est bien isolé de l`oxygène; la dégradation du PEO était causée par des contraintes mécaniques. En résumant, les mélanges ont été préparés à 120°C, 90 rpm, pour 5 min.

Pour les mélanges préparés par solution, le solvant utilisé a été le chloroforme. Même pour ces mélanges on a varié les paramètres (vitesse d'agitation, température, concentration) pour obtenir les meilleures propriétés. Évidemment, une agitation plus élevée entraîne une plus grande dégradation mécanique. Il est intéressant de noter que, même en solution, augmenter la température provoque une diminution du poids moléculaire final du PEO; au contraire la concentration de la solution, pour les valeurs examinées (5 g/L – 50 g/L) n`avait pas d'effet. Les mesures de la viscosité intrinsèque ont montré que le polymère était plus dégradé quand il était traité en masse. Cela était prévisible, vu que le PEO mélangé en masse est exposé à des températures et des vitesses de cisaillement beaucoup plus élevées.

Caractérisation rhéologique

La figure 4.5 présente le comportement viscoélastique du mélange (PEO, SBM 233), (composition présentée au tableau 2.1); la viscosité complexe et le module élastique sont représentés en fonction de la fréquence. Aussi, les courbes du PEO pur et PEO pur traité dans la même façon que les mélanges (dans le mini mélangeur ou en solution) sont tracées. Le comportement rhéologique est typique de la plupart des mélanges de polymères, mais les bas taux de déformation et la zone terminale ne sont pas atteints aux basses fréquences (6.28 x 10^{-2} s^{-1} rad/s). Les mélanges contenant jusqu`à 5% du polymère montrent un comportement très similaire au PEO pur. Le PEO pur, qui a été traité, montre une chute évidente de la viscosité complexe et du module élastique. Au contraire, la viscosité complexe et le module élastique augmentaient avec la concentration du copolymère dans la matrice du PEO. L`augmentation était plus grande pour les mélanges préparés par solution. Le comportement rhéologique pour tous les autres mélanges PEO/copolymère bloc était similaire.

Le tableau 4.3 rapporte les augmentations de la viscosité complexe, du module élastique et de l`élasticité. Toutes ces mesures ont été effectuées à 100°C et 0.01 Hz, pour des mélanges contenant 5% en poids du copolymère. Les augmentations sont calculées par rapport au PEO pur. Les valeurs entre parenthèses correspondent à l`augmentation par rapport au PEO pur (échantillons moulés directement de la poudre). Les valeurs qui ne sont pas entre parenthèses représentent l`augmentation par rapport au PEO traité dans le mini mélangeur ou par solution sous les mêmes conditions de mélanges. C`est évident que les augmentations des modules élastiques sont plus grandes que les augmentations de la viscosité complexe ou les diminutions sont plus faibles. Par conséquence, l`élasticité augmente quand le copolymère est mélangé avec le PEO. Il est évident que l`effet positif du copolymère est plus grand pour les mélanges obtenus par solution. La plus grande augmentation a été trouvée pour les mélanges PEO/SBM 233, où *G'* augmentait de 170% et *G'/G"* de 47%, comparé à leurs

références. Dans les mélanges préparés à l`état fondu, l`augmentation de l`élasticité due à l`addition du copolymère n`était pas toujours suffisante pour compenser la diminution causée par la dégradation.

L`allure de toutes les courbes rhéologiques sont typiques des fluides rhéofluidifiants. On s`attendait qu'après l'ajout des deux copolymères SBM et MAM toutes les fonctions du matériau auraient augmenté. Ce qui nous intéressait était leur augmentation relative, qui était aussi liée à l`élasticité à l`état fondu (*G'/G"*). On sait que *G'* donne une mesure de la quantité d`énergie emmagasinée dans le polymère, et que le module visqueux *G"* est lié à l`énergie perdue. *G'/G"* est donc le rapport de l`énergie emmagasinée sur l'énergie perdue. Premièrement, on voit que juste à cause de la dégradation, le module élastique diminue plus que la viscosité complexe; cela provoque une diminution de l`élasticité à l`état fondu. Quelques mesures faites par la chromatographie par perméation de gel (GPC) ont montré que la distribution des poids moléculaires du PEO pur devient plus étroite quand il est exposé à dégradation mécanique. La raison est que les chaînes plus longues sont plus sensibles au cisaillement et elles sont les premières à se casser en des molécules plus courtes. Comme il a était montré par Wong et al. (1998), l`élasticité est reliée à la distribution des poids moléculaires, et elle diminue quand la distribution devient plus étroite. En tout cas, on peut voir qu'après addition du copolymère, le module élastique est récupéré et il augmente plus que la viscosité complexe.

Les propriétés rhéologiques dépendent du procédé de mélange. Le fait que deux méthodes différentes provoquent des différences dans le comportement relatif des mélanges qui ont exactement la même composition suggère que la morphologie créée est aussi différente. On sait que l`amélioration des propriétés mécaniques et rhéologiques dépend de la taille des domaines du copolymère; une plus petite taille (dans notre cas elle est de l`ordre du nanomètre) donne des meilleures propriétés. Une bonne dispersion des domaines du copolymère dans la matrice est aussi très importante.

Quand on mélange par solution, la viscosité de la solution est beaucoup plus faible que celle du polymère à l`état fondu; on s`attend, par conséquence, une meilleure dispersion du copolymère. En comparant les différents grades, on peut voir clairement à l'aide du tableau 4.3, que le mélange PEO/SBM 233 a les plus grandes augmentations du module élastique et de la viscosité complexe, ainsi que du rapport de l`élasticité *G'/G"*. Le SBM 233 est le grade qui contient la plus petite quantité du PMMA, qui est le bloc compatible avec le PEO, et par conséquence, la plus grande quantité de blocs incompatibles styrène et butadiène (les blocs qui créent la séparation des phases).

Mesures de la viscosité élongationelle

Les mesures de la viscosité élongationelle en fonction du temps ont été faites pour deux échantillons, le PEO pur passé à travers l`extrudeuse bi vis et un mélange du PEO et 5% SBM E20, préparé avec la même extrudeuse. La figure 4.8 montre la viscosité élongationelle pour les deux échantillons, en fonction du temps. La vitesse d'élongation a été gardée constante, à quatre différentes valeurs. Les données ont été prises avec un rhéomètre RER, qui est sûrement un instrument puissant pour mesurer la viscosité élongationelle, mais qui a aussi des désavantages, comme le fait que les échantillons sont fondus dans l`huile chaude, et que les densités de l`huile et des échantillons n`étaient pas exactement identiques (0.900 g/cm$^3$ pour l`huile et 1.072 g/cm3 pour le mélange). Cela a causé des déformations non uniformes et des erreurs expérimentales. Néanmoins, les résultats sont significatifs puisque la reproductibilité est acceptable. La viscosité élongationelle augmente après l'ajout du copolymère.

Caractérisation mécanique

Des tests mécaniques ont été faits pour investiguer si l`addition du copolymère a un impact sur les propriétés mécaniques du PEO pur à l`état solide. Même si le but

principal était d`améliorer l`élasticité du PEO à l`état fondu, on espère d'obtenir un mélange qui garde les propriétés mécaniques du polymère pur. Trois types de tests ont été faits : tests de traction et analyse mécanique dynamique en flexion et en torsion.

Tests de traction

La figure 4.9 montre des courbes typiques contrainte-déformation des mélanges PEO/5% SBM E22. Les courbes pour les autres mélanges ont la même allure. Il est montré que le PEO et ses mélanges sont tous des matériaux fragiles. L`addition du copolymère ne change pas la forme des courbes. On peut voir que, après l`addition du copolymère, il y a une amélioration de l`élongation à la rupture. Cela était prévisible puisque que les copolymères sont des élastomères. Les figures 4.10 et 4.11 montrent une comparaison du module de Young et de la contrainte à la rupture de tous les mélanges, préparés avec le mini mélangeur ou par solution. Les lignes continues référent au PEO pur traité de la même façon que les mélanges. Les mélanges obtenus en masse ont une contrainte à la rupture plus élevée. La courbe contrainte-déformation du PEO pur passé à travers le mini mélangeur est similaire à la courbe du PEO pur. Au contraire, le PEO pur traité par solution montre une forte diminution de la contrainte à rupture. Comparés à leurs références, tous les mélanges montrent une augmentation de la contrainte à la rupture après addition du copolymère, à l`exception de deux cas, c'est-à-dire en passant de 2% à 5% en concentration pour deux mélanges PEO/MAM préparés avec le mini mélangeur.

Les résultats des tests de traction indiquent qu'au moins pour les mélanges obtenus par le processus à l`état fondu les propriétés sont maintenues. Le copolymère a une bonne influence sur la contrainte à la rupture pour les mélanges obtenus en masse ou par solution; la dégradation mécanique ne provoque pas une grande perte des propriétés en traction, vu que le PEO pur et le PEO traité ont presque la même courbe. Toutefois, il y a une grande différence entre les mélanges obtenus par les deux différentes méthodes.

Cette différence n`est pas un effet de la dégradation. Si c`était le cas, le PEO passé dans le mini mélangeur devrait montrer une plus grande perte. Cela pourrait être un effet des traces du solvant encore présentes dans les éprouvettes. Après séchage des éprouvettes dans le four à des températures proches au point de fusion (50°C), les propriétés en traction augmentaient, en prouvant que la perte de propriétés mécaniques était due à la présence du solvant. De toute façon, on ne peut conserver le PEO pour plusieurs jours à ces températures, puisque cela favoriserait la dégradation à l`état solide.

L`augmentation de la contrainte à la rupture est causée par la présence du copolymère et par la morphologie qui est créée. La miscibilité thermodynamique entre le PEO et le PMMA favorise la dispersion des domaines du copolymère à l`ordre du nanomètre. La nano structuration et la micro séparation des phases résultent en une augmentation des propriétés mécaniques. On a essayé de visualiser la morphologie en MEB, mais on n'a pas eu de succès, comme il est prévisible quand la morphologie est composée de nano phases.

Analyse mécanique dynamique

Des tests d'analyse mécanique dynamique ont été faits en flexion et en torsion. L`impact du copolymère et de la dégradation était plus ou moins le même sur les propriétés en flexion et en torsion. Le module élastique généralement augmentait avec la quantité du copolymère. Les propriétés des échantillons obtenues avec la mini extrudeuse étaient, comme dans les cas des tests de traction, meilleures que les propriétés des échantillons obtenues par solution. Cela a été interprété comme dû à l`effet des traces de solvant encore présent malgré le séchage prolongé.

Conclusions

Le but de cette étude était d`améliorer la processabilité de l`oxyde de polyéthylène à l`état fondu, sans affecter ses propriétés à l`état solide. Des variables importantes dans la discussion de la processabilité sont l`élasticité (*G'/G"*), la viscosité en cisaillement et la viscosité élongationelle. De 1% à 5% des copolymères SBM et MAM ont été additionnés au PEO pur et les propriétés rhéologiques et mécaniques des mélanges ont été investiguées. Les propriétés dépendent du procédé de mélange. Les chaînes de PEO sont très fragiles quand elles sont exposées au cisaillement. C`est impossible d`éviter complètement la dégradation. En traitant le PEO dans un mélangeur mécanique, la dégradation dépendait beaucoup de la température, et, comme prévu, dépendait aussi de la vitesse de rotation des vis. Par contre en solution, la dépendance de la température n`était pas forte. La dégradation a été quantifiée à l'aide de la viscosité intrinsèque. Les mélanges faits avec une extrudeuse bi-vis avaient une réduction plus sévère du poids moléculaire moyen, avec réductions de l`ordre de 40%.

La caractérisation rhéologique a montré que le copolymère avait un effet positif sur le PEO pur; le module élastique augmentait plus que la viscosité complexe; par conséquence, l`élasticité augmentait. L`effet était plus évident pour les mélanges obtenus par solution. La viscosité élongationelle a été mesurée, en fonction du temps, et elle augmentait avec l`ajout du copolymère. Les propriétés mécaniques ont été aussi étudiées. Le copolymère avait un effet bénéfique sur les propriétés. La contrainte à la rupture et le module élastique, mesuré en flexion et en torsion, étaient améliorés. Au contraire, la contrainte à la rupture des mélanges obtenus par solution était réduite; cela a été expliqué par la présence de traces du solvant.

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LIST OF NOMENCLATURE AND ABBREVIATIONS

Nomenclature:

G': storage modulus (shear)

G'': loss modulus (shear)

E': storage modulus (DMA in flexion)

E'': loss modulus (DMA in flexion)

M_w: weight average molecular weight

M_n: number average molecular weight

M_v: viscosity average molecular weight

η^*: complex viscosity

η^+: stress growth coefficient

ω: frequency

δ: phase angle

Abbreviations:

ARES: Advanced Rheometric Expansion System

AS: poly(acrylonitrile-co-styrene)

ASTM: American Society for Testing and Materials

DMA: Dynamic Mechanical Analysis

DSC: Differential Scanning Calorimetry

GPC: Gel Permeation Chromatography

HDPE: high density polyethylene

LDPE: low density polyethylene

LLDPE: linear low density polyethylene

LVDT: linear variable differential transformer

MAM: copolymer of methylmethacrylate-butylacrylate-methylmethacrylate

MWD: molecular weight distribution

PB: poly(butadiene)

PBA: polybutylacrylate

PEO: poly(etyhelene oxide)

PMMA: poly(methyl methacrylate)

PS: poly(styrene)

PVC: poly(vinyl chloride)

RER: Rheometrics Extensional Rheometer

RME: Elongational Melt Rheometer

RPM: rotations per minute

SAOS: small amplitude oscillatory shear

SB: copolymer poly(styrene-butadiene)

SBM: copolymer of poly(styrene-butadiene-methyl methacrylate)

SEM: scanning electron microscope

TEM: transmission electron microscope

THF: tetrahydrofuran

UHMW: ultra high molecular weight

CHAPTER 1

INTRODUCTION

1.1. Problematic

This project involved three entities:
CREPEC, (Centre De Recherche Sur Les Polymères Et Les Composites – Center Of Research For Polymers And Composite Materials); Avestor, a Canadian industry world leader in the production of polymer batteries; Arkema, France, the chemical branch of the multinational company Total.

In the polymer batteries produced by Avestor (schema represented in Figure 1.1), polyethylene oxide is used as the electrolyte. Very thin layers of PEO are assembled between a cathode of vanadium oxide and an anode of metallic lithium; in the production line, in order to create this multilayered structure, lamination is a reliable and economic process. However, it is very difficult to obtain films of very small thicknesses without problems such as instabilities or ruptures in the melt. It is sometimes useful to put additives in the polymer melt in order to improve the melt strength and the rheological properties. In our work we study the effect on PEO of block copolymers, which have become very popular in recent years because of their ability to create self-assembled nanostructures. The copolymer domains, as small as nanometers and dispersed in the PEO matrix, should reinforce the melt and let us obtain a blend that can be processed in a more effective way. Arkema supplied seven grades of the block copolymers SBM and MAM, which are now produced in a large scale.

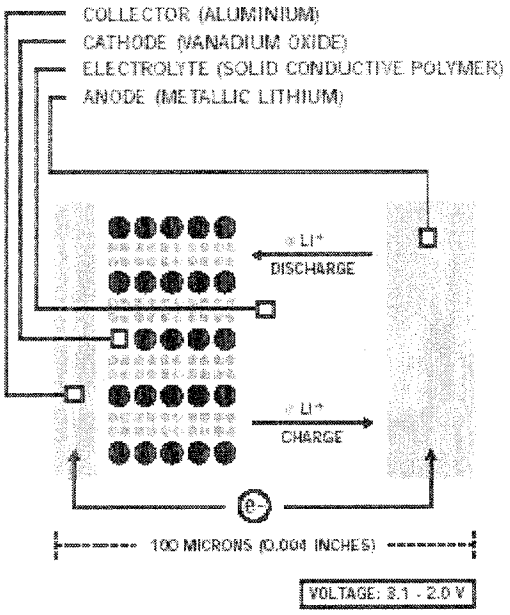

Figure 1.1: Schema of the polymer battery. (Source: www.avestor.com)

1.2. Objectives

The objective of this project was to improve the processability of polyethylene oxide. We know that processability of a polymer depends on such factors as elasticity in the melt state, elongational viscosity and shear viscosity. Addition of small percentages of the two triblock copolymers SBM and MAM should improve the elasticity without increasing too much the shear viscosity. Also, mechanical and electrical properties should not be affected. We verified these assumptions through a systematic work of rheological characterization and mechanical characterization. We also tried to compare different blending methods, in order to find the one which improved the most the processability. Several grades of SBM and MAM were added to PEO, so that we could make some conclusions on the characteristics of the copolymer which give the best results.

1.3. Content

This thesis is divided into six chapters. After this introductory chapter, the second chapter presents an overview on the PEO, the copolymers and the processability, which involves elongational properties. The third chapter presents a description of the methodology, with a general description of all the methods used and specific information on how we carried out the experiments. The fourth chapter contains the article: "Rheological and mechanical properties of PEO/block copolymer blends", submitted to *Polymer Engineering & Science* in February 2005. In the article the main results are presented, such as the rheological characterization of the blends, the measurements of the elongational viscosity and the mechanical characterization, including experiments on tensile properties and dynamic mechanical properties in flexion and in torsion. In the fifth chapter we present the results of DSC, GPC, and we make some considerations about stability of PEO and the blending technique. These results were not presented in the article but are nevertheless useful in order to fully understand our work. After the conclusions and prospective, discussed in the sixth chapter, follows a list of the bibliography and the appendix, in which the rheological characterization is presented in detail.

CHAPTER 2

LITERATURE REVIEW

2.1. Description of PEO

Polyethylene oxide has a lot of interesting properties, which make it useful in many different fields. It is obtained by heterogeneous catalytic polymerization of ethylene oxide monomer. It is a soft semi-crystalline thermoplastic and can be dissolved into water, thanks to hydration of the ether oxygen. In water it displays interesting drag reducing and flocculating properties. It has a lot of commercial applications, due to the wide range of molecular weight in which it is commercially available (100 000-8 000 000 g/mol). It is used for disposable laundry bags, packaging for agricultural seeding, wet-tack adhesives. Films of high molecular weight PEO are tough, ductile, heat-sealable and, because of their high degree of cristallinity, resist well to atmospheric moisture. Recently PEO has found increasing use as a conducting medium in light-weight, high energy polymer batteries. Several studies have been conducted on electrical properties, starting from the 80 s.

Blends of PEO have also been investigated in the last decades; PEO has been blended with PMMA, PS, PVC. Polymer blends have been largely studied because they provide an economic way to generate new materials. By carefully choosing the components of the blends a large variety of properties can be obtained. Polymers can be miscible or immiscible. When immiscible polymers are blended the blend assumes a multiphase structure.

2.2. Degradation of PEO

A blend can be obtained by many processing techniques; mainly by processing the polymers in the melt state, for example in extruders or in mechanical blenders, or by solution casting technique, where the polymers are dissolved in a common solvent, which is evaporated after the blend is obtained. During the blending process the polymer can degrade, through three factors: temperature; reaction with oxygen, favored by higher temperatures; shear. Polyethylene oxide is sensitive to all three of these elements.

Thermal decomposition takes place in a range of temperature between 235°C and 255°C (Fares et al. 1994). When PEO is heated to these temperatures, random scission of C-C and C-O bonds occurs, forming radicals which depolymerize in low molecular weight materials, and also in some volatile species, such as ethylene, formaldehyde, and acetaldehyde. The cleavages are more frequent in the C-O bonds, which are less stable then the C-C bonds.

Aerobic degradation takes place either in the bulk or in solution; again, it is favored by the fact that the carbon-oxygen bond present in the PEO chain has a lower energy compared to a carbon-carbon bond. Previous studies have shown how degradation accelerates at elevated temperature and with ultraviolet light.

Thermal oxidation is dependent on PEO's molecular weight. It has been showed, by Maclaine et al. (1975), that cristallinity of pure PEO reaches a maximum around 6000 g/mol, and then decreases with increasing molecular weight. Because of their higher degree of cristallinity, low molecular weight PEOs are more resistant to thermal oxidation. High molecular weight PEOs are, as a consequence, more sensitive to oxygen.

Mechanical degradation is also a very important issue for polyethylene oxide, which degrades under the effect of shear both in bulk and in solution. In solution a polymer is exposed to smaller shear then in the bulk. Anyhow, in the blending process the shear force that is necessary to apply in order to obtain a good mixing is large enough to

provoke mechanical degradation of the polymer. Nakano et al. (1971) have reported that the scission of the chains is not due to interaction between polymer chains, and thus it does not depend on the concentration of the polymer in solution, but rather to intra molecular forces due to the velocity gradients that exist in the different regions of the solution. However, the dependence of mechanical degradation upon the concentration of the solution has been widely disputed. D'Almeida et al. (1997), also studying solutions of polyethylene oxide, pointed out that the majority of the studies on mechanical degradation in solution were based on experiments in which the shear rate, not the shear stress, was kept constant. This would invalidate the conclusions. In contradiction with Nakano et al. (1971), they showed how, in their experiments, degradation increased as the concentration solution decreased. They explained this by saying that increasing the concentration also increases the interactions among the molecules, thus reducing the hydrodynamic volumes. Molecules of higher hydrodynamic volume will degrade preferentially. Also, they discussed the effect of the solution temperature over degradation, concluding that increasing the temperature from 30°C to 50°C does not provoke clear effects; they explained that the thermal energy is absorbed by the macromolecules to increase their internal energy. On the contrary, increasing the shearing time will increase the quantity of molecules to be degraded, until a limiting M_w is reached at which the shear stress is no longer large enough to cause degradation.

Finally, special care has to be given to how the polyethylene oxide is stored. The first observation is that PEO must never be stored at temperatures higher then its melting point (64°C). Let's remember that PEO is a semi crystalline polymer, essentially constituted of two phases, an amorphous phase, and a second phase that contains the spherulitic crystals. Oxygen permeability depends on chain mobility; it is therefore much higher in the amorphous region then it is in the crystalline region. If samples of PEO are stored below its melting point, only the amorphous region will be exposed to thermal oxidation; on the contrary when it is stored above its melting point, it is

completely exposed to attack from oxygen, and the oxidation rate increases a lot. Scheirs et al. (1991) studied the solid-state thermal oxidation of a powder of PEO. They observed how the molecular weight of PEO, kept at 60°C in air, slowly decreased during the initial 23 days, after which the rate of degradation greatly increased because of the auto-accelerating stage of the free-radical degradative process. After 30 days the powder was transformed into a soft, waxy solid. Bortel et al. (1979) studied degradation at the solid state of some high molecular weight PEOs. They observed an increase of the cristallinity in the degradation process. They explained that the most stable configuration of the PEO they studied had a degree of cristallinity of at least 70%. A lower cristallinity would lead to exceptionally high strains in the helical crystalline structure. The longer molecules, in the process of adjusting to a more crystalline configuration, would break into smaller molecules.

2.3. Description of the copolymers

Block copolymers have drawn a lot of interest in the recent years. Some scientists claim that in the future years the field of block copolymers will be one of the most expanding areas for the generation of new sophisticated materials, in particular in the creation of new nano-structured materials. Block copolymers contain two or more polymer segments in the chains, and can create self assembled structures, even at the nanoscale; the domain spacing will depend on the molecular weight, the segment size, and the strength of interaction between the blocks. Self organization can be achieved by processing the polymer either in the bulk or in solution. Many literature reviews have been dedicated to this subject (Lodge 2003, Hamley 2003, Förster 2002). The two copolymers we take in consideration for our project are SBM and MAM.

2.3.1. SBM

SBM is a linear triblock copolymer, styrene-butadiene-methylmetacrilate. It is obtained by living anionic polymerization. The blocks are grown in sequence one after another: the styrene block is created first, then, when the desired length of the polystyrene block is reached, monomer of butadiene is added. Finally, monomer of methylmethacrylate is added. The blocks are connected by covalent bonds. Usually some non-negligible quantities of the copolymer styrene-butadiene are present in the final product. Some traces of the pure homopolymer polystyrene are also present. At the end of the polymerization some stabilizers are introduced to avoid problems of degradation.

The blocks that constitute SBM are incompatible; this provokes micro-phase separation at a nanoscale; the fact that it is composed by three blocks makes it compatible with a large number of polymers; a large number of morphologies can be obtained.

Previous studies on these copolymers didn't show any evidence of degradation due to shear or temperature (Lapeyre 2001).

2.3.2. MAM

MAM is a symmetric triblock copolymer of the type ABA. The A bloc is methylmethacrylate and the B bloc is butylacrylate. It is obtained by radical polymerization. The block polybutylacrylate is obtained first, then monomer of methtylmetacrylate is added at its ends. We obtained from Arkema two grades of this copolymer, different in the molecular weight and in the length of the blocks. The details about the characteristics of the materials we used are presented in Table 2.1.

Table 2.1: Characteristics of the polymers used. (Source: Aldrich; Arkema)

PEO (Polyethylene oxide) - Sigma-Aldrich – Mv: 100000 g/mol		
SBM (Stytene-butadiene-methylmethacrilate) - Arkema (France)		
Grade	Molecular weight	Composition
AF-X 004	Mw ~ 100 kg/mol	S/B/M ~10/45/45 with 30 % of dibloc SB
AF-X 233	Mw ~ 100 kg/mol	S/B/M ~30/40/25 with ~40 % of dibloc SB
AF-X 250	Mw ~ 50 kg/mol	S/B/M ~60/10/30 with 45 % of dibloc SB
AF-X E20	Mn ~ 50 kg/mol	S/B/M ~33/33/34 with 25% of diblock SB
AF-X E22	Mn ~ 50 kg/mol	S/B/M ~25/25/50 with 10 % of dibloc SB
MAM (Methylmethacrilate-butylacrylate-methylmethacrilate) - Arkema (France)		
DC 42	Mw ~ 102 kg/mol	PBA 35%, PMMA 58.5% + 6.5% of methacrylique acide in the block PMMA
DC 46	Mw ~ 130 kg/mol	PBA 32.4%, PMMA 67.6%

2.4. Homopolymer-copolymer blends

Mechanical and rheological properties are directly affected by the morphology of the polymer blend. In our case small quantities of the block copolymers SBM and MAM were added to PEO. Both these copolymers contain in their chain a block of polymethylmethacrylate. PEO is thermodynamically compatible with PMMA, while it is incompatible with the other blocks, styrene, butadiene and butylacrylate. The presence of the PMMA block enabled us to blend the polymers in the bulk, as the polymer/copolymer interface will have a low interfacial tension; no addition of any compatibilizer is needed. Nowadays it is possible to design materials at the nanoscale; there are basically two approaches, the top-down approach, through atom-by-atom or molecule-by-molecule approach, or the bottom-up approach, through self-organization. Evidently the approach we used is the so called bottom-up, as we just mix the two polymers and take advantage of the thermodynamic compatibility between PEO and PMMA. A homopolymer can be blended with a miscible copolymer in bulk or in solution. If it is prepared in solution, during solvent removal and subsequent annealing,

the molecular species comprising such blends organize in such a way as to lower the system free energy and ideally attain thermodynamic equilibrium.

In the blends the incompatible blocks will phase separate, and will organize in domains; a low interfacial tension, in immiscible polymer blends, result in a smaller size of the domains of the dispersed phase. The rheological and mechanical properties of the blend are known to depend on the size and dispersion of these domains. Best properties are given by the smallest size of the domains and obviously by a good dispersion of the domains in the matrix. If the domains have larger sizes, if for example their size is in the order of magnitude of a micron, the incompatible domains will still phase separate, but we will speak of macro phase separation, which will sometimes result in a loss of the mechanical properties. Figure 2.1 represents the expected configuration assumed by our PEO/SBM blend.

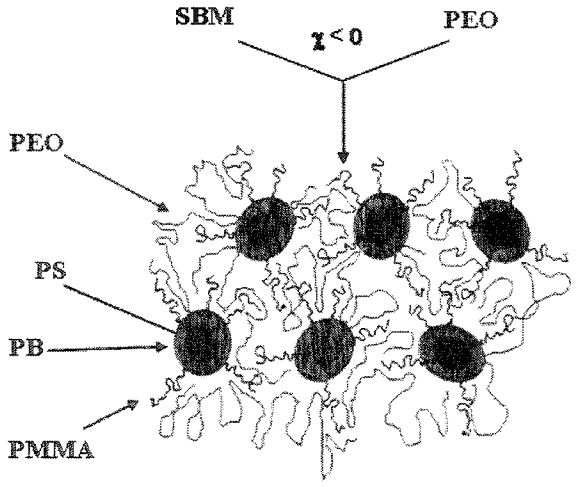

Figure 2.1: Expected organization of PEO/SBM blends (Source: Arkema)

2.5. Discussion on processability

For many applications PEO is used in thin films. A reliable process used in order to create polymer batteries is lamination (Figure 2.2). It is possible to create multilayered structures; indeed, the polymer batteries produced by Avestor are formed by many layers of vanadium oxide, metallic lithium and polyethylene oxide, which serve, respectively, as the cathode, the anode and the electrolyte. Electricity is collected by aluminum rods. The thickness of these layers, all together, is as little as 100 microns. (Figure 1.1). As a result there is a very high active surface, which gives high performances.

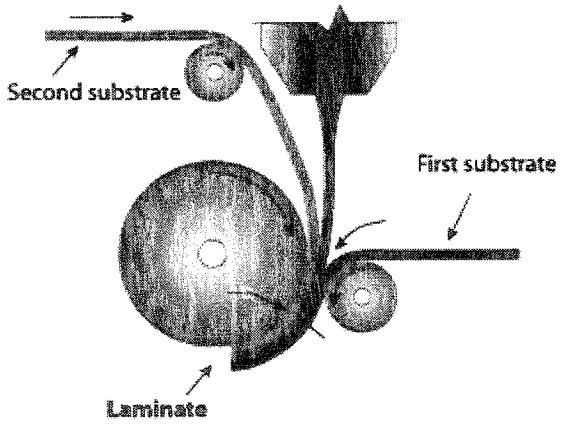

Figure 2.2: Sketch of the lamination process. (Source: http://academic.sun.ac.za)

Blends have been used in order to improve the processability of polymer. Shear and elongational properties are both important to establish the good processability of a polymer. The connection between rheology and processability is still poorly understood. In the past shear rheology has been the most studied. It is well accepted that, in order to have a good processability, the shear viscosity has to be as low as possible. However, the connection between the melt elasticity and processability is not as clear. Fang et al. (2003) tried to establish a relationship in the case of a film blowing

process. To compare the elastic behavior of different fluids, they followed Han's et al. (1986) suggestions, that used logarithmic plots of G' and G''. The relationship between G' and G'' was found to be independent of temperature. They found that, the larger the value of G', the more stable the bubble during the film blowing process. However, for many processes such as film blowing, blow molding, melt spinning, the elongational properties are equally important. In film blowing, for example, the bubble instability and melt extensibility can be correlated to measurements of elongational viscosity. The study of the elongational properties is challenging, because it is difficult to generate a steady elongational flow, and it is difficult to isolate the shear effects that typically occur along with the elongational flow. However, many techniques have been developed in recent years. Scientists as Münstedt developed some very advanced uniaxial elongational rheometers (Münstedt 1979). A very important property is strain hardening, that is the increase in elongational viscosity when a sample is exposed to large strains. Increasing the strain hardening properties generally increases the processability of a polymer for many industrial operations. Studies have shown that the strain hardening property is increased for polymers with a very long relaxation time, which comes from a wide molecular weight distribution and long chain branching.

Takahashi et al. (1999) have studied the influence of miscibility on the elongational viscosity of a blend. They prepared a miscible blend (98.5 wt% of poly(acrylonitrile-*co*-styrene) and 1.5 wt% of ultra high molecular weight PMMA) and an immiscible blend (98.5 wt% AS and 1.5 wt% UHMW–PS). They found that when the UHMW polymer was immiscible with the matrix, the dispersed domains did not increase the strain hardening property. On the contrary, for the case of miscible blends, the deformation of the UHMW polymer entangled with the surrounding matrix caused a sharp increase of the strain-hardening property. In another study, Takahashi et al. (1998) measured the elongational viscosities of random and block copolymers. They found that, while the random copolymer showed a strain hardening property, the block

copolymer showed strain softening. This behavior was interpreted with the damping function using the Bernstein-Kearsley-Zapas model.

A lot of studies have been done on blends in order to improve the extensional viscosity of a polymer. Ajii et al. (2003), for example, investigated the strain hardening property of some low density polyethylenes, and found that the addition of 10%-20% of LDPE to LLDPE resins enhances its strain hardening behavior without effecting significantly the melting and crystallization temperatures. Yamaguchi et al. (2002) found that a small amount of crosslinked HDPE enhances the melt strength and the strain hardening properties of HDPE. The concept was applied to thermoforming and processability for thermoforming was found to increase with the increase of the strain hardening. In our study on PEO and its blends with SBM we will focus on the shear rheology. However, some information on the extensional rheology will also be collected. In any case, in the future, more experimentation should be done in order to better understand the elongational properties of PEO and its blends.

CHAPTER 3

METHODOLOGY

3.1. Introduction

This chapter presents a description of the methodology used to carry out the experiments. Each section gives a general presentation of the method, with the most important equations and definitions, followed by more specific information on how these methods were applied in our particular situation.

3.2. Materials used

Polyethylene oxide (PEO) (*Mv* 100000 g/mol, polydispersity 6.9) was obtained by Aldrich. Copolymers SBM and MAM were obtained from Arkema. Characteristics of the materials used are presented in Table 2.1 (Chapter 2). Six grades were in the form of pellets; one grade was in the form of small pellets; grade SBM 233 was both in the form of pellets and in powder. PEO was in a powder form.

3.3. Preparation of the blends

SBM and MAM, which are elastomers, do not have a melting point, as at high temperatures they decompose before melting. When mixed in the bulk, they solubilize in the molten PEO. In solution, they are not soluble in water, but are soluble in chloroform, benzene, THF, esters.

Blends were prepared by two different techniques:

- melt processing, i.e. blending the polymers in bulk

- solution casting technique in chloroform.

In this thesis blends obtained in the bulk with three mechanical blenders were investigated; for the work of characterization the Haake Minilab was used. A final blend was prepared with a twin screw extruder and we also tried to obtain some blends with the Branbender Plasti-Corder, unsuccessfully. Some conclusions could nevertheless be drawn.

1. Haake Minilab: it is a small compounder, equipped with two conical twin screws, which is operable with small quantities of material (5-6 g), and which has a recycling channel, that enables us to control the residence time of the polymer in the mixer. It can be equipped with co or counter rotating screws. Blends were prepared with co-rotating screws, which generally assure a better blending and higher shear. The chamber is connected with nitrogen, so that an inert environment can be assured during blending.

   The material is introduced through a tube and forced in the chamber with a piston, 2 g at a time; in the meantime the screws turn at a low speed. When all the polymer is introduced (it takes about 1 minute), nitrogen can be connected, the screw speed is set to the desired value and time is started.

   Several tests were performed in order to determine the best parameters, which were found to be 120°C, 90 rpm and 5 min.
2. Twin screw extruder from Leistritz (model ZHS 18HP). A blend of PEO and 5% SBM E20 was prepared, at 120°C and 90 rpm. A vacuum was connected to the extruder so that an inert atmosphere could be provided. The extruded material was passed through a chill roll (also from Leistritz), so that it could be rapidly cooled down.
3. BRABENDER Plasti-Corder: it is constituted by twin-rotors counter-rotating and a volume of the chamber of 25 ml. The instrument lets us control the rotation speed of the screws. Nitrogen can be connected so that we can blend the polymers in an inert environment. The two polymers were introduced in the

chamber at the same time; the time needed to fill it up was of approximately 30 seconds, after which nitrogen was connected.

Blends were also obtained by solution casting technique. The solvent used was chloroform. The polymers were left in solution at a temperature of 61°C for 24 h. A large amount of solvent is required, because we need to work with a dilute solution, to have a low solution viscosity and assure a good mixing. Each blend was made by putting 4 g of the polymers in 200 ml of chloroform. Mixing was assured by heat convection. Afterwards, the solvent was evaporated at ambient temperature; the final blend was put in an oven and dried at 40°C until the weight of the sample became constant; practically they were all dried for more then 3 days. Samples were molded with a press. Before each test every sample was kept for at least 24 hours in an oven at 40°C with a vacuum, so that either solvent residues or humidity could be eliminated. Before the mechanical tests samples were removed from the oven and put in a vacuum chamber at ambient temperature.

3.4. Rheological characterization

Rheological measurements were made using two stress controlled rheometers equipped with two parallel plates with a diameter of about 25 mm. The gap between the plates was set to 1.25 mm. The rheometers were a SR5000 of Rheometric Scientific and a CSM of Bohlin. All the tests were performed in an inert nitrogen environment.

The characterization was made through dynamic rheological measurements, performing small amplitude oscillatory shear tests (SAOS). SAOS tests can be stress controlled or strain controlled. When the test is stress controlled, a sinusoidal shear stress is imposed on the melted sample by the upper plate, and the instrument records its strain. When it is strain controlled, the instrument imposes a strain and the stress is recorded. If the tested material was perfectly elastic, the stress and the strain would be exactly in phase; if, on the contrary, the fluid was Newtonian, they would be completely out of phase

(90°). For viscoelastic fluids, such as the majority of polymers, the signals are out of phase with an angle $\delta<90°$. Defining τ_0 as the amplitude of the stress signal and γ_0 the amplitude of the strain signal, we can write the following definitions:

Elastic modulus: $$G'(w) \equiv \frac{\tau_o}{\gamma_0}\cos\delta$$

Viscous modulus: $$G''(w) \equiv \frac{\tau_o}{\gamma_0}\sin\delta$$

Complex viscosity: $$\eta^* \equiv -\frac{\tau_{21}(t)}{\dot{\gamma}_{21}(t)}$$

G' refers to the in phase component, *G"* to the out of phase component.

The Cox-Merz rule states that $\eta(\dot{\gamma}) = \left|\eta^*(\omega)\right|_{\dot{\gamma}=\omega}$, when $\dot{\gamma}(s^{-1}) = \omega(rad/s)$. If it is valid, by measuring the complex viscosity we can obtain information on the steady shear viscosity.

Three blends at three different concentrations (1%, 2%, 5% in weight) of the copolymer were prepared with all the five grades of SBM and the two grades of MAM we received from Arkema. Time sweep tests were performed at 150°C for 1 h in order to check the thermal stability of the blends. Stress sweep tests were made, at the frequencies of 0.01 Hz and 50 Hz in order to find the stress value to impose in the subsequent frequency sweep tests. In fact, for the Cox-Merz rule to be valid, the SAOS frequency sweep tests must be done in the linear zone of the polymer for all the duration of the experiment. A value of 400 Pa was found to be good for all the blends, from 0.01 Hz to 50 Hz.

Frequency sweep tests were performed at 100°C, between the frequencies of 0.01 Hz and 50 Hz. Some measurements were then continued backwards, from 50 Hz and 0.01, to assure that the polymer did not degrade in the rheometer.

Before starting the rheological characterization a lot of tests were made in order to find the best processing method to obtain the best rheological data; first of all to see the

impact of the blending processing conditions in the mini mixer on degradation of pure PEO (obviously, the more the complex viscosity decreases, the more the molecular weight of the polymer has decreased). We varied the temperature, the screw speed, the residence time in the mixer, and then we measured the complex viscosity at low frequencies.

3.5. Measurements of the molecular weight: intrinsic viscosity

3.5.1. Description of the method

Comparison between the molecular weight of the PEOs processed in different ways was made with viscosimetric methods. As we know there is a relationship between the molecular weight in viscosity of a polymer and its viscosity in solution. The relationship is based on the observation that the viscosity in solution is in fact a measure of the resistance that a fluid opposes to the flow, which depends on the frictional forces between the molecules in solution. These frictional forces depend on the size of the molecule and thus on the molecular weight. In the method we applied, a solution of the polymer is passed into a capillary tube; we measure the time that the fluid takes to flow, under the only effect of gravity, between two marks. The Poiseuille equation (eq. 1) is then used in order to relate the viscosity to the flow rate:

$$\nu = \frac{\pi P r^4}{8\eta l} \tag{1}$$

Where P is the pressure difference maintaining the flow, r and l are the radius and length of the capillary, and η is the viscosity of the liquid. The procedure which lets us calculate the molecular weight is very simple. First we calculate the relative viscosity, i.e., the viscosity of the solution on the viscosity of the pure solvent. Introducing the Poiseuille equation into this definition of relative viscosity, and considering that the

pressure that drives the flow is proportional to the density of the solution and the solvent (which for dilute solutions can be considered constant) we obtain the following expression:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \approx \frac{t}{t_0} \tag{2}$$

where t is the time taken from the solution to flow between the marks (Figure 3.1). The subscript $_0$ refers to the pure solvent, while no subscript is used for the solution. ρ is the density of the solution (for dilute solutions we can assume $\rho=\rho_0$). Plotting the relative viscosity versus the concentration, we find a curve that we can approximate using a power series:

$$\eta_{rel} = 1 + [\eta]c + k'c^2 + k''c^3 + k'''c^4 + \ldots \tag{3}$$

where c is the solution concentration and $[\eta]$ is called intrinsic viscosity. If the solution is dilute we can neglect the terms c^3 and higher and write:

$$\left(\frac{\eta_{rel} - 1}{c}\right) = \frac{1}{c}\left(\frac{\eta - \eta_0}{\eta_0}\right) = [\eta] + kc \tag{4}$$

We define the specific viscosity as:

$$\eta_{sp} = \eta_{rel} - 1 = \left(\frac{\eta - \eta_0}{\eta_0}\right) \tag{5}$$

which basically represents the increase in the solvent viscosity due to addition of the polymer on the solvent viscosity. From eq. (5) we can notice that, if we let c go to 0, the specific viscosity gives the value of the intrinsic viscosity; in symbols:

$$[\eta] = \left(\frac{\eta_{sp}}{c} \right)_{c \to 0} \tag{6}$$

The intrinsic viscosity is then related to the average molecular weight through the Mark-Houking-Sakurada equation:

$$[\eta] = K \cdot M_V{}^a \tag{7}$$

The constants, K and a, depend on the solvent, the polymer, the temperature, the polydispersity of the polymer.

3.5.2. Experimental

Five solutions of PEO in water were prepared and passed through a Cannon-Fenske viscosimeter, as represented in Figure 3.1. Concentrations were 0.2 g/L, 0.5 g/L, 0.75 dl/L, 1 g/L, and 2 g/L. The polymer was left in solution for several days before the tests, so that it could be perfectly dissolved. The time taken by the solution to flow between the two marks was calculated. The reduced and inherent viscosities were plotted in function of the polymer concentration. Linear plots were drawn, and their intercept with the viscosity axis was the intrinsic viscosity. The molecular weight in viscosity was then calculated with the Mark-Sakurada equation. The constant a was found in the literature, and was 0.78 (Carreau, De Kee et Chhabra, 1997); k (0.127 mL/g) was calculated from the nominal value of Mv of the pure PEO.

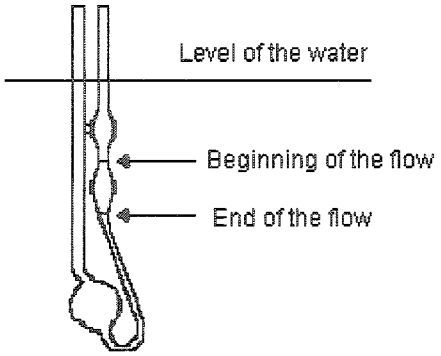

Figure 3.1: Sketch of the Cannon-Fenske viscosimeter

3.6. Traction tests

The stress-deformation curves were obtained with a Instron 4400 R machine. The reference ASTM designation for this kind of tests is the D 638 – 02a. The samples had the following dimensions (type V):

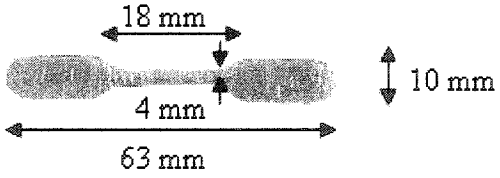

Figure 3.2: Schema of the sample used for the tensile tests

The small dimensions of the sample were chosen considering that we had limited quantities of the material, as blending in the mini mixer, 6 g at the time, takes an enormous amount of time. The tests were made at the laboratory conditions, at around 25°C of temperature; the samples were removed from the vacuum at ambient temperature just before the beginning of the test. We tested many samples for each blend, and the curves were plotted after obtaining 5 samples that gave the same results and that broke in the narrow cross sectional test section, as indicated in the ASTM norms. In order to obtain this kind of reproducibility, an average of 10 samples needed

to be tested each time, probably due to the easiness by which micro flaws are introduced in PEO. The speed of deformation was set at 0.5 mm/min. Such a speed was taken in order to obtain more precise data and more reproducible results, as it maximized the time of rupture of the sample to around 90 s.

3.7. Dynamical mechanical properties in flexion (DMA)

Dynamic mechanical analysis was performed in a dynamic mechanical analyzer from TA instruments. The ASTM norm reference is the D 4092 – 01. The samples, mounted in a three-point bending arrangement (dual-cantilever configuration) were rectangular, approximately of this size (in mm):

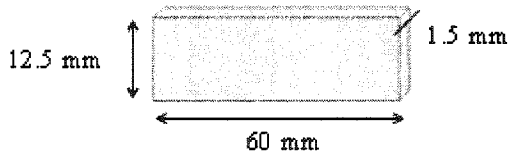

Figure 3.3: Schema of the sample used for dynamic mechanical analysis

Real length of the samples was 60 mm but, subtracting the part which needed to be fixed in the clamp, the free length was 35 mm. The machine applies a sinusoidal force, in the center of the sample, and records its displacements. As for the dynamic rheological tests, for a viscoelastic material the signals for the stress applied and the strain will be out of phase. Imposing a sinusoidal stress:

$$\sigma = \sigma_0 \sin(\omega t)$$

The out of phase sinusoidal strain can be written as a sum of two components:

$$\varepsilon = \varepsilon_0 \sin(\omega t + \delta) = \varepsilon_0 \left[\sin(\omega t)\cos\delta + \cos(\omega t)\sin\delta\right]$$

We can define a complex modulus E^*, a storage modulus E', a loss modulus E'' as follows:

$$E^* = \frac{\sigma(t)}{\varepsilon(t)} = E' + iE''$$

Where:

Storage modulus: $E' = E\cos\delta$

Loss modulus: $E'' = E\sin\delta$

Loss tangent: $\tan\delta = E''/E'$

with $E = \frac{\sigma}{\varepsilon}$.

The storage modulus is related to the amount of energy that is actually stored in the material. The loss modulus refers to the dissipated energy.

The tested samples were blends of PEO and all the seven grades of block copolymers we had. The percentage of the block copolymers was of 2% and 5%, made in both the methods previously described. Pure PEO was also tested to have a basis of comparison. Also pure PEO processed in the mixer and in solution was tested to have an idea of the impact of the processing method on the properties of PEO, more precisely to know the impact of degradation and of the residual presence of some traces of solvent. At first strain sweeps were performed in order to find the linear zone, at a temperature of 30°C and 50°C. A value of strain of 15 μm seemed to be in the linear zone for all the blends, between these two temperatures. Afterwards strain controlled temperature ramps were performed, between 30°C and 50°C. The fixed amplitude of the strain was 15 μm for all the blends and the heating rate was 1°C/min. The lower temperature limit was chosen mainly because of a failure in the cooling system of the machine at the time of the experiments. The upper limit was set at 50°C so that we would not get too closed to

the melting point of PEO at 64°C. In any case the maximum temperature at which our material is used in the polymer battery application is about 40°C; therefore a characterization in this range of temperatures seems to be sufficient for our objectives. Experiments were performed at least two times to assure reproducibility.

3.8. Dynamical mechanical properties in torsion

The instrument used in order to test the mechanical properties in torsion was an ARES rheometer of *Rheometrics Scientific*. The ASTM reference for this kind of test is the D 5279-01. The rectangular samples were of the same kind as those previously described for the DMA; the geometry was adjusted in order to have a 43 mm of free length. A characterization of the two modules in torsion in function of the frequency was performed. During experiments humidity and temperature could be considered constant and tests were made at ambient temperature, around 25°C. At first strain sweeps were performed in order to find the linear zone, at a frequency of 0.01 Hz and of 100 Hz. A value of strain of 5 % seemed to be in the linear zone for all the blends, between these two frequencies. Afterwards strain controlled frequency sweeps were performed, between 0.01 Hz and 100 Hz at a fixed strain of 5 %, for all the blends.
As for the DMA, we tested samples of pure PEO, pure PEO processed in the mixer and in solution, and blends with 2% and 5% percentages in weight of copolymers.

3.9. Differential scanning calorimetry (DSC)

Cristallinity of the blends was determined by measurements in a Perkin-Elmer DSC calorimeter. Samples of about 50 mg were heated and cooled, along with a reference, at a rate of 5°C/min. Measurements were made in an inert atmosphere between 40°C and 100°C. Samples were heated a first time so that their thermal history could be erased, then cooled at the same rate, and then reheated a second time. The degree of

cristallinity was calculated with the classic formula: $\alpha = \frac{\Delta H_m}{\Delta H_m^0}$, where $\Delta H_m{}^0$ is the heat of fusion for the polymer (PEO) 100% crystalline. According to values reported in the literature it is 205 J/g (Khasanova et al. 2003).

3.10. Gel permeation chromatography

GPC is a really useful technique used to find the molecular weight distribution of a polymer. A solution of the polymer is passed into a column packed with beads, which contain pores of different sizes. The short chains can pass through all the pores, even the smallest ones, while largest chains can only pass through the largest ones. Short and long chains separate through a complex process. At the end of the column there is a detector. Largest chains, which pass through a small number of pores, exit first, while the shortest chain, which go through a longer path, exit last. A sketch of GPC technique is presented in Figure 3.4. This technique can be used to find the molecular weight distribution of a polymer.

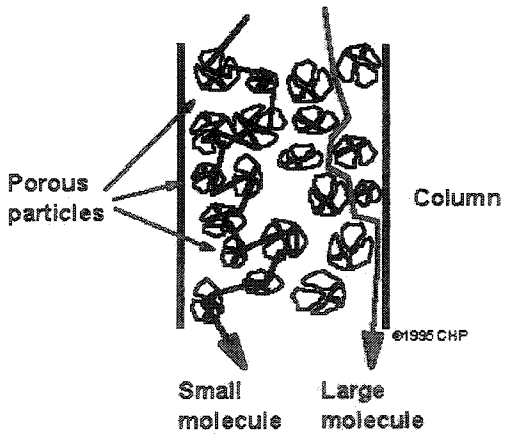

Figure 3.4: Schematic of a size-exclusion chromatography column. (Source: http://www.chemistry.adelaide.edu.au/external/soc-rel/content/size-exc.htm)

Some gel permeation chromatography measurements were made on two samples of polyethylene oxide in order to investigate its degradation after blending in the mini mixer. A sample of pure PEO and a sample of pure PEO passed through the mini mixer at 120°C, 90 rpm, 5 min, were tested. The experiments were performed at Avestor. The solvent used was a blend of 50% (volume) acetonitrile and 50% of a water solution 5% of sodium acetate.

3.11. Elongational viscosity

A measurement of the elongational viscosity of PEO and a blend of PEO and 5% SBM was performed at IMI (Industrial Materials Institute, NRC, Boucherville, Qc). The machine used was a Rheometrics Extensional Rheometer, RER-9000. It is a limited strain elongational rheometer, originally developed by Münstedt at BASF. The idea is to melt a cylindrical shaped specimen in hot oil and stretch it either at constant strain rate or at constant stress. The experimental configuration proposed to hold the specimen between a reference LVDT and a moveable rod. The sample preparation procedure, which is customized for every polymer family, has to be conducted with a lot of care, in order to remove all residual stresses that, when the sample is melted, might have an effect on the sample shape. The melted specimen is immersed in a bath of hot silicone oil (dimethylsiloxane oil (Dow 200, 100 cts)), which is maintained at a constant temperature of 100° C. For this study, the measurements were performed at a constant strain rate. This is accomplished by exponentially varying the velocity of one end of the sample in function of time. Stretching starts at the pre-selected strain rate. The force resulting from the controlled uniaxial stretching is measured by the deformation of a calibrated reference leaf spring coupled to a LVDT (linear variable differential transformer).

As for the sample preparation, the granules were transfer-molded under vacuum using the Rheometric RSV-2100 sample preparation kit in conjunction with a Yokogawa

programmable temperature controller model UP25. The granules were melted under vacuum, and then molded, first heated to 100°C and kept at this temperature for 4 min before transferring the melt to the mold. The mold assembly was then placed under light pressure and allowed to cool down to room temperature. The uniformity of the resulting cylinder-shaped specimens was verified, the average diameter was found to be d=6.1 ± 0.05 mm diameter. The sample length used in this study varied from 22 to 24 mm. The end surfaces of the molded specimens were cleaned and then fixed to clean aluminum ties using a high temperature epoxy (24h curing). The oil to be used in the bath was chosen so that the densities of the oil and of the samples could be as close as possible. Differences in the densities would in fact cause non uniform deformations in the stretching process, and the specimen would break more easily giving experimental errors. The density of the samples was measured using a PVT apparatus from Haake (PVT 100). The densities were measured at 100°C and 15, 20, 30, 50, 80 MPa; a value for atmospheric pressure was then found through extrapolation.

CHAPTER 4

RHEOLOGICAL AND MECHANICAL PROPERTIES OF PEO/BLOCK COPOLYMER BLENDS

4.1. Article presentation

This chapter presents the article, submitted to *Polymer Engineering & Science* in February 2005 by A. Ferretti, P.J. Carreau and P. Gerard with the title "Rheological and mechanical properties of PEO and block copolymer blends".

The most important results are presented in this section. We present the rheological characterization of all the blends, prepared with the mini mixer and by solution casting technique; the effect of the blending method on pure PEO, with the results of the measurements on the intrinsic viscosity; then measurement of the elongational viscosity, performed with a RER rheometer; the complete mechanical characterization is then presented, with the results of the traction tests, DMA and torsion tests. Anyhow, only the graphs which we considered to be essential for the comprehension of this project are presented; rheological results are presented in detail in the appendix.

4.2. Rheological and mechanical properties of PEO/block copolymer blends

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4.2.1. Abstract

Small quantities of block copolymers from two families, styrene-butadiene-methylmethacrylate (SBM) and methylmethacrylate-butylacrylate-methylmethacrylate (MAM) have been added to a polyethylene oxide (PEO) in order to improve its processability, namely increasing its elastic modulus without increasing too much its shear viscosity. The copolymers contain one block of polymethylmethacrylate (PMMA) that is compatible with PEO; the other blocks create nano phases, dispersed in the PEO matrix. Considerable efforts were devoted to finding the best blending method, either melt processing or solution casting. PEO is very sensitive to shear, and was found to degrade both in the bulk and in solution. Degradation, which cannot be avoided, was quantified through intrinsic viscosity measurements. The rheological characterization of blends containing 1, 2, 5 wt% block copolymer was carried out. The elastic modulus was found to increase more then the complex viscosity. Blends obtained by solution casting technique gave better results. The elongational viscosity obtained for one blend containing 5 wt% of SBM showed a slight increase with respect to the pure PEO. Tensile tests showed that the copolymer generally increased the mechanical properties of the blends prepared using a mini mixer or a twin-screw

extruder compared to the pure PEO. On the contrary, small traces of the solvent, still present in the solution casting samples, drastically reduced their tensile strength.

4.2.2. Introduction

Polyethylene oxide (PEO) is a soft semi-crystalline thermoplastic which displays a lot of interesting properties and finds many applications due to the wide range of molecular weight in which it is commercially available (10^5-8×10^6 g/mol). It is soluble in water. Films of high molecular weight PEO are tough, ductile, heat-sealable and, because of their high degree of crystallization, resist well to atmospheric moisture [1]. Also, it has recently found increasing use as a conducting medium in light-weight, high energy polymer batteries [2]. In the polymer battery, very thin layers of PEO are assembled in a sandwich structure. The most economical process through which such a structure is created is lamination. Thin layers of PEO are obtained until now by the cast film technique using a solvent. Hence, it is desirable to improve the processability of pure PEO, so that thin films can be obtained by extrusion in a more effective and more economic way.

Processability of a polymer is directly affected by its shear viscosity, elasticity and by its elongational properties. Our work focuses on the linear viscoelastic properties. Some preliminary measurements of the elongational viscosity, made with a RER rheometer, are nevertheless presented. We know that, in order to improve the processability, the shear viscosity has to be as low as possible. Also, the melt elasticity related to the ratio of the elastic to the loss modulus, (G'/G''), should be as high as possible, as shown by Fang et al. [3] for polyethylenes in film blowing. They found that the bubble stability improved as the ratio of G'/G'' increased.

Block copolymers, are becoming very popular, in particular because of their self-assembling properties. They can organize in very complicated structures due to the thermodynamic interactions between the blocks [4-6]. For the blends investigated in this work, PEO is always compatible with one of the blocks of the copolymer,

polymethylmetacrylate (PMMA); the other incompatible blocks (styrene, butadiene, butylacrylate) will phase separate. There is no need for a compatibilizing agent, as it is already "incorporated" in the copolymer. The copolymer domains are of the order of nm. [4-7].

In working with PEO, however, we have to keep in mind that it is a very fragile material, which is easily degraded. For this reason, it is a very difficult material to study. In the literature there are many discrepancies regarding data on PEO. It has been reported to degrade under the effect temperature, around 225°C [8]. It is also very sensitive to thermal oxidation, which is highly dependent on molecular weight. Maclain et al. [9] found that the crystallinity of PEO reaches a maximum around a molecular weight of 6000 g/mol, and then decreases as the molecular weight increases. Being more crystalline, low molecular weight PEO has better resistance to the attack of oxygen. Mechanical degradation has been reported to take place both in solution and in bulk [10,12].

Special care has to be given to the conditions in which it is stored. Scheirs et al. [13] studied the oxidation of a powder of PEO, kept at 60° C in contact with air. They found that the molecular weight decreased because of oxidation, at a slow rate for the first 23 days. After 23 days, there was an accelerating stage of the free-radical degradation process, and the molecular weight decreased dramatically. Bortel et al. [14] studied the solid state oxidation of high molecular weight PEO. They claimed that the degradation was due to exceptionally high strains in the helical crystalline structure, and that scission of the chains occurred as they tried to reorganize themselves to reach a degree of cristallinity of 70%.

For the majority of the studies on homopolymer-copolymer blends, the blends were prepared by a solution casting technique. We know that industrially it is preferable to prepare blends in the bulk (molten state), to avoid the high costs of the solvent removal and recovery. In our work, we prepared the blends both ways, so that we could compare the results.

4.2.3. Experimental

4.2.3.1. Materials

PEO (Mv=10^5 g/mol; polydispersity 6.9) was purchased from Aldrich. The 5 grades of the triblock copolymer SBM Nanostrength™ (styrene, butadiene, methylmethacrylate), obtained by anionic polymerization, and the 2 grades of the symmetric acrylic triblock copolymer MAM Nanostrength™ (methylmethacrylate, butylacrylate, methylmethacrylate), obtained by controlled radical polymerization, were supplied by ARKEMA (France). The SBM copolymers contain some non negligible quantities of the diblock copolymer SB. Different grades of different molecular weights and variable lengths of the blocks have been investigated. Characteristics of the copolymers are presented in Table 4.1.

4.2.3.2. Blend preparation

Two blending methods were investigated and compared: melt processing and solution casting technique. Blends obtained by melt processing were prepared in a mini mixer (Haake Minilab). It is a small compounder, equipped with two conical screws and it has a recycling channel, which enables us to control the residence time of the polymer in the mixer. A final blend of PEO and 5% SBM E20 was prepared using a twin-screw extruder in the co-rotational mode (Leistritz ZSE 18HP), at 120°C and 90 rpm. Blends obtained by solution casting were prepared in chloroform. The polymers were dissolved (20g/L) and left for 24h at 61°C. No mechanical stirrers were used and mixing was achieved by natural convection. The solvent was evaporated at ambient temperature and the blends were then dried in a vacuum oven for several days at 40°C.

4.2.3.3. Intrinsic viscosity measurements

The viscosity average molecular weight was used in order to quantify the extent of the mechanical degradation caused by the different blending methods. The PEO was dissolved in water at different concentrations, and the viscosity of dilute solution was then obtained using a Cannon-Fenske viscometer at 25°C. The reduced viscosity ($\eta_{red} = \frac{(t - t_0)/t_0}{c}$) and the inherent viscosity ($\eta_{inh} = \frac{\ln(t/t_0)}{c}$) were plotted as a function of the polymer concentration in the solution, and their linear interpolation was traced. (t: time taken by the solution to flow between 2 marks; t_0 refers to the pure solvent, which was water in this work). Their limit as the concentration c reaches 0 is the value of the intrinsic viscosity [15]. An example is presented in Figure 4.1. Both the reduced viscosity and the inherent viscosity values extrapolate to the same value, suggesting that the measurements are meaningful and that the intercept is the intrinsic viscosity $[\eta]$. M_v was then calculated using the Mark-Houking-Sakurada equation [15]:

$$[\eta] = K \cdot M_v{}^a \qquad (1)$$

where K and a are constants, which depend on the solvent, temperature, the polymer and its polydispersity. The exponent a was set to be 0.78. [15]. Mv of the pure polymer obtained from Aldrich was used to calculate the constant K, which was found to be equal to 0.127 mL/g. This is considerably different from values reported in the literature where K was found to be in the range 0.0125-0.05 mL/g for PEO having narrower molecular weight distributions.

4.2.3.4. Linear viscoelastic measurements

The linear viscoelastic data were obtained using two stress controlled rheometers (a SR5000 of Rheometric Scientific and a CSM of Bohlin) equipped with two parallel

plates with a diameter of 25 mm. All the tests were performed under an inert nitrogen environment.

The effect of the copolymer was quantified from results of dynamic frequency sweeps tests from 0.01 Hz to 50 Hz, at 100°C. The imposed stress was set to 400 Pa, which was found to be in the linear viscoelastic region for all the blends. Time sweep tests were also performed to verify the thermal stability of the blends.

4.2.3.5. Elongational viscosity

Measurements of the elongational viscosity were made at IMI (Industrial Materials Institute, NRC, Boucherville, QC), with an elongational RER rheometer (Rheometrics RER 9000), similar the one originally developed by Münstedt [16]. The measurements were performed at 100°C and a constant strain rate. The deformation of the molten specimen, immersed in a bath of hot silicone oil (dimethylsiloxane oil (Dow 200, 100 cts)), was accomplished by exponentially varying the velocity of one end of the sample with time. The density of the oil (0.900 g/cm^3) was close to the density of the polymer at 100°C (1.012 g/cm^3 for pure PEO and of 1.072 g/cm^3 for the blend, measured using a Thermo Haake PVT 100). The samples were carefully prepared so that all the residual stresses could be removed, to avoid deformations when the sample was melted. The granules were transfer-molded under vacuum using the Rheometric RSV-2100 sample preparation kit in conjunction with a Yokogawa programmable temperature controller model UP25. The uniformity of the resulting cylinder-shaped specimens was verified, and the average diameter was found to be d=6.1 ± 0.05 mm diameter. The sample length used in this study varied from 22 to 24 mm. The end surfaces of the molded specimens were cleaned and then fixed to aluminum ties using a high temperature epoxy (24h curing).

The RER rheometer has some drawbacks, one serious being that the specimen is melted in hot oil, and that oil and sample densities, at test temperature, were not exactly equal. This led to non-uniform deformation, premature breakage (low strain at break) and consequently to experimental errors. Nevertheless, the results are meaningful in the sense that they do represent the material behavior under low elongational rates (reproducibility is acceptable, believed to be within ± 15 %).

4.2.3.6. Tensile measurements

The stress-deformations curves were obtained using an Instron 4400 R. (ASTM D638-02a, samples of type V). The tests were made at lab conditions, around 25°C, at 0.5 mm/min. Curves were traced after obtaining 5 measurements which gave similar results and for which the samples broke in a narrow cross sectional test section. Samples were obtained by molding in the hot press at 100° C. They were then dried at 40°C in a vacuum for at least 24 h, so that humidity could be removed.

4.2.3.7. Dynamic mechanical properties in flexion and in torsion

Dynamic mechanical analysis was performed using a dynamic mechanical analyzer from TA Instruments (ASTM D 4092 – 01). The rectangular samples were mounted in a three-point bending arrangement (dual-cantilever configuration). The machine applies a sinusoidal force, in the center of the sample, and records its displacements. Some strain controlled temperature ramps were performed, between 30 and 50°C, at constant amplitude of 15 μm, this value had been previously verified to be in the linear zone for all the samples.

Mechanical properties in torsion were investigated using an ARES rheometer of Rheometrics Scientific (ASTM D 5279-01). The storage modulus was measured as a function of the frequency. The tests were made at ambient temperature and the humidity and temperature could be considered constant. During the strain controlled

frequency sweeps the maximum strain was set to be 0.05, which had been previously verified to be in the linear region for all the samples.

4.2.4. Search for the best processing method

Figure 4.2 shows the complex viscosity, the elastic and viscous moduli of the PEO, measured at 1 Hz, strain of 0.05 and 150°C, and plotted as functions of time. The results show no sign of a decrease in any of these material functions. The PEO is stable at this temperature.

Figure 4.3 shows the loss of the complex viscosity of PEO after processing in the mini mixer as a function of the rotational speed of the mixer screws. The dynamic rheological measurements were made at 100°C and 0.01 Hz. The results show that the complex viscosity decreases with the increase of the screw speed, and also decreases dramatically with the increase of temperature in the mini mixer. For example, for a screw speed of 90 rpm, the loss in η^* after 5 min is about 18% when the mixer is operated at 100°, 23% when it is operated at 120°C and rises to 33% for 140°C.

Figure 4.4 compares the loss of the complex viscosity of the PEO as a function of time when blending was made under inert atmosphere or when the polymer was left in contact with air. We can see that under nitrogen the complex viscosity tends to be stabilized after 5 min. The molecular weight of the PEO still decreased but the rate of its decrease is small. On the contrary, without nitrogen, the complex viscosity keeps decreasing at a high rate. We can conclude that with the nitrogen purge the mini mixer is well isolated from oxygen and that the PEO degradation is mainly caused by mechanical degradation, enhanced by temperature.

Table 4.2 gives the results from the intrinsic viscosity measurements. They were performed on pure PEO, pure PEO processed in solution, through the mini mixer, and through the twin-screw extruder. Note that the measured values of the complex

viscosity are not sufficient to estimate the reduction in molecular weight due to degradation caused by different blending methods. For example in the cast film samples, solvent left after drying in traces would act as a plasticizer and cause a sensitive drop in the complex viscosity. The results from the intrinsic viscosity measurements are more informative and show that the PEO recovered from the solution technique had the lowest drop in the molecular weight (~18%), followed by the PEO processed in the mini mixer under nitrogen at 90 rpm and 150°C (~27%) and the PEO processed in the twin screw extruder at 120°C and 90 rpm (~39%). These results are expected as the deformation rate is considerably larger in the twin-screw extruder than in the mini mixer. However, the significant drop in the molecular weight when the PEO is processed in solution is surprising as virtually no mechanical mixing was imposed on the sample.

The first conclusion we draw is that PEO is thermally stable at 150°C, in agreement with literature results [8]. As the copolymers do not degrade either at that temperature, we could blend the polymers at 150°C without worrying about thermal degradation. By quantifying the decrease of the complex viscosity we can assess the extent of the mechanical degradation of PEO. The strong dependence of η^* on the screw speed (Fig.3) indicates that there is an important mechanical degradation, enhanced by increases in the mixing temperature and presence of air. As widely explained, the degradation of PEO cannot be avoided, as it occurs as soon as it is exposed to shear. However, in order to obtain a good dispersion of the copolymer in the PEO matrix, we need to apply enough strain or deformation during the blending step, which would also favor the complete dissolution of the copolymer pellets; higher strains would promote the formation of smaller domains of the copolymer in the PEO matrix, which would then be better dispersed. We can conclude the same for temperature. A high processing temperature would lead to a severe degradation of PEO, but on the contrary would favor the diffusion and reduce the dissolution time of the copolymer in the matrix. The problem is, therefore, to find the optimum processing conditions. As already

mentioned, a most important parameter influencing the mechanical degradation of PEO is temperature. We tried to operate the mini mixer at the lowest temperature, which was found to be 120°C. At lower temperatures the copolymer was not well dispersed in the matrix, as visible from inspection of the samples from the mini mixer. Many screw speeds were tested and the best from the rheological results was found to be 90 rpm. The blend was left in the mini mixer long enough to reach a good homogeneity, which was 5 min.

As it is listed in Table 4.1, some of the copolymer grades we received were in the form of powder, some in pellets. SBM 233 was both in pellets and in powder. These copolymers, which are elastomers, would not melt in the extruder, but would dissolve in the molten polyethylene oxide. We tried to obtain blends from both pellets and powder to see if the larger size of the pellets would force us to operate the mini mixer or the twin-screw extruder in more drastic conditions and for longer residence times. There was no evident advantage in using the powder instead of the pellets. We can therefore conclude that the size of the pellets was not a very important variable in the blending process.

We recall that the blends were all prepared under the exact same conditions, so that the effect of the copolymer could be quantified. The parameters were chosen so that the copolymer grade, which needed a higher temperature and a faster screw speed, could be well dissolved; these grades were SBM004 and SBM233. Less drastic conditions could be used for other grades. This difference in the "easiness" of dissolving is not related to the rigidity of the pellets, as SBM004 was by far the less rigid. Copolymer grades of lower molecular weight required less drastic conditions. To sum up, all blends prepared in the mini mixer were processed under inert atmosphere, at 120°C, screw speed of 90 rpm, during 5 min.

Blending by solution casting was made in chloroform, as it was the only common solvent of PEO, SBM and MAM. Even for the solution technique we tried to vary the

parameters (mixing speed, temperature, solution concentration) to obtain the best properties. Obviously, higher mixing rates result in a greater mechanical degradation. It is interesting to notice that, even in solution, increasing the operating temperature slightly decreased the final molecular weight of PEO; on the contrary the concentration of the polymer solution, in the range we examined (5–50 g/L), did not have any effect. For the following results the polymers were dissolved (20 g/L) and left for 24h at 61°C without mechanical agitation.

Measurements of the intrinsic viscosity showed that the PEO was more degraded when processed in bulk (see Table 4.2). This was expected, as in the bulk it was exposed to much higher strain (shear and elongational) components and much higher temperatures. The fact that PEO obtained by solution or in the mini mixer had more or less the same curve of complex viscosity suggested that some traces of solvent were still present in the sample. Even though samples were dried for several days in the vacuum at 40° C the solvent was probably not totally removed. PEO degrades even in the solid state, and should not be kept for long times at temperature above 25° C [13,14].

4.2.5. Rheological characterization

Figure 4.5 reports the viscoelastic behavior of PEO and SBM 233 blends (composition presented in Table 4.1), as the complex viscosity (Fig. 5a) and elastic modulus (Fig. 5b) versus frequency. Also, curves of pure PEO and pure PEO processed in the same way as the blends (in the mini mixer or in solution) are plotted. The rheological behavior is typical of most polymer melts, but the low shear rate and terminal zone were not reached at the lowest frequencies (6.28×10^{-2} s^{-1}). The blends containing up to 5% copolymer exhibit a very similar behavior than the PEO matrix. The processed PEO showed a visible drop in the complex viscosity and in the elastic modulus. On the contrary, the complex viscosity and the elastic modulus increased as we increased the concentration of copolymer in the PEO matrix. The increase was greater for blends

prepared by the solution casting technique. The rheological behavior for all the other PEO/block copolymer blends was quite similar.

Table 4.3 represents the increases in the complex viscosity, elastic modulus and elasticity, taken from dynamical rheological measurements made at 100°C and 0.01 Hz, for blends containing 5% in weight of copolymer. Percent increases are with respect to the pure PEO. The values in parentheses refer to the increases from the pure PEO samples molded directly from the powder. Values not in parentheses represent the increases from processed PEO, in the mini mixer or in solution under the same conditions as the blends. It is clear that in every case the increases in the elastic modulus are greater then the increases in the complex viscosity or the decreases are less, as a consequence the elasticity (G'/G'') increases as a copolymer is blended to the PEO. Again it is evident that the benefic effect of the copolymers is greater for blends obtained by the solution casting technique. The largest increases were found for the PEO/SBM 233 blend, where G' increased by as much as 170% and G'/G'' by 47%, compared to the reference PEO. For the blends prepared in the bulk, the increases of the elasticity due to the addition of the copolymers were not always as large due to the PEO degradation.

Figure 4.6 plots the elastic modulus and the complex viscosity, measured at 100°C, 0.01 Hz and 400 Pa, of PEO/SBM 233 blends as a function of the copolymer concentration. We can see that, for the range of concentration studied, the relationships between the material functions and the concentration of the copolymer are almost linear, suggesting miscibility of the copolymer with the PEO. The results for the other blends are similar and are not shown here.

Figure 4.7 reports a characteristic elastic time, $\lambda = G'/\omega G''$, as a function of the frequency for the pure PEO processed in the mini mixer, in solution, and in the twin screw extruder, compared to the curves for a blend of PEO and 5% SBM E20.

Comparing the three blending methods, we notice that the increase in elasticity for the blend prepared with the twin-screw extruder, compared to its reference, is the largest among the three. However, it is not sufficient to recover the large decrease provoked by the mechanical degradation.

The shapes of all the rheological curves are those of a shear-thinning fluid. It was expected that after addition of any of the two block copolymers SBM and MAM, all the material functions would increase. Anyhow, what we were concerned about was their relative increases and more the melt elasticity (related to *G'/G"*). We know that *G'* is a measure of the amount of energy stored in the polymer, while the viscous modulus *G"* is connected to the amount of energy dissipated. *G'/G"* is therefore the ratio of the energy stored on the energy lost. First of all, we notice, just because of degradation the elastic modulus decreases more then the complex viscosity, provoking a loss in the melt elasticity. Some measurements done with gel permeation chromatography (GPC) showed how the molecular weight distribution of pure PEO narrows as it is exposed to mechanical degradation. This is because the longest chains are more sensitive to shear and they are the first to break into shorter chains. As shown by Wong et al. [17], elasticity is related to the molecular weight distribution, and it decreases as the MWD narrows. Nevertheless, we notice that after addition of the copolymer, the elastic modulus is recovered and it increases more then the complex viscosity. Hence, elasticity is increased. In some cases the increase is quite important.

We notice from Figure 4.7 that blending in the twin screw extruder is very effective (the difference between the elasticity curves of the blend and their reference is larger). It is clear that in the twin screw extruder the polymer is exposed to much higher strains resulting in a greater degradation of the PEO. On the other hand, higher strains promote more effective organization of the copolymer in the matrix, thus increasing more the elasticity.

Comparing the different grades we can clearly see, from Table 4.3, that the PEO/SBM 233 blend has the largest increases of the elastic modulus and of the complex viscosity, as well as of the ratio *G'/ G"*, which is related to the elasticity. SBM 233 is the grade that contains the least quantity of PMMA, which is the compatible block with PEO, and thus the greater quantity of the incompatible blocks styrene and butadiene, the blocks that create a phase separation.

4.2.6. Elongational viscosity

Measurements of the elongational viscosity as a function of time were carried out for two samples of PEO; pure PEO passed through the twin screw extruder and a blend of PEO and 5% SBM E20, prepared with the twin screw extruder. Figure 4.8 shows the uniaxial elongational viscosity growth function for the two samples as a function of time. The elongational rate was kept constant, set at four different values (0.1 s^{-1}, 0.3 s^{-1}, 0.5 s^{-1}, 1 s^{-1}). In the figure the solid lines correspond to the predictions from the linear viscoelasticity multiplied by three ($3\eta^{+}(t)$). The predictions have been calculated using a three element (6 parameters) Maxwell model [19]:

$$\underline{\underline{\sigma}}(t) = -\int_{-\infty}^{t} \left[\sum_{k=1}^{N} \left(\frac{\eta_k}{\lambda_k} \right) e^{-\frac{(t-t')}{\lambda_k}} \right] \underline{\underline{\dot{\gamma}}}(t')\, dt' \qquad (2)$$

The coefficients have been calculated from the relaxation spectrum, obtained from the linear viscoelastic data. The good agreement between the predictions and the experimental data suggests that the measurements are accurate. We notice that the elongational viscosity increases monotonously with time for short times and for low imposed elongational rates, as expected from linear viscoelasticity. However, we observe a marked strain hardening for long enough time even at the lowest elongational rate (0.1 s^{-1}), which is not common for linear polymers. The addition of the copolymer

does not change the general behavior of the pure PEO, but the elongational viscosity is markedly increased. This is quite visible from the figure at the lowest elongational rate (0.1 s^{-1}), but due to instrument limitations, the gain at larger elongational rates is not clear. The increase in the elongational viscosity is believed to be beneficial for processing thin films of PEO, but more work is needed to confirm that hypothesis.

4.2.7. Mechanical characterization

Mechanical tests were performed in order to investigate if the addition of the copolymer has an impact on the mechanical properties of the pure PEO at the solid state. While the main goal is to improve the melt elasticity of PEO we hope to obtain a blend that retains the mechanical properties of the pure polymer. Three kinds of tests were performed: tensile tests and dynamic mechanical analysis in flexion and in torsion.

4.2.8. Tensile tests

Figure 4.9 shows typical stress-strain curves obtained for the PEO/5% SBM E22 blends. The curves for the other blends have exactly the same behavior. It is clear from the figure that PEO and its blends are all fragile materials. Addition of the copolymer does not change the shape of the curves. However, we notice that the addition of the copolymer improves the elongation at break; this is expected, as the copolymers are elastomers. There is a very small range that conforms to Hooke's law, in which the deformation and stress are truly proportional. We can define the Young modulus as the slope of the tangent to the first part of the curves.

Figure 4.10 and 4.11 show a comparison of the Young modulus and of the stress at break, respectively, for all the blends, prepared either in the mini mixer or in solution (error bars are shown to indicate the accuracy of the measurements). The horizontal straight lines refer to the PEO processed in the same way as the blends. The stress

deformation curve of the pure PEO processed through the mini mixer was similar to the curve of the pure PEO. On the contrary, pure PEO processed in solution showed a sharp decrease in the tensile strength. Blends obtained in the bulk showed better tensile properties. The Young modulus of the blends obtained by extrusion is larger than for the blends obtained in solution, but the difference is not significant. Compared to their reference, all the blends show an increase of the tensile strength with increasing quantity of the copolymer, except two cases, i.e. increasing the concentration from 2% to 5% for the two PEO/MAM blends prepared using the mini mixer.

From these tensile tests we can say that, at least for the blends obtained by melt processing, the properties are maintained. The copolymer has a good influence on the tensile strength for blends obtained both in the bulk and in solution. The mechanical degradation does not provoke a great loss in the tensile properties, as the pure PEO and the PEO processed in the mini mixer give more or less the same results. However, there are larges differences between blends prepared by the two different blending methods. These differences are not due to degradation, as, if this was the case, the PEO processed through the mini mixer should depict larger losses. This is believed to be the effect of traces of solvent still present in the samples, which acts as a plasticizer. Ilshiyama et al. [20] studied the influence of humidity on tensile properties of PMMA and found that increasing percentages of humidity could considerably reduce both the Young modulus and the tensile strength of PMMA. Water had a swelling effect and decreased the glass transition temperature of the polymer, thus decreasing the cohesive force between molecular chains. We suspect similar effects of traces of water (humidity) and of solvent (chloroform), acting as plasticizer for our samples. The tensile properties of samples dried for several weeks and at 50°C slightly increased, proving that the loss in mechanical properties was largely due to the presence of the solvent. However, we could not rule the possibility of degradation of the PEO kept for several days at that temperature.

The increase in the tensile strength is induced by the presence of the copolymer and by the morphology that is created. The thermodynamic miscibility between PEO and PMMA [21-24] favors the dispersion of the copolymer domains at the nanometer scale. As already mentioned, some non negligible quantities of the copolymer styrene-butadiene are present in SBM; neither of these blocks is compatible with PEO. A question that arises is whether there are some parts of the SB blocks that independently separate from the rest of the copolymer and disperse in the PEO matrix. If there was phase separation the domains could not be detected by scanning electron microscopy, and hence are probably in the SBM domains at the nanoscale.

We observe in Figure 4.11 that increasing the concentration of MAM from 2% to 5% for samples prepared using the mini mixer provokes a loss in the stress at break. This is evidence that the copolymer was not well dispersed and dissolved in the molten PEO matrix, as we did not observe the same behavior for the blends obtained by solution. Hence, it is not a problem of solubility of the copolymer in the PEO, but it is more difficult to disperse larger quantities of the high molecular weight MAM copolymers in the bulk. Also, the better tensile properties of the blends prepared in solution, compared to their PEO reference, could be attributed to a better dispersion and the total dissolution of the copolymer when blended in low viscosity solution during 24 h. In summary, the significant increases in the tensile strength (stress at break) observed for blends containing a small quantity of a lower molecular weight copolymer suggest the total miscibility of these copolymers with PEO.

4.2.9. Dynamic mechanical properties

Figure 4.12 and 4.13 present the loss tangent, measured from dynamic mechanical analysis for the pure PEO, the pure PEO processed in solution, and PEO/5% block copolymer blends prepared in solution. The results obtained in flexion are plotted as a function of temperature in Figure 4.12 whereas the results in torsion are presented as a

function of frequency in Figure 4.13. As that the loss modulus is almost constant, while the storage modulus decreases in this range of temperature, tan δ (=*E"/E'*) is shown in Figure 4.12 to increase with temperature. Quantities of the copolymer up to 5% have no influence on the shape of the curves. However, tan δ decreases significantly due to the presence of the copolymer, reflecting the large increases of the storage modulus and the enhancements of the mechanical properties as shown by the tensile results. The graphs of the other blends that we prepared had a similar behavior and are not presented here. Again, the presence of the copolymer does not change the shape of the curves of tan δ vs ω of Figure 4.13. The minimum in the curves depends on the imposed strain amplitude and moves towards higher frequencies with increasing strain amplitude. The graphs of the other blends, which are not shown, are similar. It is interesting to note by comparing the results of both figures that the effect of the copolymer on tan δ for the blends obtained is about the same for measurements made in flexion as in torsion. From our dynamic mechanical data for the blends, we can conclude that the copolymer has a beneficial effect with respect to the pure PEO. As already mentioned for the tensile properties, the copolymers with a lower molecular weight seem to be slightly more effective, possibility because they can be dispersed and dissolved more readily in PEO.

4.2.10. Conclusions

The aim of this study was to improve the processability of polyethylene oxide in the molten state, without affecting its properties in the solid state. Important variables in the discussion of processability are melt elasticity (*G'/G"*), shear viscosity and elongational viscosity. 1 to 5% of SBM and MAM copolymers were added to pure PEO and the rheological and the mechanical properties of the blends were investigated. Properties were found to depend on the blending technique. PEO chains are very fragile when there are exposed to shear. It is impossible to totally avoid degradation when it is blended with another polymer. Processed with mechanical mixer, mechanical

degradation was found to depend strongly on temperature and, as expected, dependent on the screw speed of the mixing system. In solution, on the contrary, the dependence of degradation on temperature was not strong. We tried to apply the gentlest conditions that would let us obtain a homogeneous blend. Degradation was quantified by measurements of the intrinsic viscosity. Blends made by extrusion had a more severe reduction in its average molecular weight, of the order of 40%.

Rheological characterization showed that the copolymer had a positive effect with respect to the pure PEO, as the elastic modulus improved more than the complex viscosity, therefore, elasticity was enhanced. The effect was more evident for blends obtained by the solution casting technique. The elongational viscosity was measured, as a function of time, and the addition of a copolymer to the PEO was found to slightly increase the straight hardening of the blend compared to the pure matrix. Mechanical properties were also investigated and the copolymer was shown to have beneficial effects on the tensile strength as well on the storage modulus in flexion or in torsion. Lower tensile strength for blends prepared by solution and for the pure PEO processed in solution was attributed to the presence of traces of solvent acting as a plasticizer.

4.2.11. Acknowledgments

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4.2.12. References

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Table 4.1: Characteristics of the copolymers (Source: ARKEMA)

SBM (Stytene-butadiene-methylmethacrylate) - Arkema (France)			
Grade	Molecular weight	Composition	Form
AF-X 004	M_n ~ 63 kg/mol	S/B/M ~11/48/41	Pellets
AF-X 233	M_n ~ 77 kg/mol	S/B/M ~35/45/20	Pellets and powder
AF-X 250	M_n ~ 45 kg/mol	S/B/M ~60/10/30	Pellets
AF-X E20	M_n ~ 36 kg/mol	S/B/M ~33/33/34	Small pellets
AF-X E22	M_n ~ 40 kg/mol	S/B/M ~25/25/50	Pellets
MAM (methylmethacrylate-butylacrylate-methylmethacrylate) - Arkema (France)			
DC 42	M_n ~ 58 kg/mol	M/A/M ~31/38/31	Pellets
DC 46	M_n ~ 71 kg/mol	M/A/M ~34/32/34	Pellets

Table 4.2: Viscosity average molecular weight.

POLYMER	**[η] (dL/g)**	**M_v (g/mol)**
Pure PEO	10.1	100 000
PEO in Mini mixer	7.9	73 020
PEO in solution	8.7	82 630
PEO in twin screw extruder	6.9	61 390

Table 4.3: Percent increases for the elastic modulus, the complex viscosity, and the elasticity of PEO/5% block copolymer blends, prepared with the mini mixer and by solution casting, measured at 100°C, 0.01 Hz and 400Pa.

	Increase in G'		Increase in η^*		Increase in (G'/G'')	
	mini mixer	solution casting	mini mixer	solution casting	mini mixer	solution casting
SBM AF-X 004	-5% (44%)	34% (95%)	-2% (32%)	15% (54%)	-3% (10%)	20% (30%)
SBM AF-X 233	-15% (29%)	87% (170%)	-13% (18%)	43% (92%)	-2% (11%)	35% (47%)
SBM AF-X 250	2% (55%)	8% (57%)	-2% (33%)	6% (43%)	0% (13%)	3% (11%)
SBM AF-X E20	-5% (44%)	12% (62%)	-7% (27%)	-5% (27%)	2% (15%)	22% (32%)
SBM AF-X E22	-4% (45%)	35% (96%)	-2% (33%)	12% (51%)	-3% (9%)	23% (33%)
MAM DC 42	2% (55%)	14% (65%)	-2% (33%)	2% (37%)	4,5% (18%)	13% (23%)
MAM DC 46	1% (62%)	19% (73%)	1% (37%)	5% (42%)	5% (20%)	15% (25%)

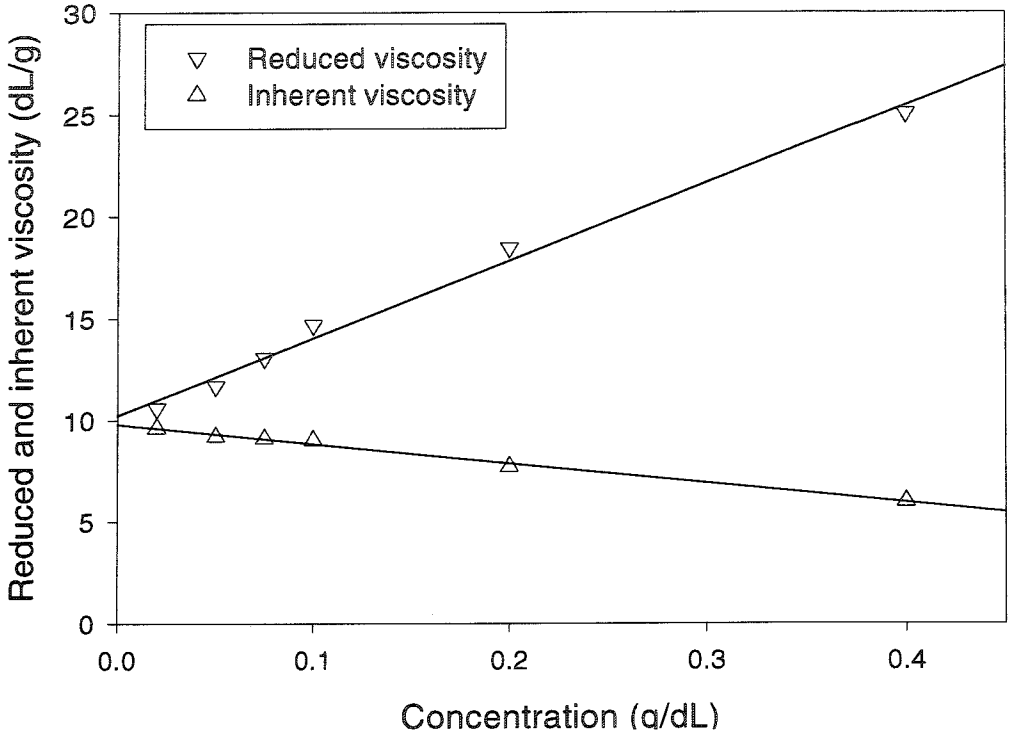


Figure 4.1: Reduced and inherent viscosities, as a function of the concentration of the PEO in the solution.

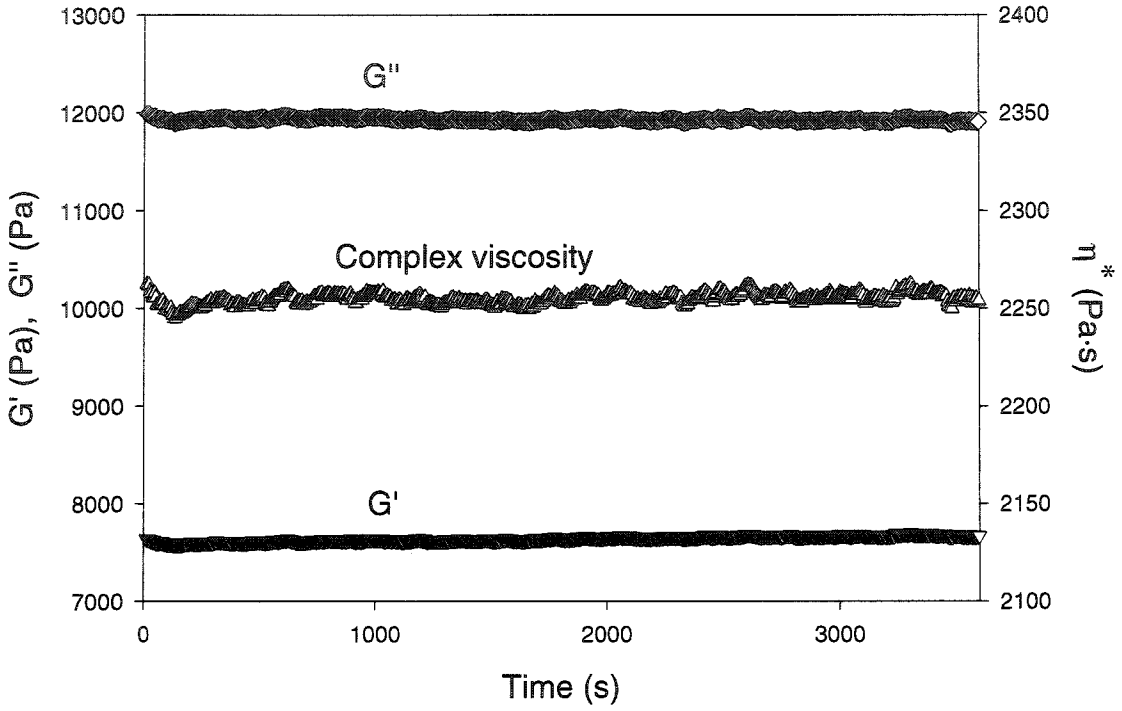


Figure 4.2: *G'*, *G"* and η^* measured at 150°C, 1 Hz and strain amplitude of 0.05 as a function of time.

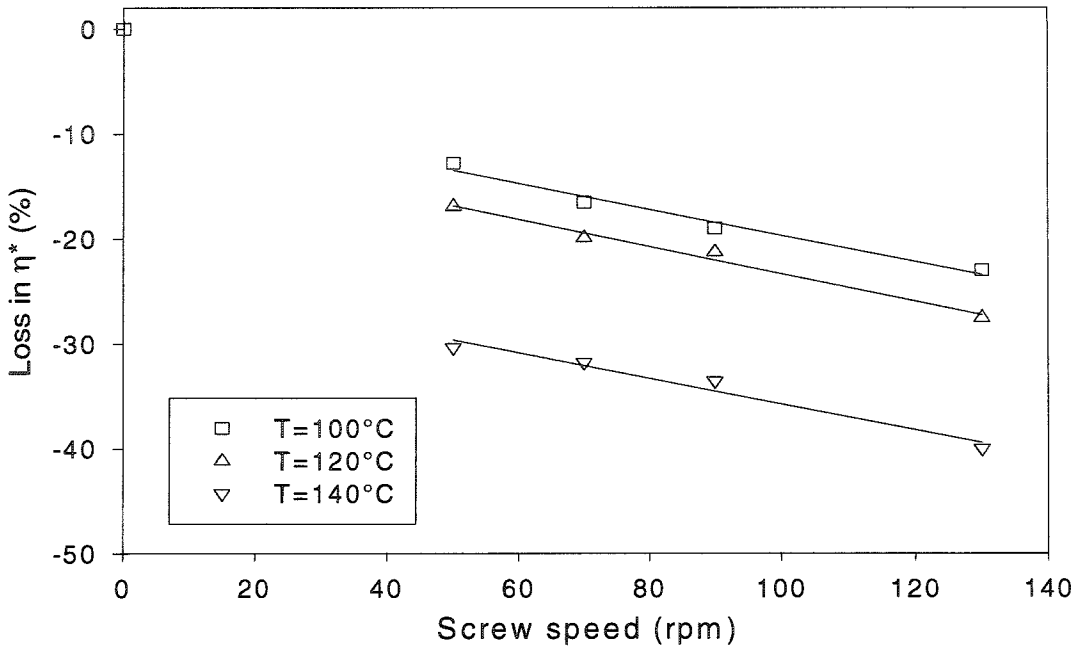


Figure 4.3: Loss in the complex viscosity of the PEO (measured at 1 Hz and 100°C) as a function of the mini mixer screw speed for three different temperatures. The samples were kept 5 min in the mini mixer.

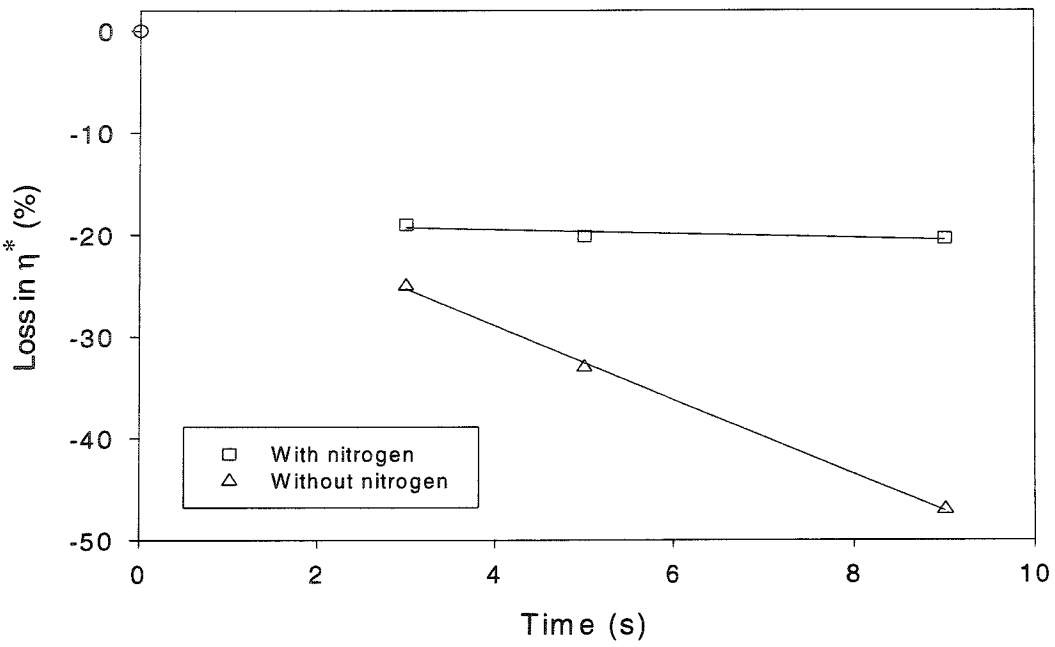
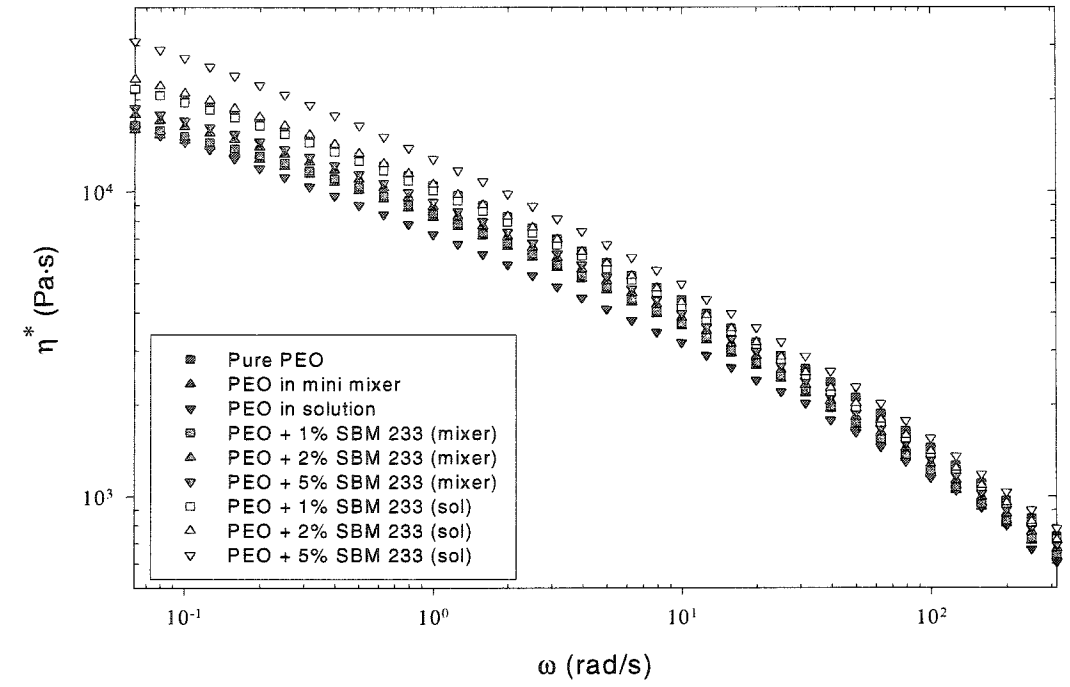
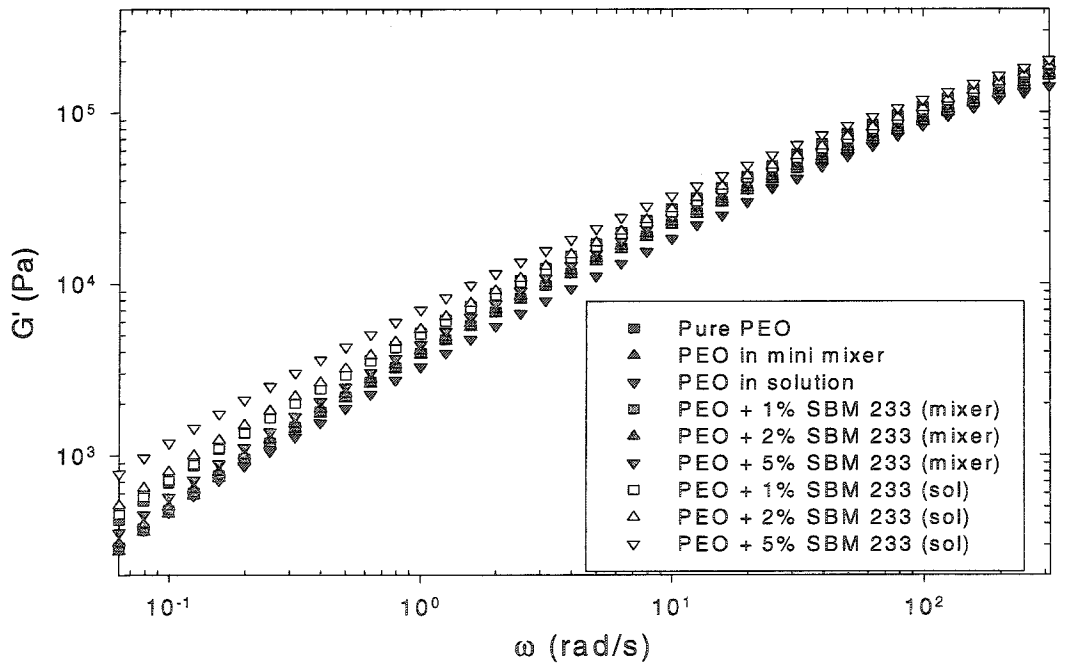


Figure 4.4: Effect of the residence time on the loss of complex viscosity of the PEO (measured at1 Hz and 100°C), processed in the mini mixer at 120° C and 90 rpm, under or without nitrogen.



a)



b)

Figure 4.5: Comparison of the viscoelastic behavior at 100°C of pure PEO, pure PEO processed in the mini mixer or in solution, and blends of PEO and 1%, 2%, 5% of SBM 233, blended in the mini mixer and in solution

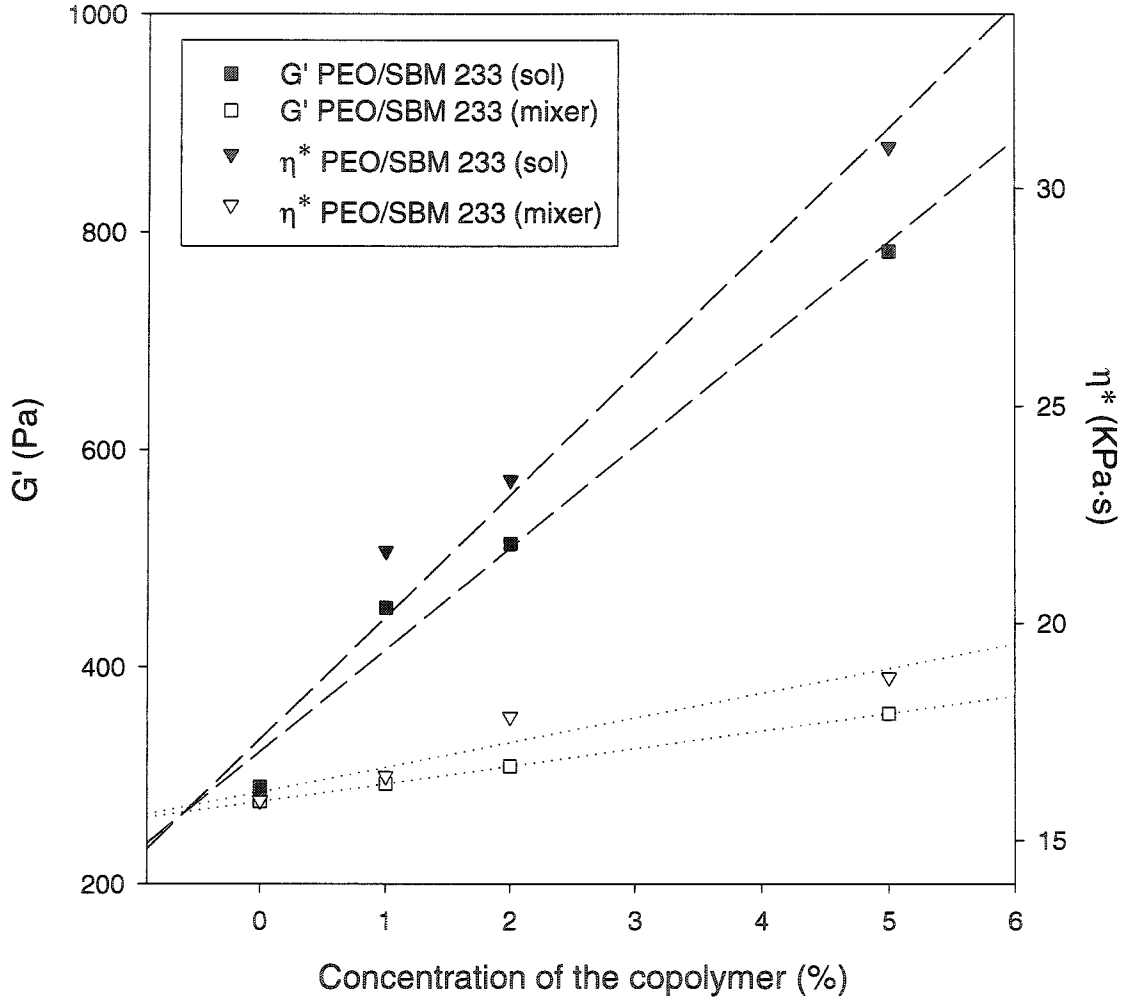


Figure 4.6: Effect of the concentration of the copolymer on the storage modulus and the complex viscosity of PEO/SBM 233 blends, prepared either in the mini mixer or in solution.

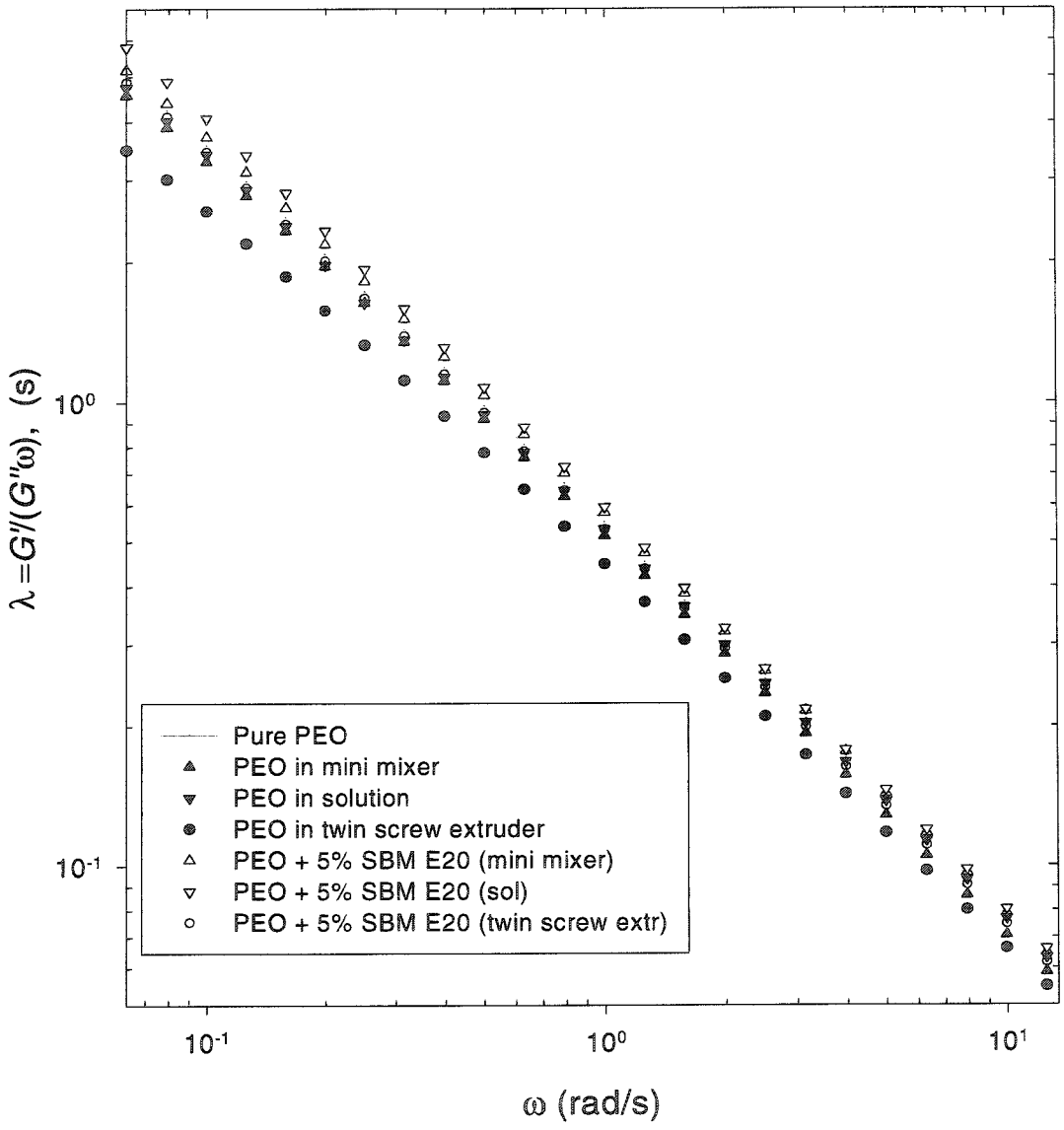


Figure 4.7: Elastic characteristic time for blends of PEO and 5% SBM E20 prepared with the mini mixer, with the twin screw extruder, and in solution, compared with pure PEO processed in the same ways and pure PEO molded directly from powder.

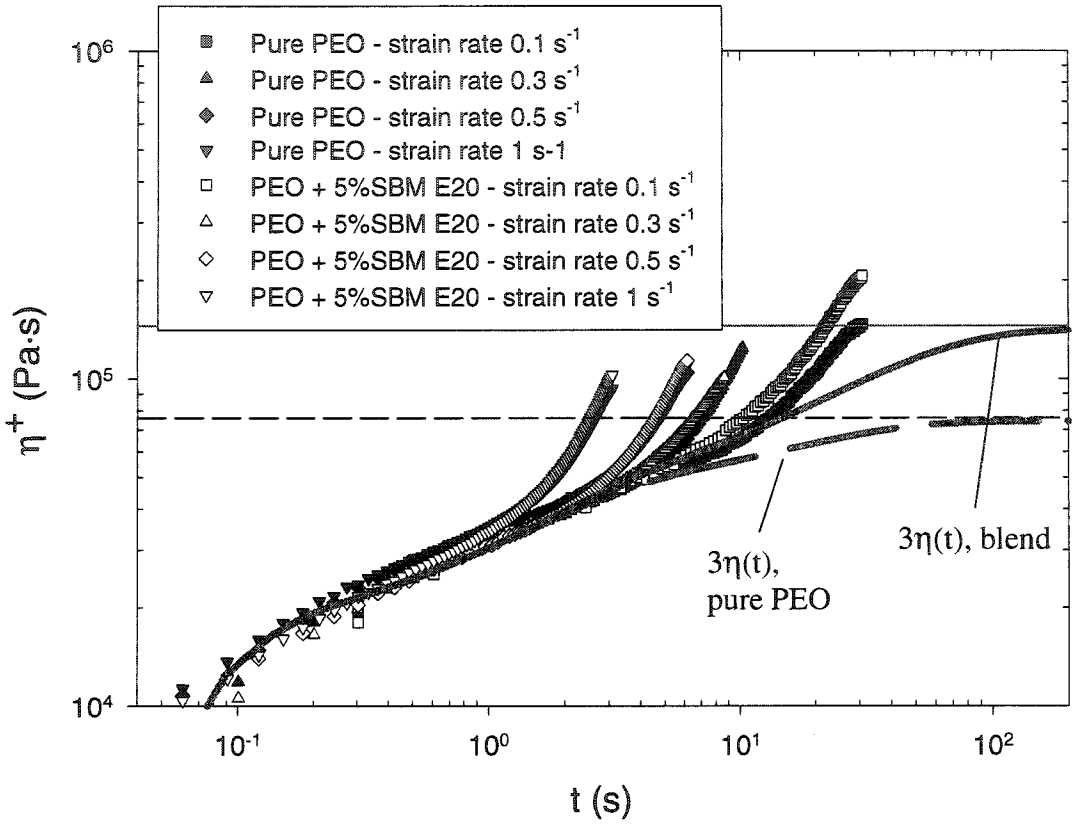


Figure 4.8: Elongational viscosity of pure PEO and a blend of PEO and 5% SBM E20 as a function of time.

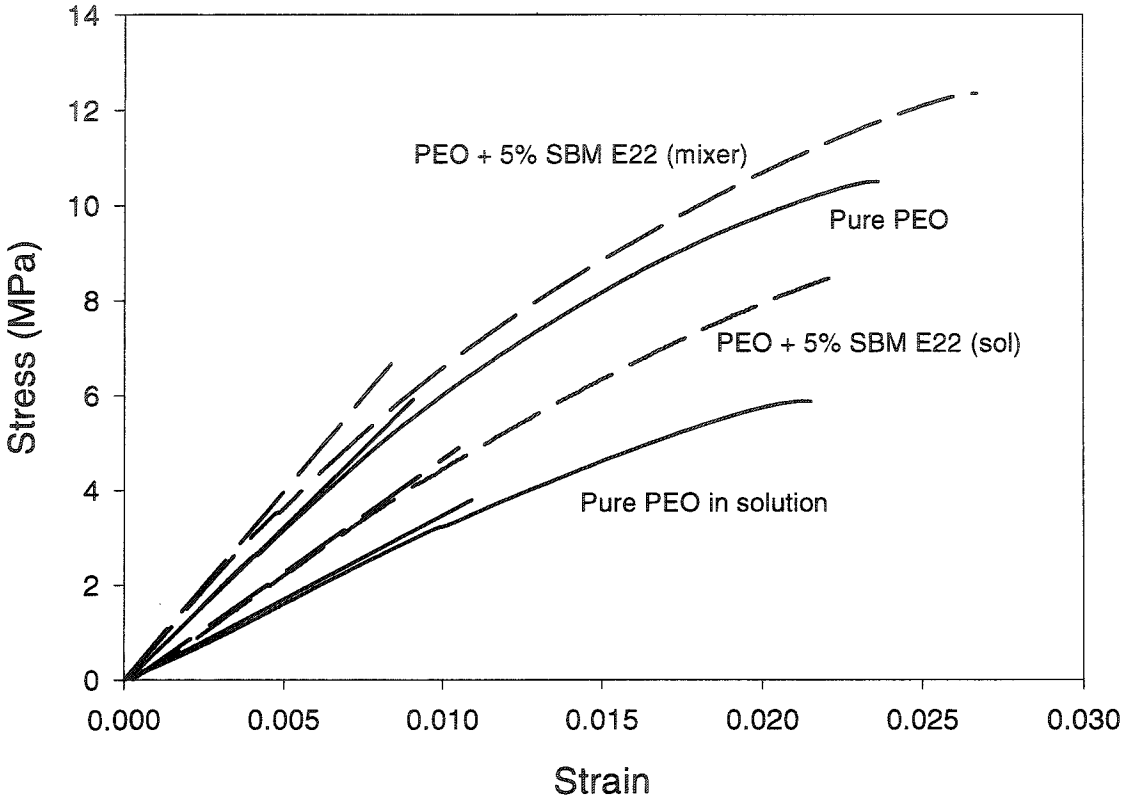


Figure 4.9: Stress-strain curves of pure PEO and PEO/5% SBM E22 blends, for samples prepared through different methods.

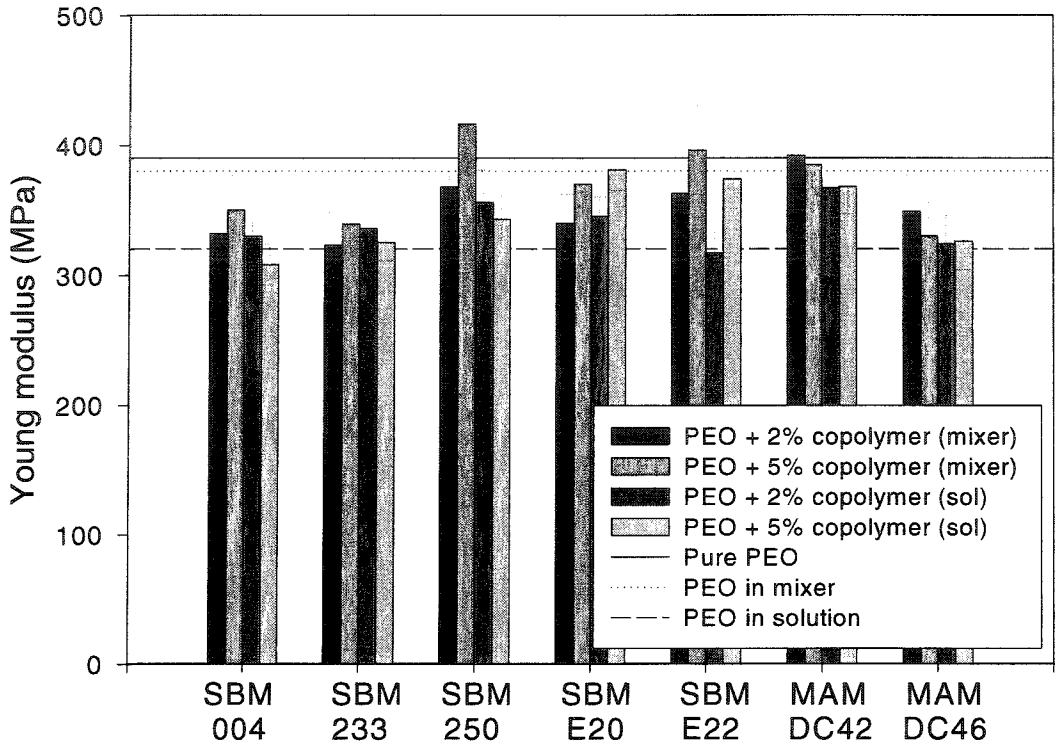


Figure 4.10: Young modulus for blends of PEO and 2% or 5% copolymer prepared both in the bulk (mini mixer) and in solution

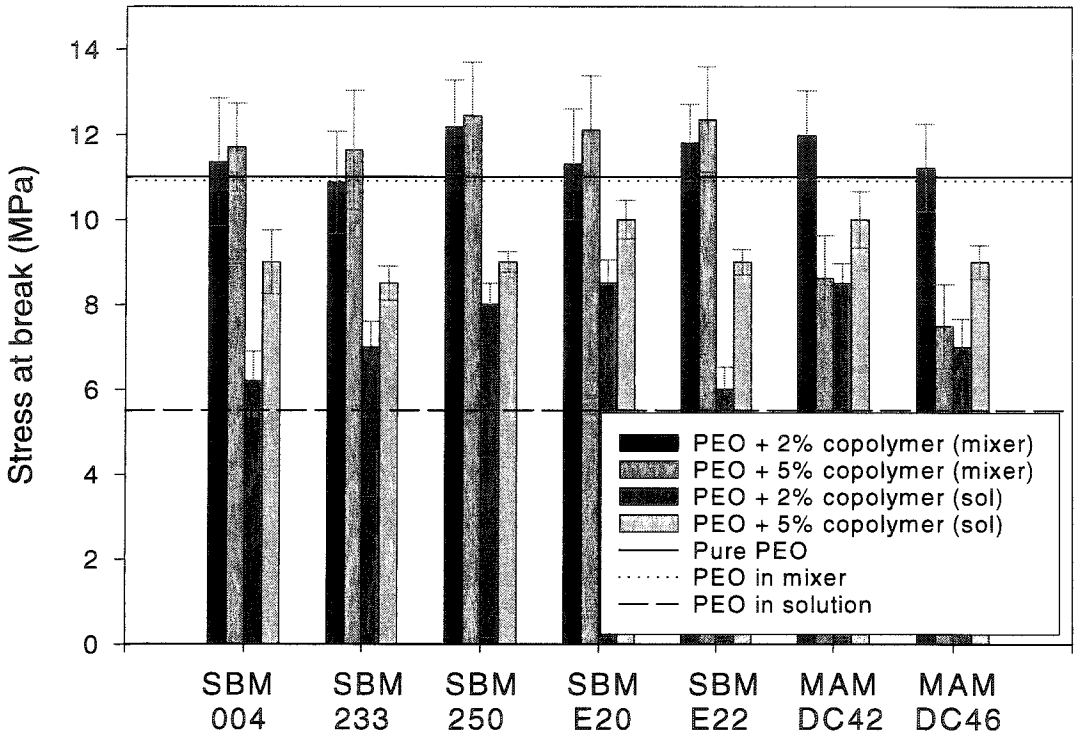


Figure 4.11: Stress at break for blends of PEO and 2% or 5% copolymer prepared both in the bulk (mini mixer) and in solution

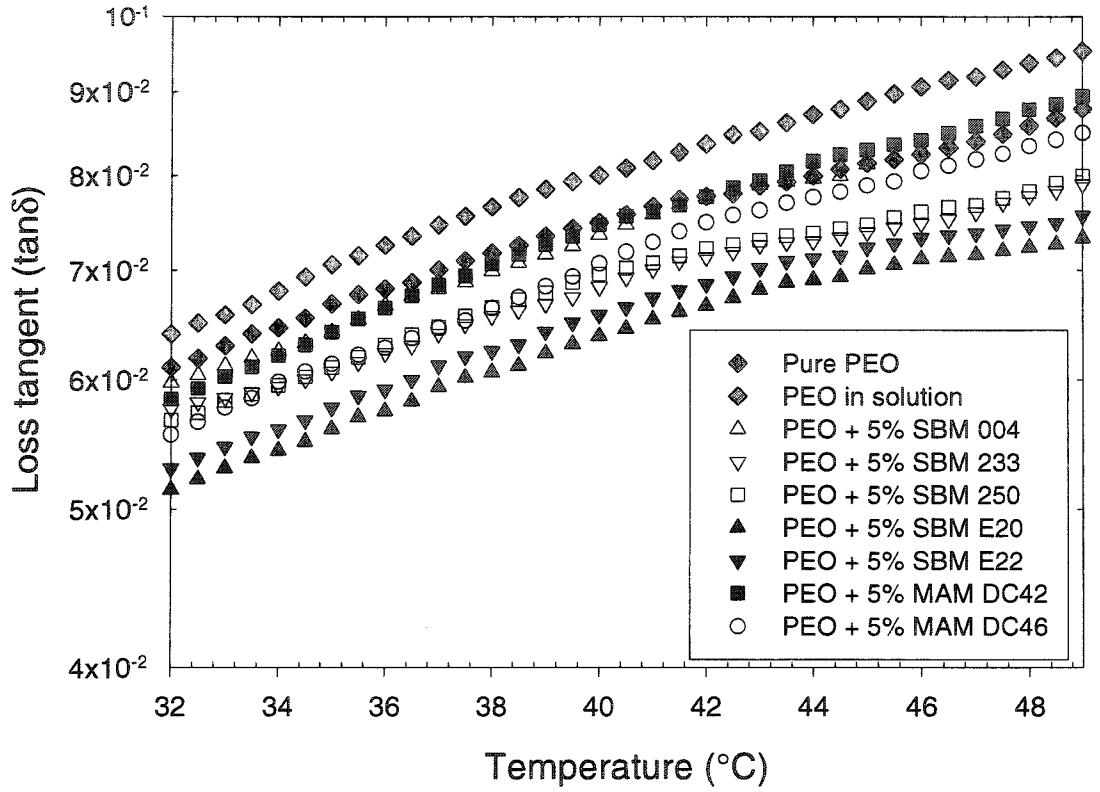


Figure 4.12: Loss tangent, measured by dynamic mechanical analysis in flexion of pure PEO and PEO/5% block copolymer blends prepared by solution

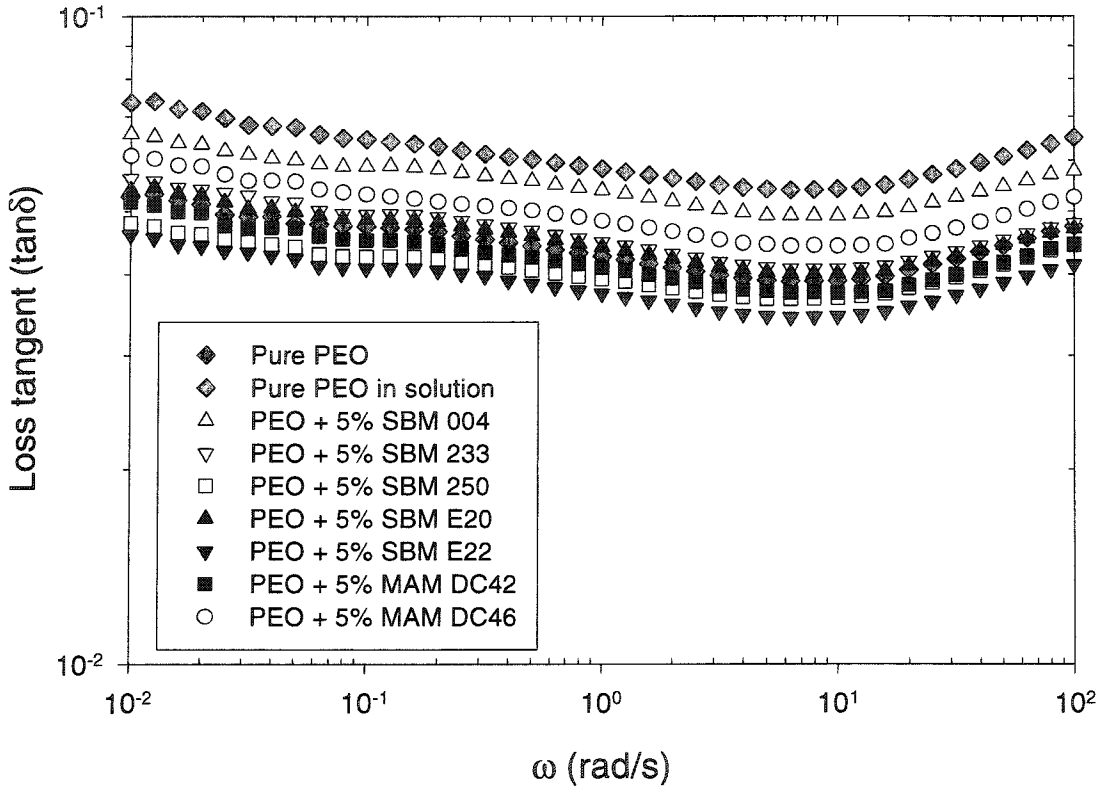


Figure 4.13: Loss tangent, measured at 25°C by dynamic mechanical analysis in torsion of pure PEO and PEO/5% block copolymer blends prepared by solution

CHAPTER 5

GENERAL DISCUSSION

5.1. Problems associated with the stability of PEO

Polyethylene oxide is a very difficult material to study; its properties change very easily with time. It is very difficult to obtain reproducible results and reliable data on PEO. There are many discrepancies in the literature. Bigger et al. (1991), for example, listed all the values of the glass transition temperature calculated for PEO from previous works, which differ in same case of as much as 20°C for samples of the same molecular weight. This was attributed to the different thermal histories experienced by the samples, as well as the different molding conditions. As discussed in the introduction, PEO tends to degrade even in the solid state. Special care has to be given to the storage conditions. It can't be stored at temperatures higher then its melting point. From rheological measurements we found a drop in the complex viscosity of as much as 40%, after it was stored for 24 hours at 80°C in a vacuum oven, and thus in a place with a low content of oxygen and humidity. Even for storage temperatures lower then the melting point, it can't be stored for long times. Again we found a drastic drop in the complex viscosity after it was stored for six months at 40°C in the same vacuum oven (Figure 5.1). Humidity has a catastrophic effect as well; samples kept for six months in ambient conditions of temperature and humidity had a drop in the viscosity even lower then 50%. Even during the molding process the PEO is degraded. We varied the molding temperature from 100°C to 150°C and found a small but sensible difference (around 2%) in the complex viscosity. This is not a thermal effect as we know that 150°C are not enough to cause thermal degradation (Fares et al. 1994); the problem is that the molding press is not isolated from ambient atmosphere, from oxygen and

humidity; in the presence of oxygen temperature plays a major role, as, if it increased, it provokes a great increase of the rate of oxidation.

Anyhow, our objective was not to have exact data on PEO. Our objective was to investigate the effect of the copolymer on pure PEO. All we had to do, then, was to give special care to the conditions in which the blends were prepared, stored, molded, and analyzed. Every step was repeated exactly in the same way for every blend. This way, the changes in the molecular weight and humidity conditions of pure PEO should not have an impact on the conclusions we obtained about the effect of the addition of the copolymer.

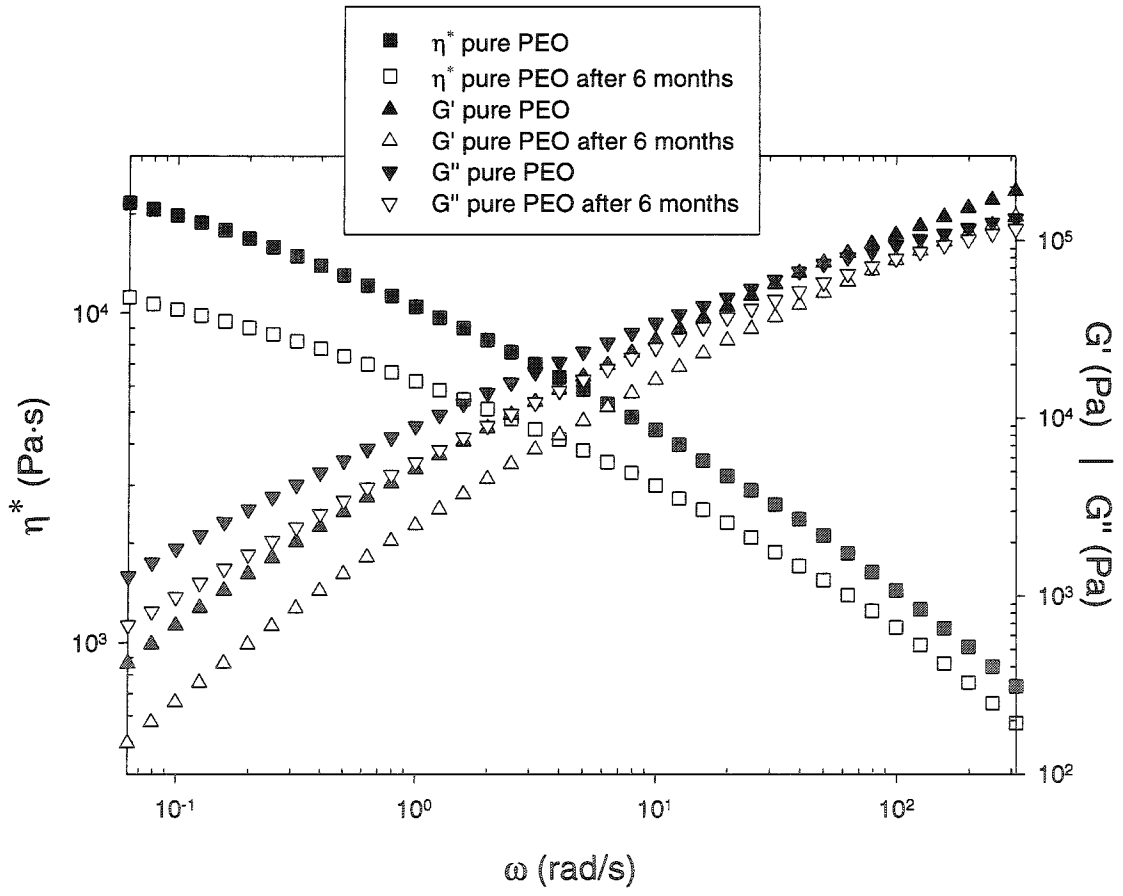


Figure 5.1 : Comparison of the viscoelastic properties of pure PEO with another sample of the same PEO, kept for six month in a vacuum oven at a temperature of 40° C.

5.2. Observations about the blending technique

5.2.1. Blending in the Brabender

We tried to investigate the different techniques that would let us obtain blends with small quantities of material. The instruments we could use were the Plasticorder Brabender and the Haake Minilab. In particular, we tried many times to obtain blends with the Brabender, unsuccessfully. This is unexpected. Indeed, the Brabender imposes much higher shear; through rheological measurements we found that the complex viscosity decreases a lot more, at the same temperature and comparable strain rate, when the polymer is processed in the Brabender. A higher shear should let us obtain better blends; on the contrary the pellets of the copolymer are always still visible; they never dissolve completely in the PEO matrix, even if it is left in the blender for a long time. Evidently the copolymer pellets cannot dissolve in a PEO that is too degraded, and which has, therefore, a very low viscosity.

5.2.2. Blending in solution

The influence of the different parameters on degradation a polymer in solution is discussed extensively in the literature. Influence of temperature, strain rate, concentration, and type of solvent was studied. We did not question the influence of the type of solvent, as chloroform was the only common solvent that was found to be usable for these kinds of blends. Toluene, for example, is also a common solvent of PEO and SBM/MAM, but not at ambient temperature. As we evaporated the solvent at ambient temperature toluene could not be used. We varied strain rate, temperature, and concentration to see their effects. Increasing strain rate also provoked an increasing in degradation of PEO, but this is quite obvious, considering the fragility of PEO's chains and the fact that they break as soon as they are exposed to shear. We tried to minimize as possible the strain rate. In order to have some clues on the effect of temperature we made some blends at ambient temperature and at 61° C, boiling point of chloroform.

The effect of temperature was not quantified in a systematic way; the strain rate could not be kept to be exactly the same, as the machinery used was different (for blending at high temperatures a condensation column was used). The mechanical energy necessary to obtain the blend was provided, in the case of blends made at 61° C, just by natural convection; strain rate was smaller then for blends made at ambient temperature. Nevertheless we found that pure PEO blended at 61° C was slightly more degraded; we can therefore conclude that, even in solution, temperature plays a role in the degradation of PEO; anyhow, as the difference was small, and as increasing the temperature let us obtain a more positive effect of the copolymer, blends were made at 61° C. The effect of concentration was also discussed. Nakano et al. (1971) found that concentration of PEO did not have a role in its degradation, thus concluding that scission of the chains is not caused by intermolecular interaction. We made blends at different concentrations (5–50 g/L), and then compared the average molecular weight in viscosity with viscosimetric measurements; we found no evident effect of concentration on *Mv* of PEO. Our result is thus in agreement with Nakano et al. (1971).

5.3. Gel permeation chromatography (GPC)

GPC was performed in order to obtain some information on the degradation of the PEO during the blending process. The experiments were performed at Avestor (Boucherville, Qc). Samples of pure PEO and of pure PEO passed to the mini mixer (T=120°C, 90 rpm, 5 min) were tested. The solvent in which they were dissolved (concentration: 0.3%) was a blend of Acetonitrile (50 % in volume) and a water solution containing 5% of sodium acetate.

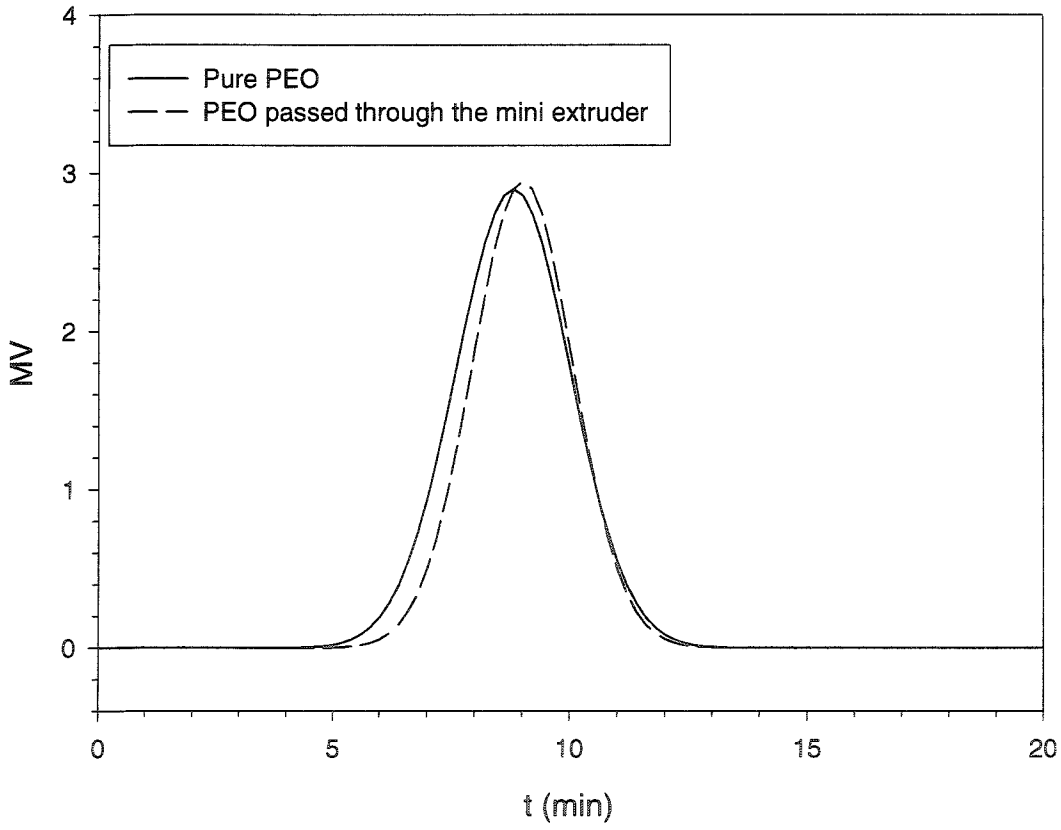


Figure 5.2: GPC graph: comparison in the molecular weight distribution between PEO taken in a powder form, PEO processed in the mini mixer.

Table 5.1: Average molecular weight and polydispersity of pure PEO and pure PEO processed in the mini mixer.

POLYMER	M_n	M_w	Pd
Pure PEO	24976	171050	6.9
PEO in Mixer	24126	110312	4,6

Experiments made on different samples gave a very good reproducibility. The data is in agreement with the measurements of the viscosity average molecular weight and seems to be accurate. The previous experiments gave no information about the molecular weight distribution of the PEO and the impact of the processing method on the MWD. This information can be obtained by looking at the GPC chromatogram (Figure 5.2), where the first signal obtained (in time) represents the largest molecules exiting from the column. We can conclude that the processed PEO has a smaller number of long chains, compared to the PEO tested without any treatment. When the PEO is exposed to shear, for example in the mini mixer, its longest chains, being the most sensitive to mechanical degradation, break into shorter chains. This causes a narrowing of the molecular weight. The conclusion is that, blending the PEO with the copolymers, we provoke a decrease of its polydispersity.

This result is in agreement with our rheological measurements. By looking at curves of the complex viscosity in the low frequency region (Figure 4.5), we notice that the slope of the initial part of the curve is larger for the pure PEO passed through the mini mixer, while it is smaller for PEO tested as received. It is well known that a higher slope of the curve corresponds to lower polydispersity and a smaller slope corresponds to higher polydispersity.

5.4. Differential scanning calorimetry (DSC)

Some DSC measurements were also performed on both the blends obtained by melt processing and by solution casting technique, to see if the copolymer has an influence on the cristallinity of the PEO. If we remember that the first application thought for these blends is as the electrolyte of a polymer battery, we know that conductivity is greatly affected by the cristallinity of the polymer; conduction takes place only in the amorphous region of the polymer (Scrosati et al. 1990).

The curves we obtained for PEO/5% copolymer blends obtained with the mini mixer are shown:

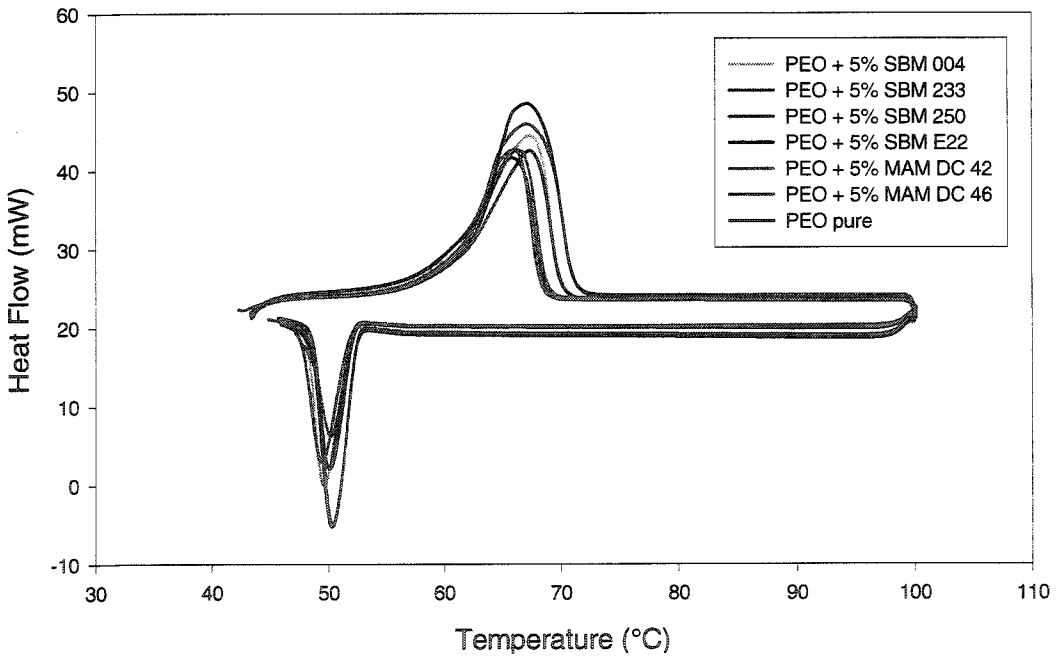


Figure 5.3: DSC scan of pure PEO and PEO/5% block copolymer blends obtained with the mini mixer (T=120°C, 90rpm, 5min). Heating rate: 5°C/min.

We see that, for all the blends, the shape of the curve is the same. Some authors (Scheirs et al. 1991) found that when PEO is exposed to severe oxidation it shows two distinct melting peaks in the DSC curves. The second peak can be related to the

formation of lower-molecular-weight material with different lamellar thickness. We didn't find any sign of this second peak. The copolymer does not have an influence on the melting point or on the temperature of crystallization of pure PEO. Cristallinity was calculated with the formula: $\alpha = \frac{\Delta H_m}{\Delta H_m^0}$. ΔH_m^0 was taken as 205 J/g (Khasanova et al. 2003). ΔH_m s and the cristallinity of the blends are listed in the following table:

Table 5.2: Cristallinity of the PEO and block copolymers blends (2% and 5% in weight) prepared both by extrusion and solution

	Extrusion		Solution	
	2%	5%	2%	5%
Pure PEO			138 J/g	**67.3%**
SBM AF-X 004	125 J/g **62.2%**	125 J/g **64.0%**	127 J/g **63.2%**	126 J/g **64.5%**
SBM AF-X 233	130 J/g **64.7%**	135 J/g **69.1%**	133 J/g **66.2%**	125 J/g **64.0%**
SBM AF-X 250	132 J/g **65.7%**	130 J/g **66.6%**	134 J/g **66.7%**	133 J/g **68.1%**
SBM AF-X E20	139 J/g **69.2%**	138 J/g **70.7%**	132 J/g **65.7%**	131 J/g **67.1%**
SBM AF-X E22	133 J/g **66.2%**	127 J/g **65.0%**	138 J/g **68.7%**	140 J/g **71.7%**
MAM DC 42	132 J/g **65.7%**	129 J/g **66.1%**	136 J/g **67.7%**	133 J/g **68.1%**
MAM DC 46	131 J/g **65.2%**	128 J/g **65.6%**	132 J/g **65.7%**	133 J/g **68.1%**

As we can see, percentages of cristallinity vary very little according to the quantity and kind of copolymer added. We can conclude that the presence of the copolymer does not have a significant effect on the crystallization of PEO.

5.5. Blend prepared with the twin screw extruder

A blend was made with a twin screw extruder from Leistritz (model ZSE 18HP). As already mentioned this project aimed at studying a blend that can be used in an industrial scale. We studied the effect of the copolymer on PEO, blending with the mini mixer and by solution casting technique. It is obvious that the mini mixer is a very useful instrument in the lab, but it has no use at a production scale. Solution casting techniques, then, are sometimes used industrially, but are expensive and the solvent is not easily removed completely. After the complete characterization of all the blends, we chose one grade of copolymer, and we made a blend in a twin screw extruder, which, although it is small if compared to an industrial extruder, can give an idea of what happens when we work with large quantities of polymer. We looked for a grade of SBM which gave good rheological properties, namely a good increase in elasticity. We chose grade E20, which is actually the SBM which increases elasticity the most. We notice, looking at Table 4.3 that we could reach even better results with the MAM copolymer; anyhow, for our experience, MAM requires more drastic conditions to be completely solubilized in the mini mixer, and higher residence times. Moreover, we only had MAM in the form of pellets, while SBM E20 was in the form of little pellets; considering the small residence time of the polymers in the extruder, we considered that we could obtain a better and more homogeneous blend with SBM E20.

It is clear that in the twin screw extruder PEO is exposed to higher shear then in the mini mixer and in solution; as a consequence, we expect a higher extent of degradation; also, PEO is extremely sensitive to thermal oxidation; even though a vacuum was applied in the chamber, the isolation from oxygen could not be as good as in the mini mixer. Our expectations were confirmed by measurements of the viscosity average molecular weight, which was found to be 61390 g/mol, against 73020 g/mol of pure PEO passed through the mini mixer, and 82630 g/mol of PEO put in solution (Table 4.2).

Figure 5.4 represents the rheological curves for the blend of PEO and 5% SBM E20, for pure PEO passed though the extruder, and therefore degraded, and for pure PEO just molded from powder, and therefore not degraded. The drop in the molecular weight provokes a great drop in the complex viscosity curve. Anyhow, the general behavior is the same that we discussed for blends prepared with the other methods, as the viscosity and the elastic modulus of pure PEO decrease because of degradation, but then increase again due to the addition of the copolymer. However, if we compare these rheological curves to the curves of the blends obtained with the mini mixer (Figure 4.5) we can notice that the differences between the curves are larger. It is obvious that the decrease after processing is larger, because of greater degradation. The fact that there is a greater increase upon addition of the copolymer, on the contrary, is surprising. We can make the same conclusions if we look at the curves of elasticity.

We calculated the zero shear viscosities for pure PEO passed to the twin screw extruder and for the blend PEO/SBM E20, using the Carreau-Yasuda model. We used the rheological data represented in Figure 5.4, interpolating the complex viscosity curves. The expression of the model is the following:

$$\frac{\eta^*(\dot{\gamma})-\eta^*_\infty}{\eta^*_0-\eta^*_\infty}=\left[1+(\omega\lambda)^a\right]^{\frac{n-1}{a}}$$

η^*_∞, the constant value that the viscosity function approaches for large values of $\dot{\gamma}$, was set to 0; η^*_0 is the zero shear viscosity. We found a η_0 of 65267 Pa·s for the blend and 29137 Pa·s for the pure PEO. The zero shear viscosities had already been calculated with the Maxwell model (the lines of the uniaxial elongational viscosity growth function shown in Figure 4.8 represent the linear viscoelasticity multiplied by three; the value for $t \to \infty$ is three times the η_0). The fact that values calculated with different models resemble each other suggests that our calculations were correct.

As for the mechanical properties, Figure 5.5 represents the stress-strain curves for pure PEO and the blend prepared in the twin screw extruder, while Figure 5.6 represents the storage modulus, calculated with DMA and plotted as a function of temperature, for the same blend. The copolymer increases the tensile strength, the Young modulus, and the storage modulus in flexion of pure PEO. These results are in line with the others. The increase in the mechanical properties, again, is more consistent in this case; we assume the copolymer is better organized and better dispersed in the PEO matrix when blending is made in the twin screw extruder.

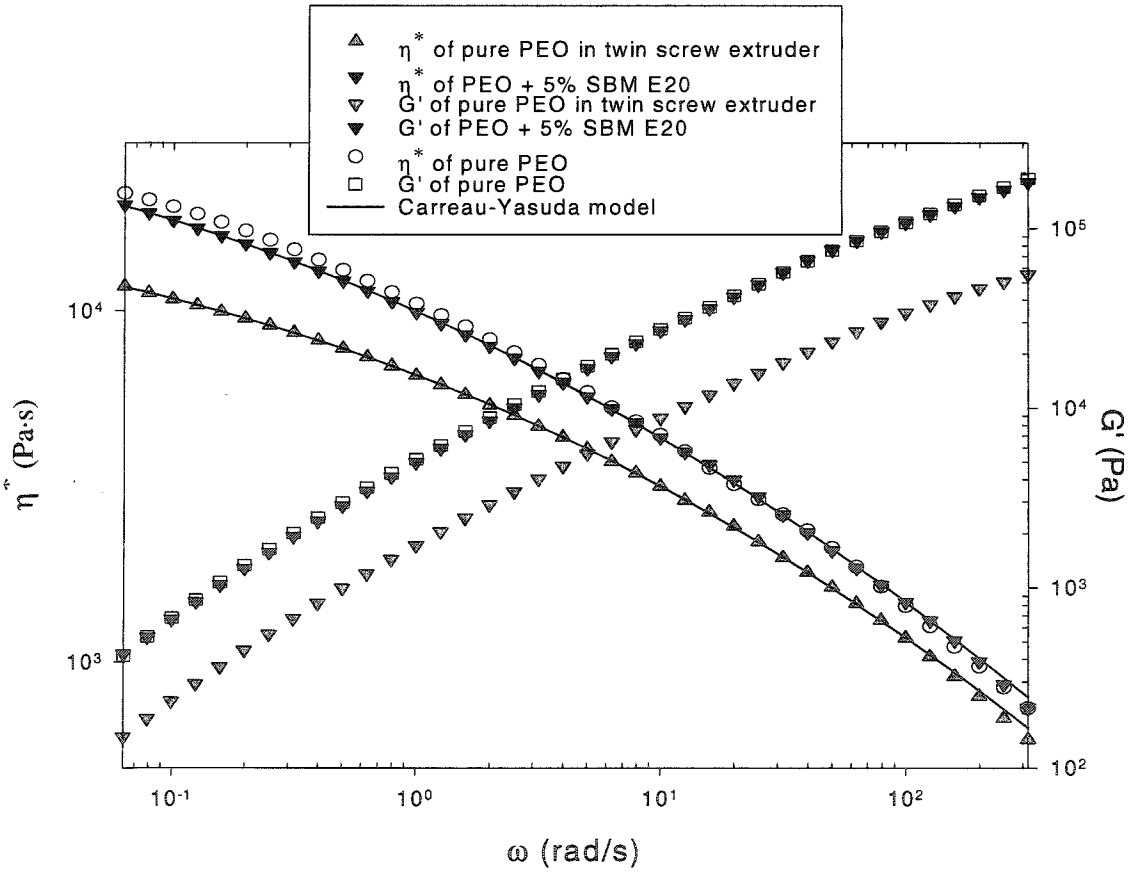


Figure 5.4: Comparison of the viscoelastic behavior at 100°C of pure PEO passed through the twin screw extruder and a blend of PEO/SBM E20 prepared with the twin screw extruder (120°C, 90 rpm). Interpolations made with the Carreau-Yasuda model.

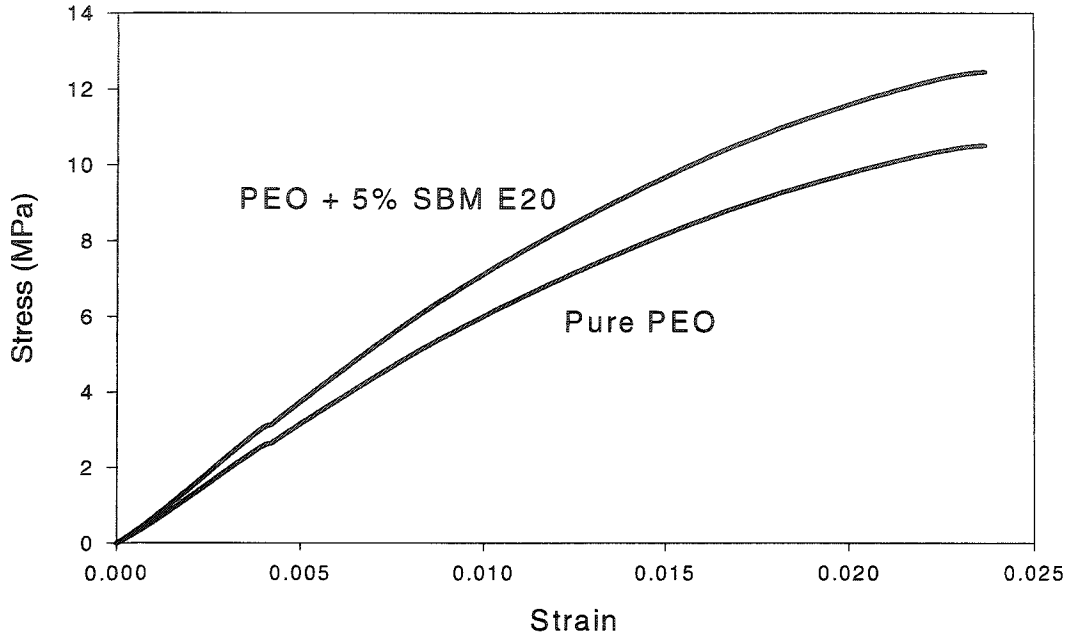


Figure 5.5: Stress-strain curve for a blend PEO and 5% SBM E20 prepared in the twin screw extruder (T=120°C, 90 rpm), compared to pure PEO.

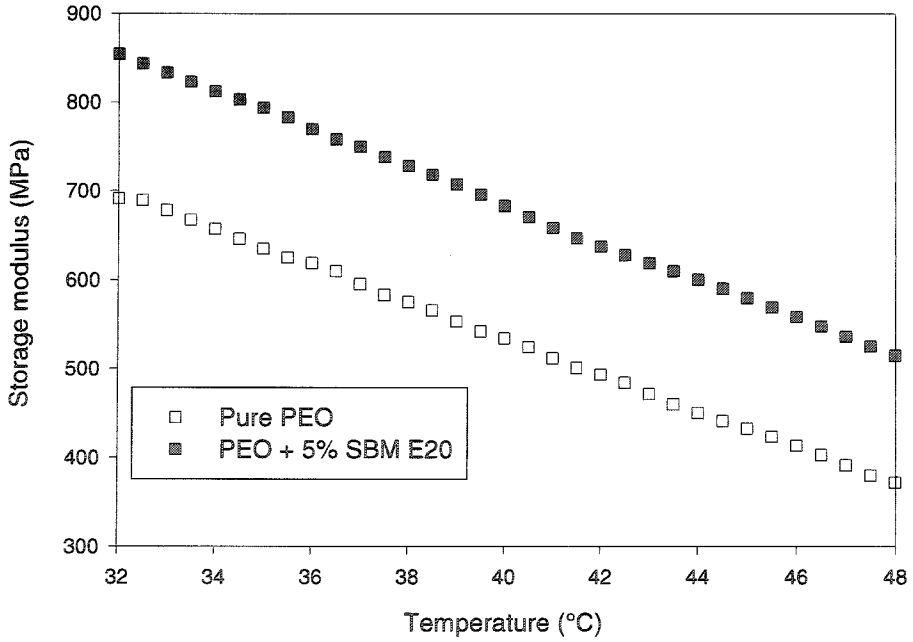


Figure 5.6: Storage modulus, measured with DMA, of a blend of PEO and 5% SBM E20 (prepared in extruder T=120°C, 90 rpm) compared to pure PEO.

CHAPTER 6

CONCLUSIONS AND PROSPECTIVE

6.1. Conclusions

The aim of this study was to improve the processability of polyethylene oxide in the melt state, without affecting its properties in the solid state. Important variables in the discussion of processability are melt elasticity (*G'/G"*), shear viscosity and elongational viscosity. From an experimental point of view, the goal was to find a blend that, while maintaining the mechanical and electrical properties of pure PEO, would increase its melt elasticity without increasing much its shear viscosity. 1 to 5% percentages of the copolymers SBM and MAM were added to pure PEO. Different blending techniques were used. A complete characterization was performed on blends obtained by melt processing in a mini mixer and solution casting techniques. At the end a blend was prepared using a twin screw extruder. Rheological and mechanical properties were found to depend considerably on the blending technique. A major problem in processing PEO is that it is very sensitive shear. Its chains break very easily because of mechanical degradation, which was found to be very dependent on temperature. Parameters such as temperature, strain rate and blending time were varied in order to find the technique that would let us obtain the best possible rheological properties. Measurements of the average molecular weight in viscosity were carried out in order to quantify degradation. As it was expected the gentlest method was found to be solution casting technique, the most drastic melt processing in the twin screw extruder.

Through a rheological characterization, performed with small amplitude oscillatory shear tests, it was possible to conclude that the copolymer increases most of the times the melt elasticity of pure PEO, as it increases its elastic modulus more than its

complex viscosity. The increase was greater for blends obtained by solution casting technique. The blend prepared with the twin screw extruder gave a good result too. We know that properties depend on the size of the copolymer domains and on their dispersion in the PEO matrix. In the twin screw extruder PEO is exposed to higher shear and the copolymer domains should therefore be smaller and better dispersed. A better dispersion is also expected for blends prepared in solution, in which the polymers are kept in contact with each other for 24 hours.

A RER rheometer was then used to make some measurements of the elongational viscosity. The uniaxial elongational step growth coefficient was plotted in function of time. Pure PEO was compared with a blend of PEO/5% SBM E20 prepared with the twin screw extruder. The copolymer increased the elongational viscosity of pure PEO, and also increased its strain hardening property, which is believed to be very important for the production of thin films.

After the rheological characterization, a complete mechanical characterization was carried out. Tensile tests and dynamic mechanical analysis in flexion and in torsion were performed. Tensile strength was found to increase with addition of the copolymer; the effect on the Young modulus was not significant. For blends obtained by solution casting technique we can say that small traces of the solvent, which is very difficult to remove completely, provoke a great decrease of the tensile strength. The samples should by left to dry for several days at a high temperature. Anyhow PEO is known to degrade even in the solid state, if it is stored at high temperature and long times. Loss in the molecular weight, evidently if not too drastic, does not cause a large loss in the mechanical properties. For blends obtained by solution a drying procedure should be carefully designed in function of the desired properties for the specific application. DMA measurements showed that the storage modulus increases after addition of the copolymer.

Cristallinity of PEO was calculated with DSC measurements and was found not to be affected by addition of the copolymer.

6.2. Prospective

We concluded that these copolymers, SBM and MAM, can improve the processability of pure PEO. We know that the extensional properties of a polymer play a major role in determining whether it has a good processability or not. More experiments on elongational properties should be carried out. Many instruments could be used: the ARES rheometer; the RME extensional rheometer of Rheometrics Scientific, available at IMI; experiments could be performed with an on line rheometer attached to the injection molding machine in our laboratory.

Some observations with TEM could be done, to have a better understanding of the morphology of the blends, and see how the processing method affects the size of the copolymer domains.

We remember that the first application that had been thought for this blend is as an electrolyte in a polymer battery. We assumed that, since the quantity of copolymer that is added is very small, the electrical properties, namely the conductivity, should not be affected. This assumption should be verified. Measurements of the conductivity should be carried out for all the blends we studied.

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APPENDIX

Complete rheological characterization

In the following section we present the complete rheological characterization of the blends of PEO and SBM and the blends of PEO and MAM that we studied.

For each blend we present the behavior of the elastic modulus (G'), of the viscous modulus (G''), of the complex viscosity (η^*) as a function of the concentration of the copolymer (1%, 2% and 5%) and the blending processing method. The curves for pure PEO and pure PEO processed in the mixer or in solution are traced for comparison.

All the measures are taken with a SR5000 rheometer; the geometry used is parallel plates (diameter: 25 mm). The gap was set to be 1.25 mm.

All the measurements are stress controlled frequency sweeps; the amplitude of the stress is set to be 400 Pa. The temperature is 100° C.

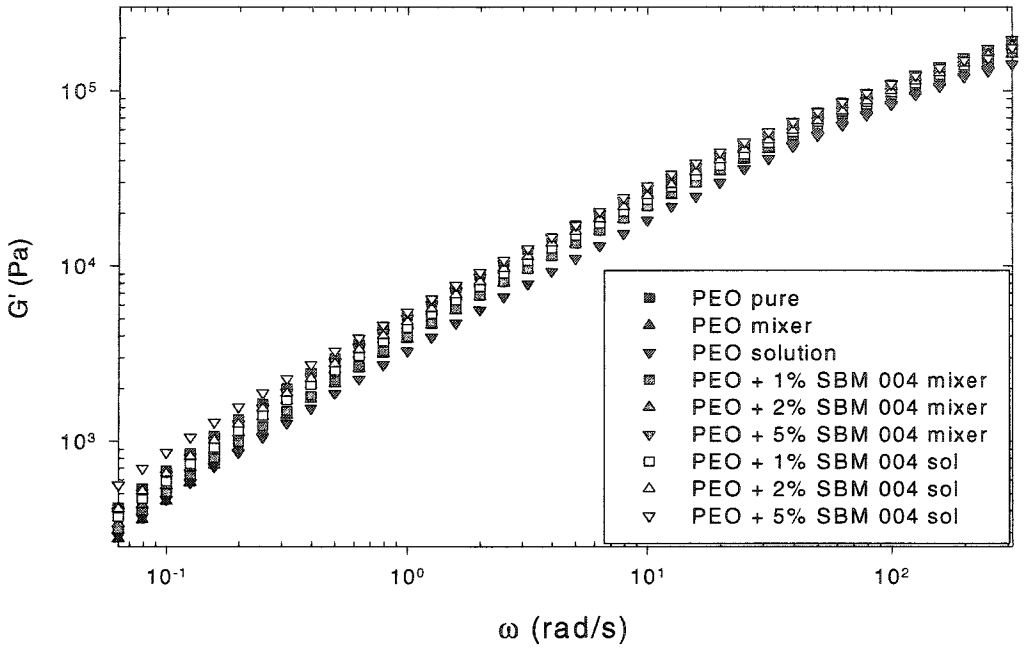

Figure A.1: G' (blend of PEO and SBM 004)

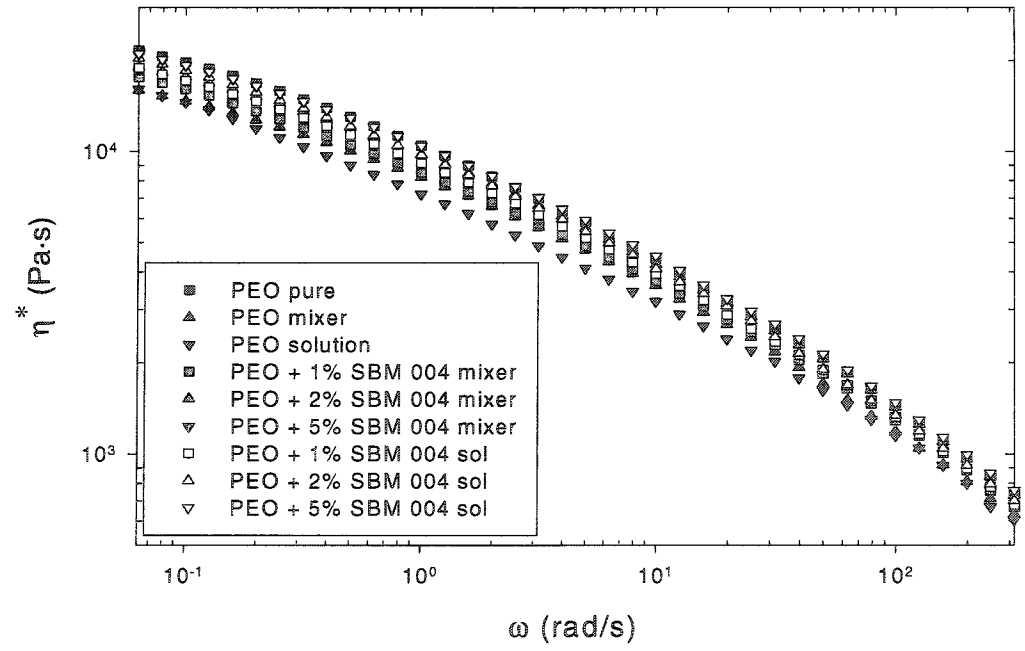

Figure A.2: η^* (blend of PEO and SBM 004)

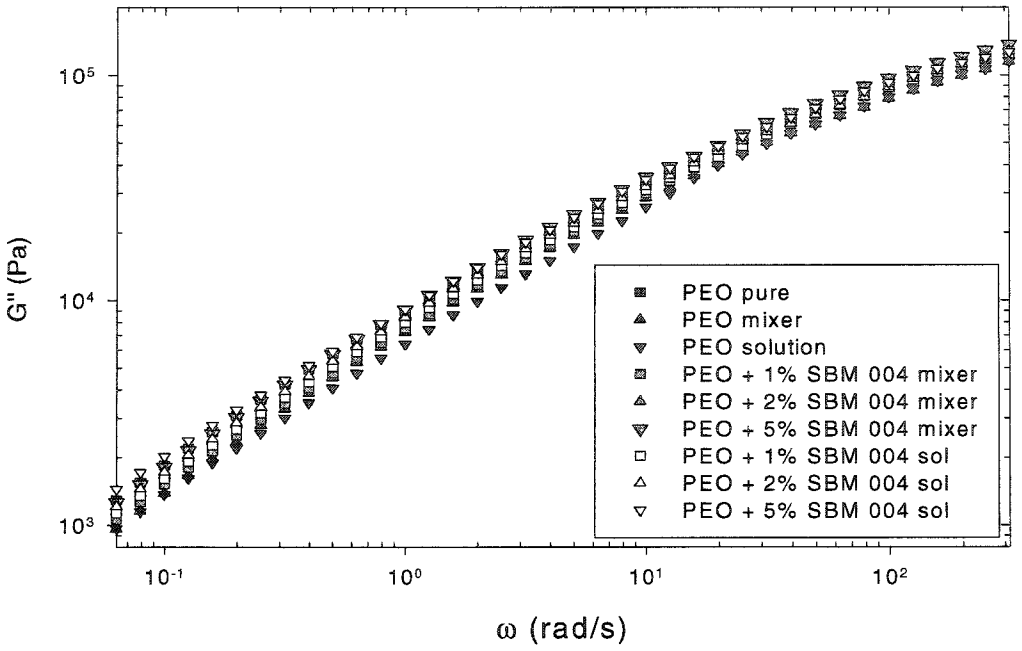

Figure A.3: G" (blend of PEO and SBM 004)

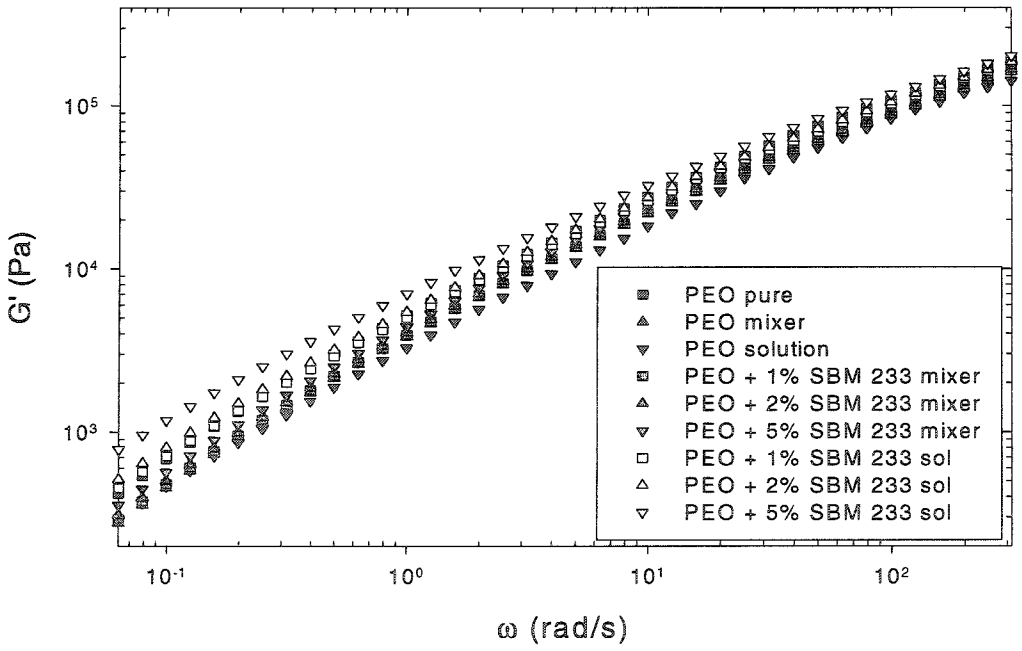

Figure A.4: G' (blend of PEO and SBM 233)

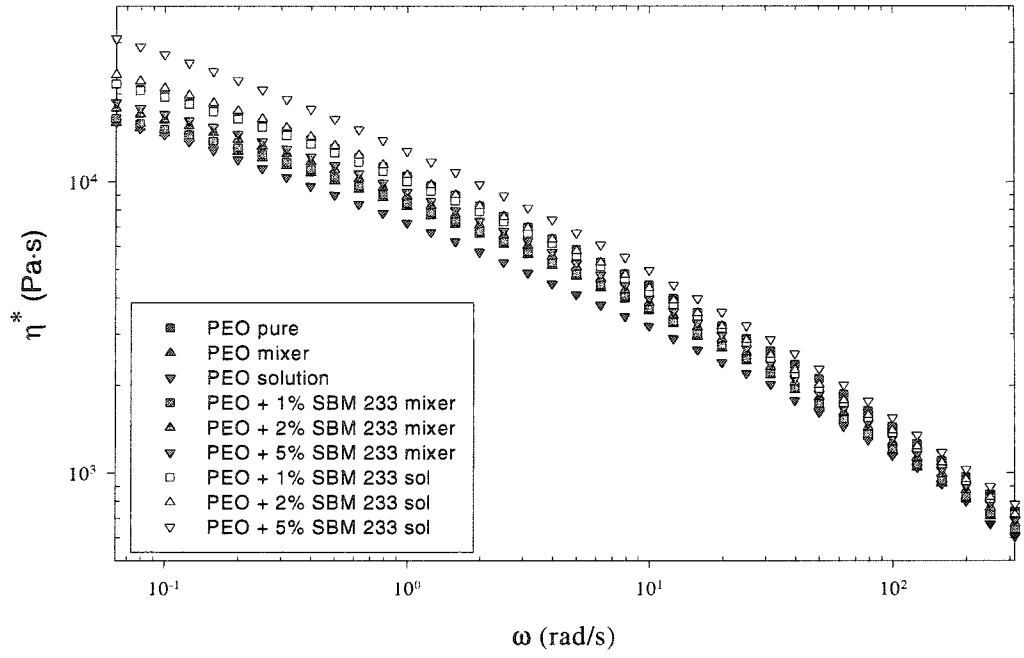

Figure A.5: η^* (blend of PEO and SBM 233)

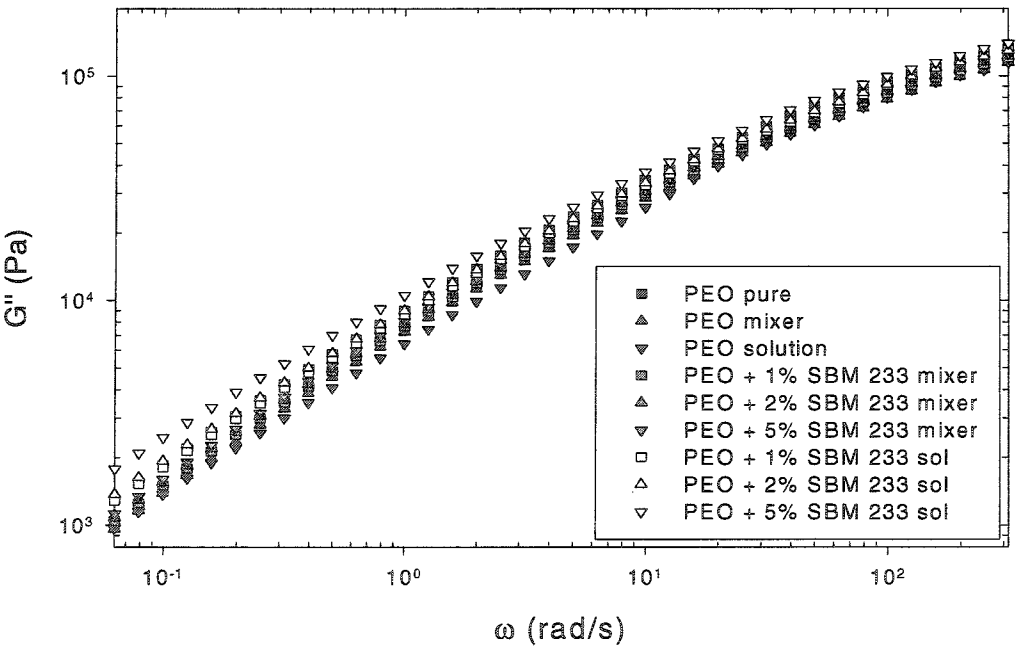

Figure A.6: G" (blend of PEO and SBM 233)

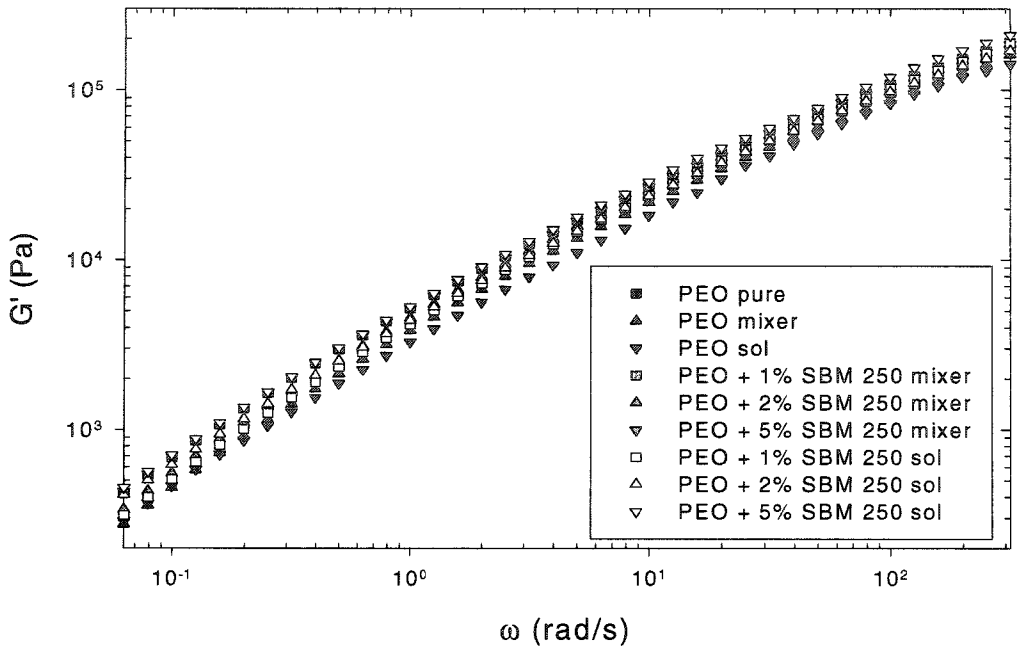

Figure A.7: G' (blend of PEO and SBM 250)

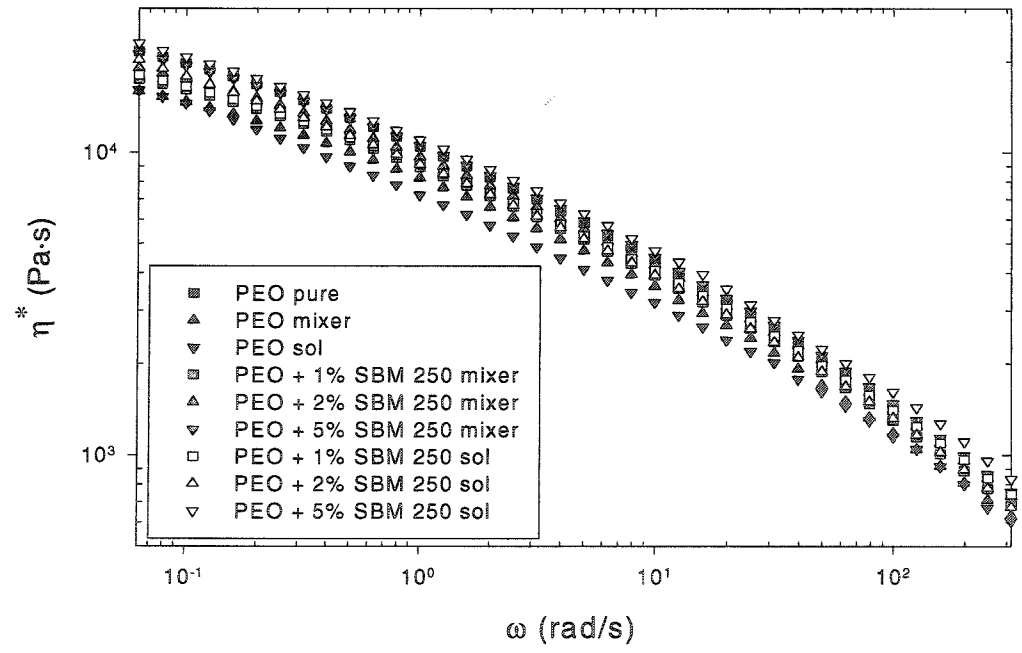

Figure A.8: η^* (blend of PEO and SBM 250)

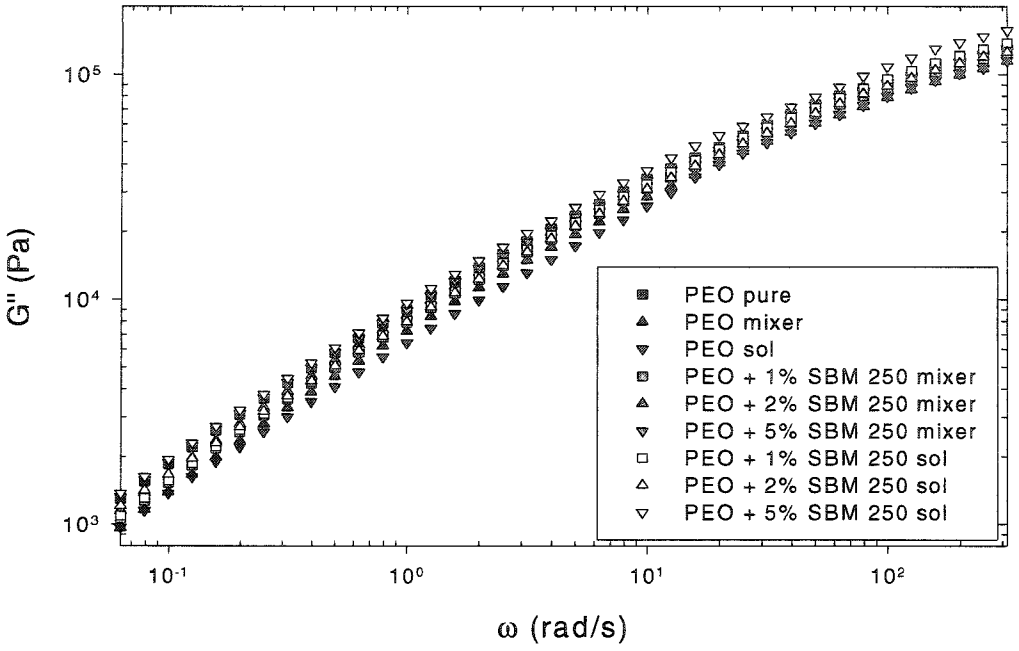

Figure A.9: G" (blend of PEO and SBM 250)

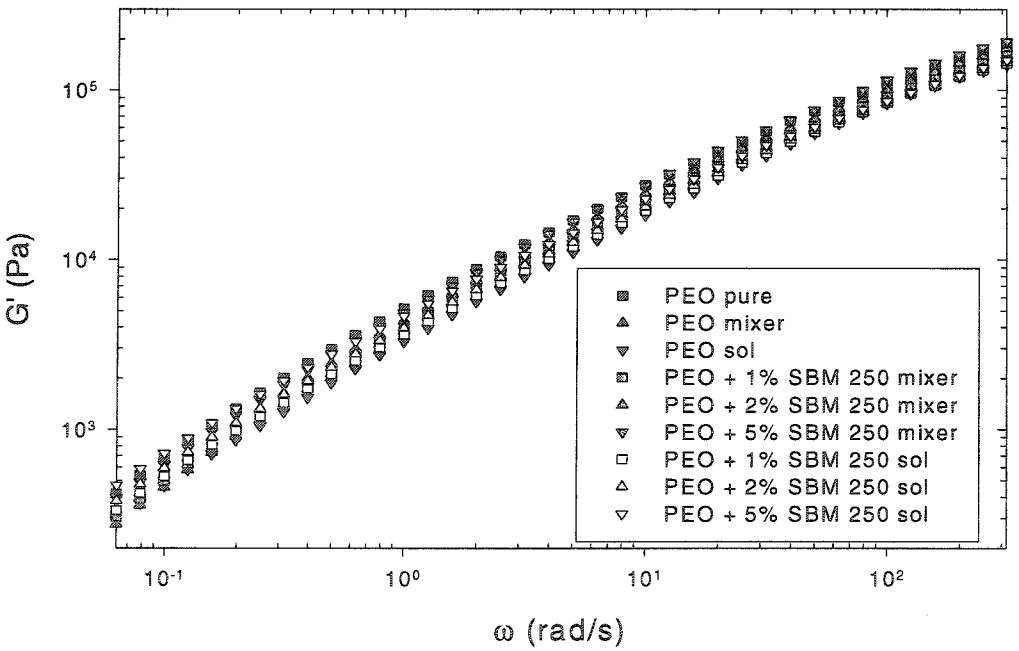

Figure A.10: G' (blend of PEO and SBM E20)

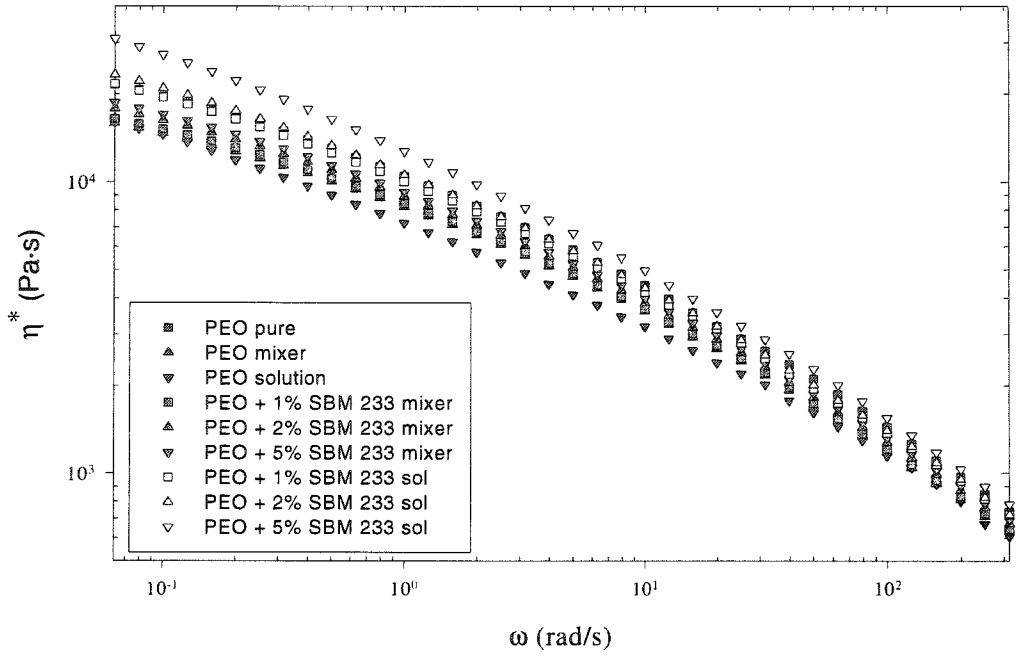

Figure A.11: η^* (blend of PEO and SBM E20)

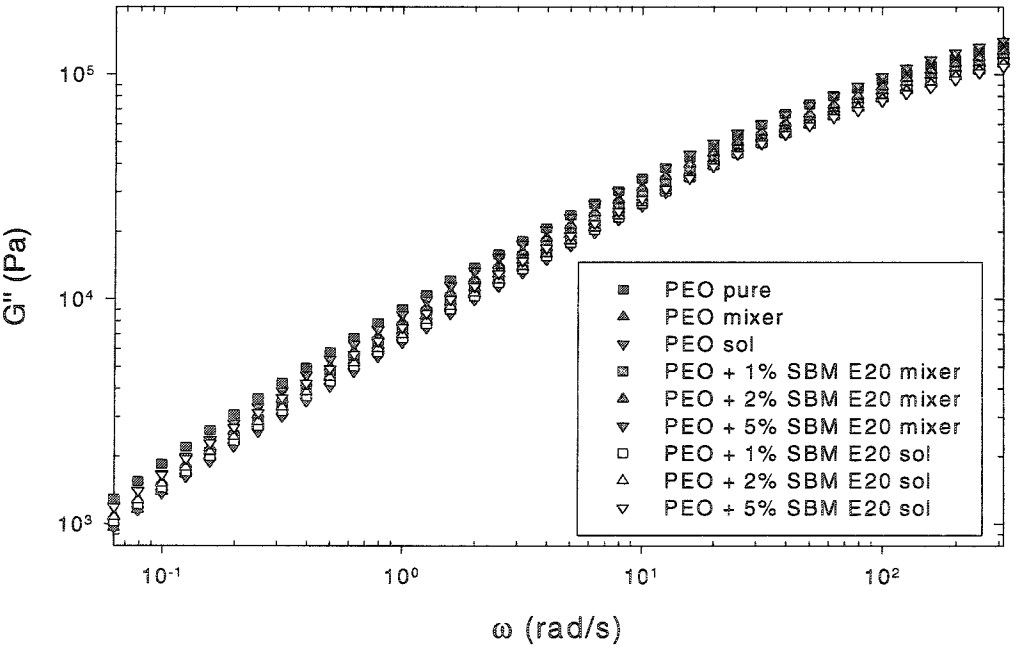

Figure A.12: G" (blend of PEO and SBM E20)

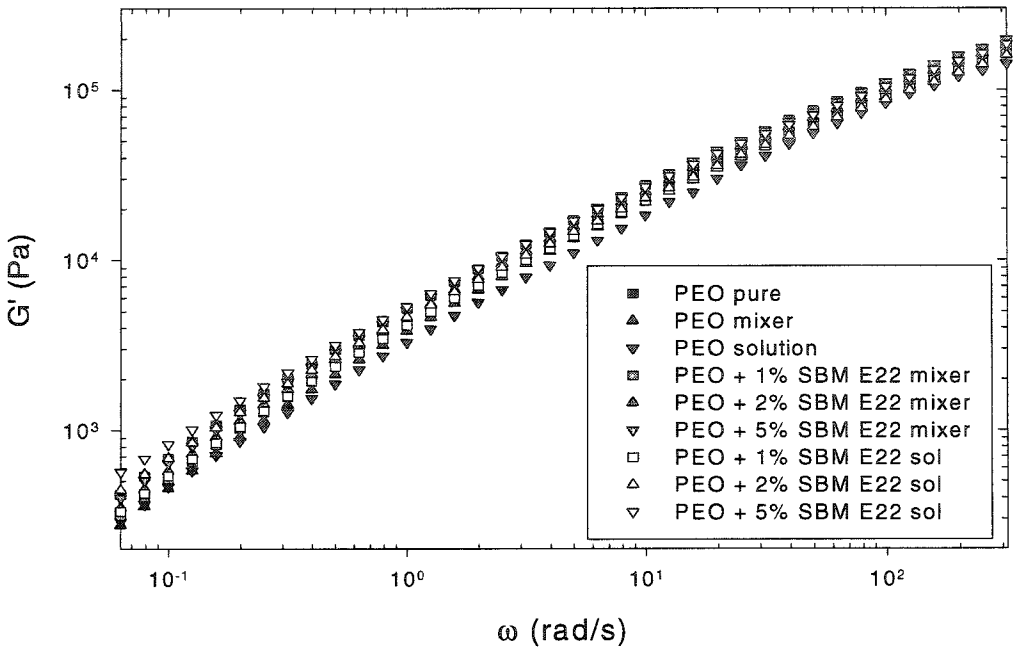

Figure A.13: G' (blend of PEO and SBM E22)

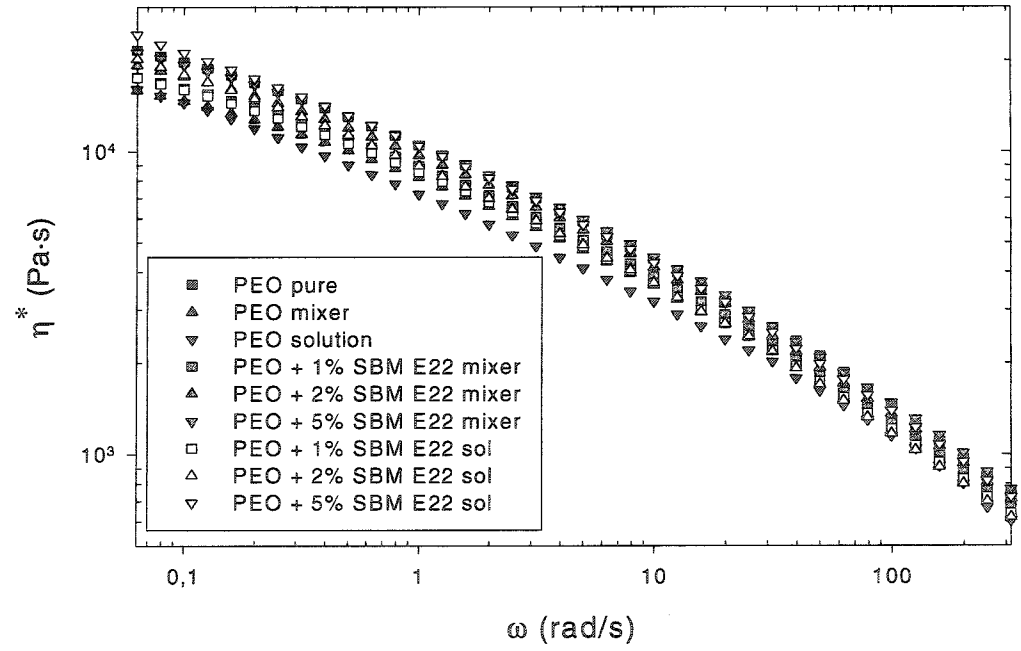

Figure A.14: η^* (blend of PEO and SBM E22)

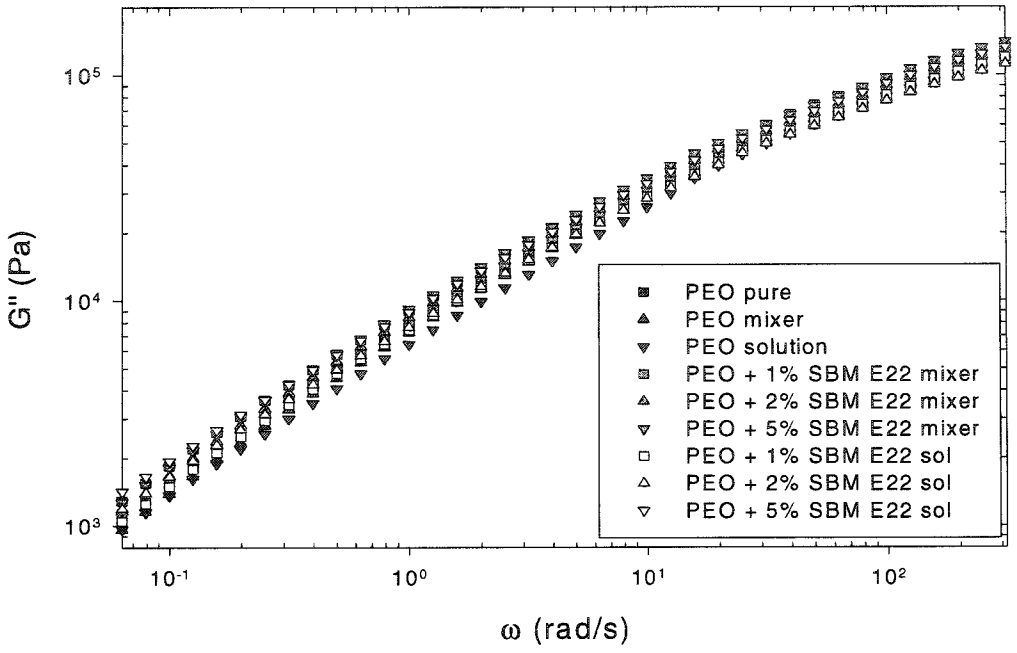

Figure A.15: G" (blend of PEO and SBM E22)

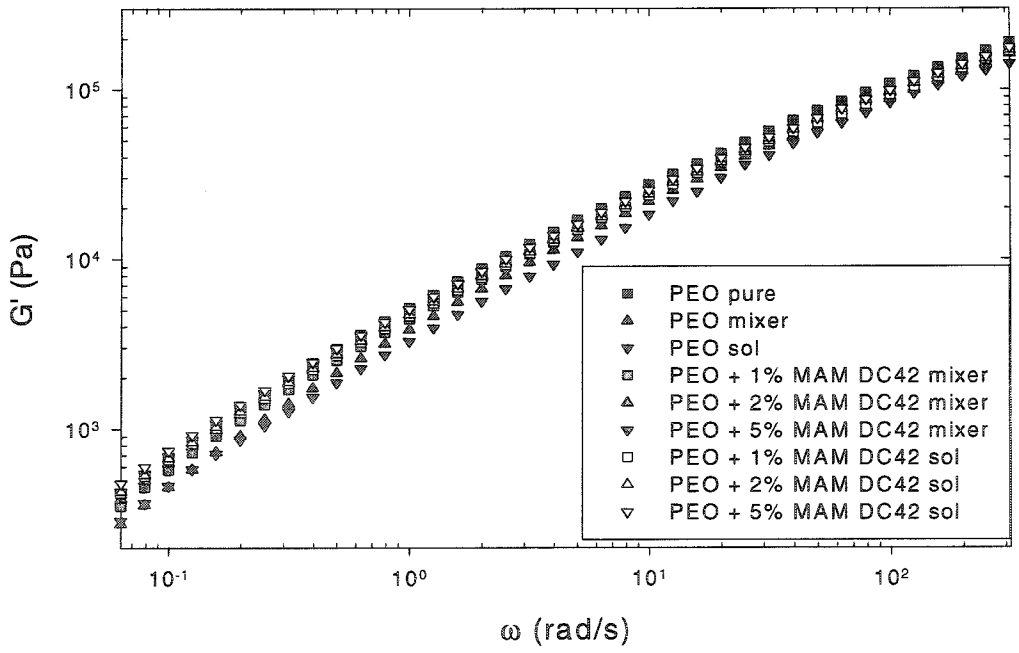

Figure A.16: G' (blend of PEO and MAM DC42)

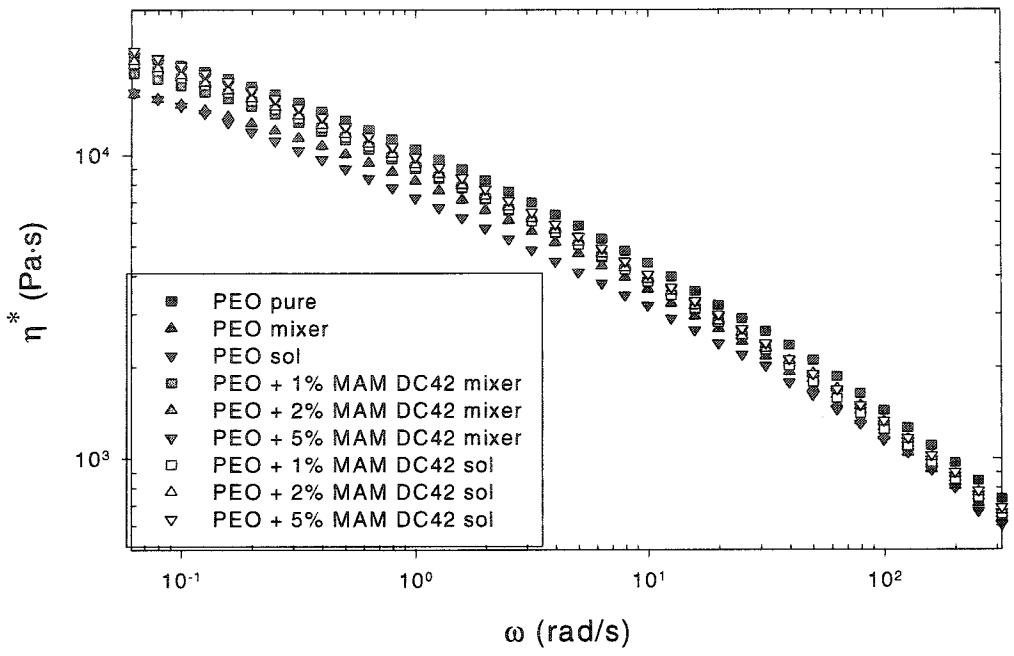

Figure A.17: η^* (blend of PEO and MAM DC42)

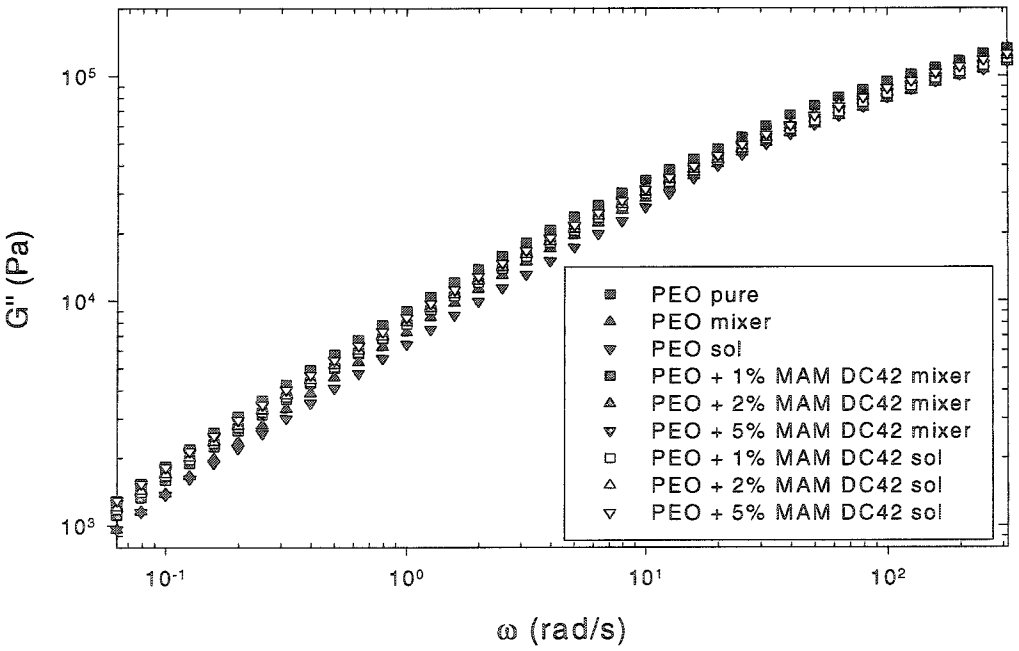

Figure A.18: G" (blend of PEO and MAM DC42)

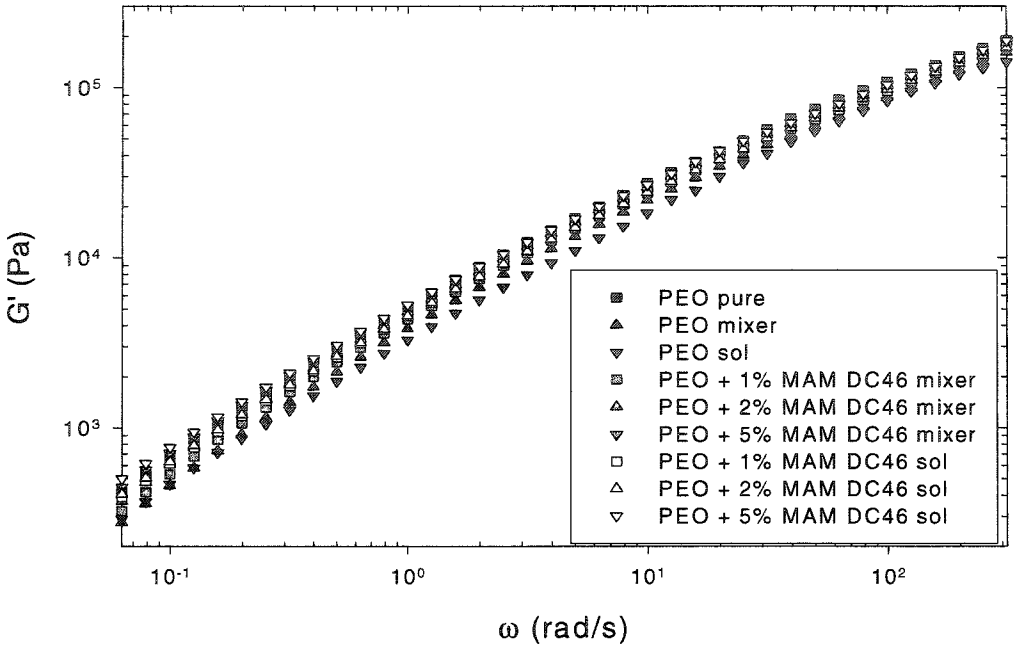

Figure A.19: G' (blend of PEO and MAM DC46)

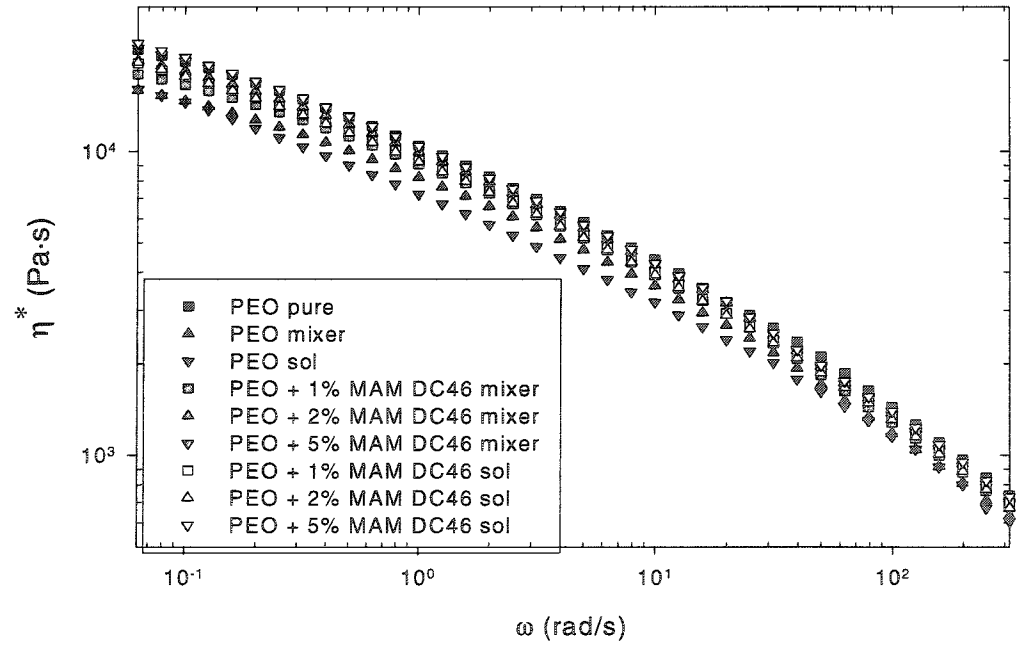

Figure A.20: η^* (blend of PEO and MAM DC46)

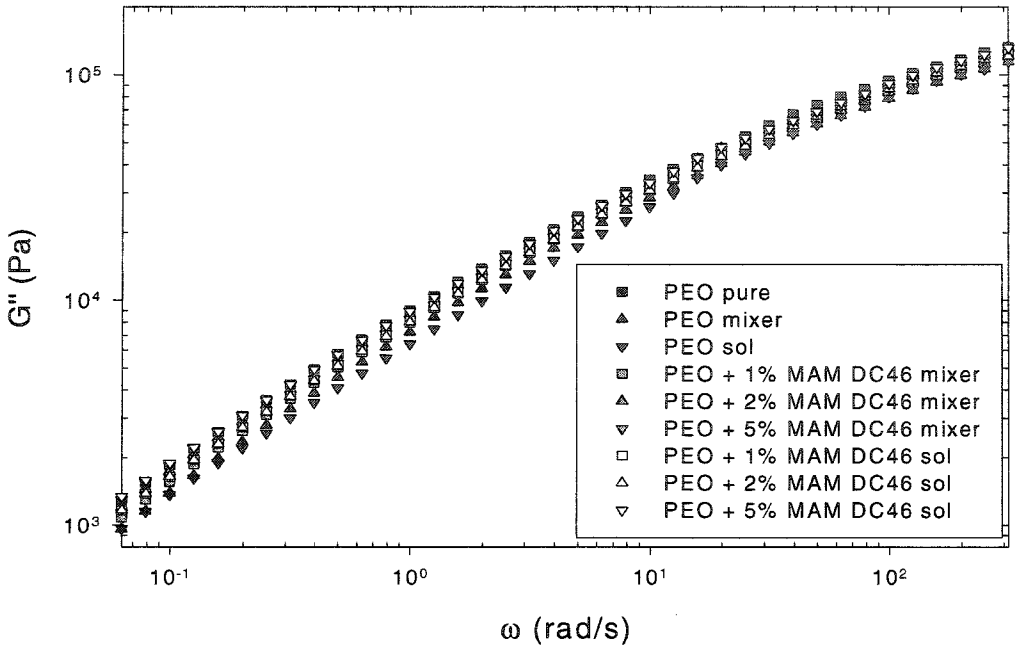

Figure A.21 G" (blend of PEO and MAM DC46)

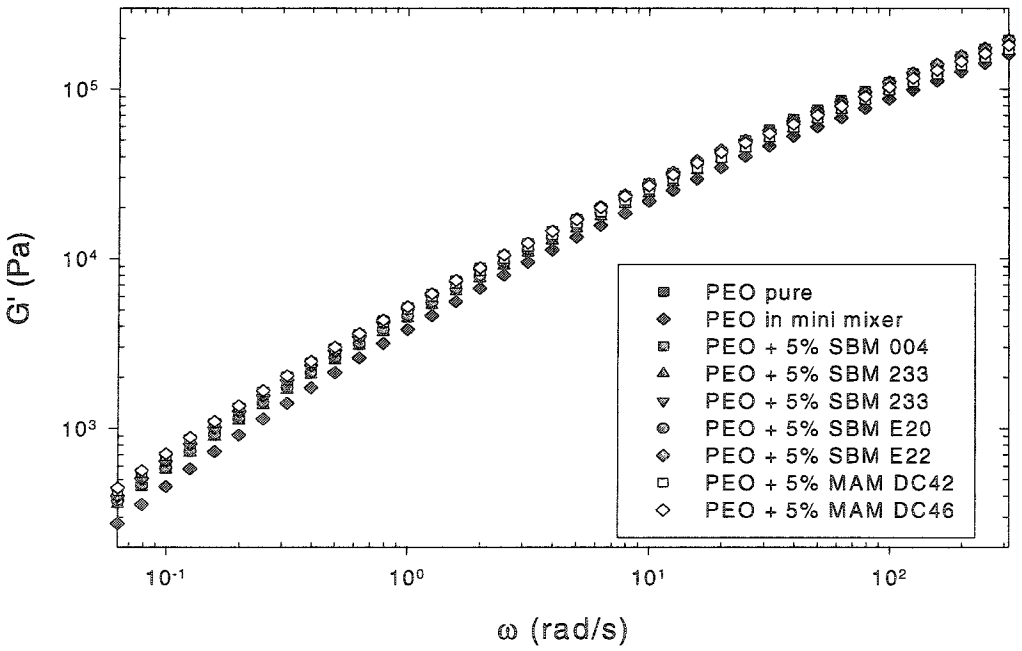

Figure A.22: G' (blend of PEO/5% block copolymer – prepared in mini mixer)

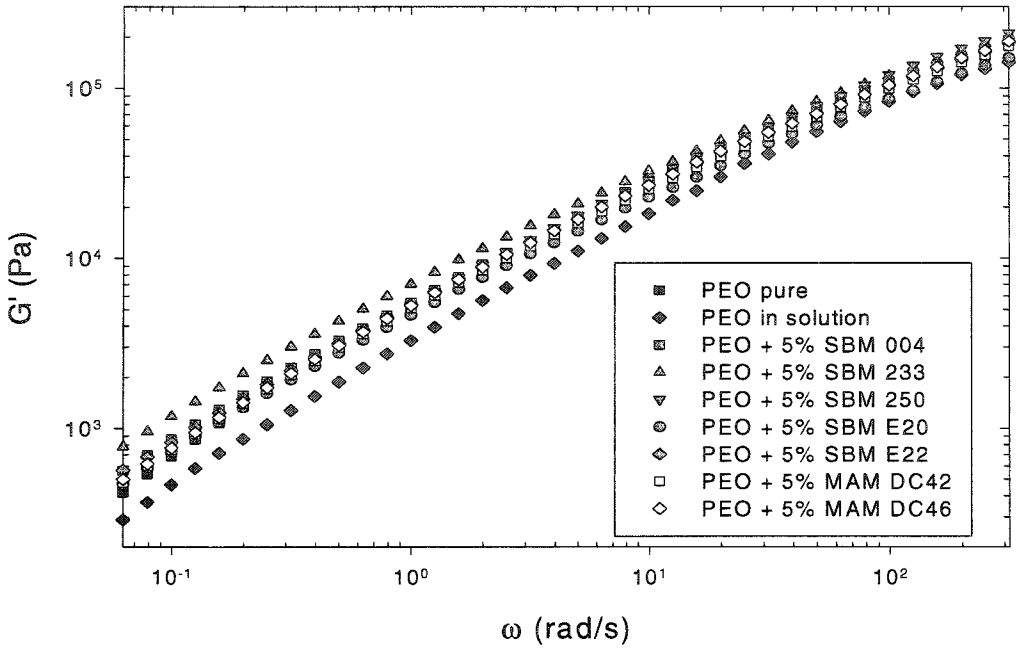

Figure A.23: G' (blend of PEO/5% block copolymer – prepared in solution)

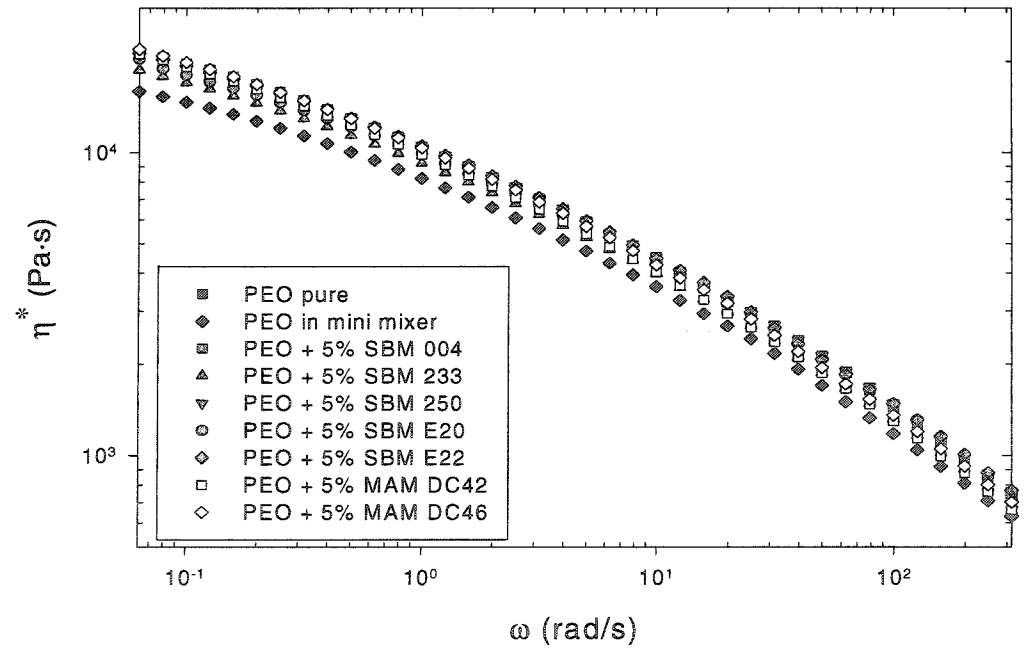

Figure A.24: η^* (blend of PEO/5% block copolymer – prepared in mini mixer)

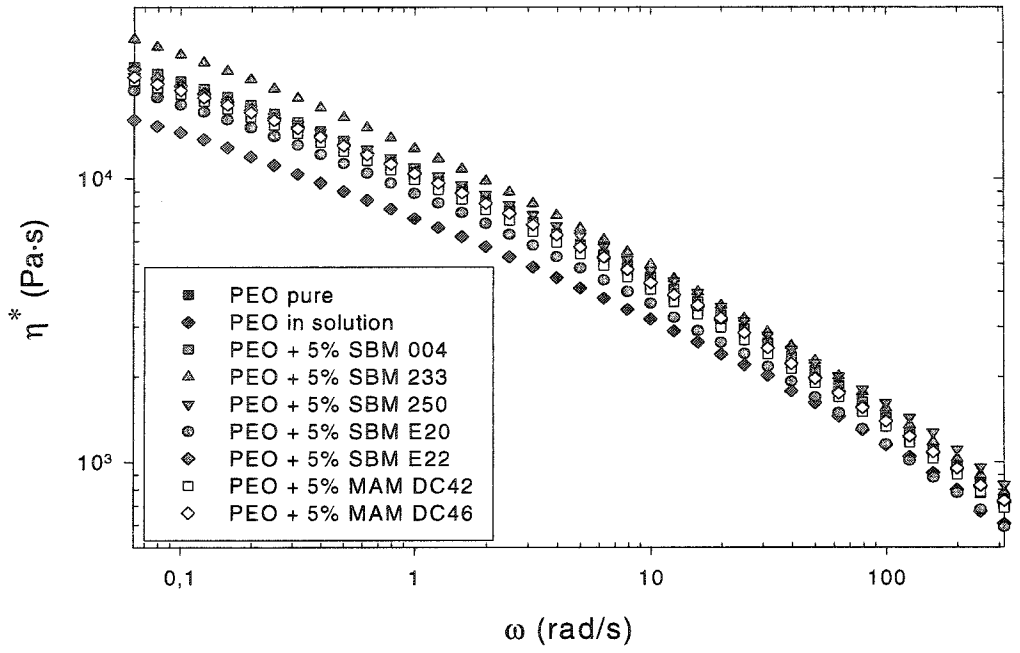

Figure A.25: η^* (blend of PEO/5% block copolymer – prepared in solution)

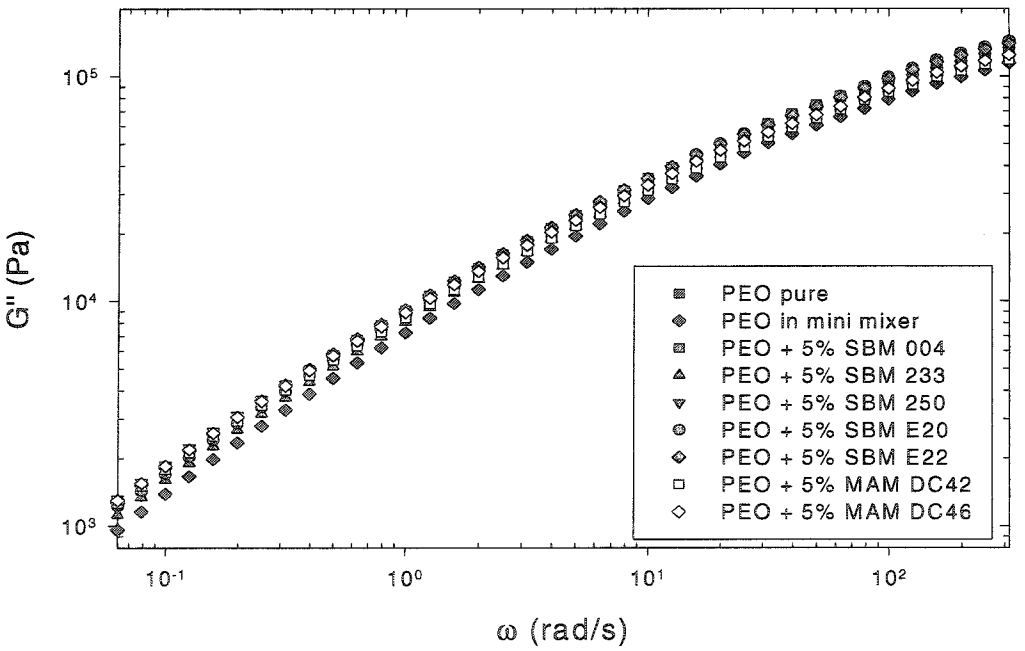

Figure A.26: G" (blend of PEO/5% block copolymer – prepared in mini mixer)

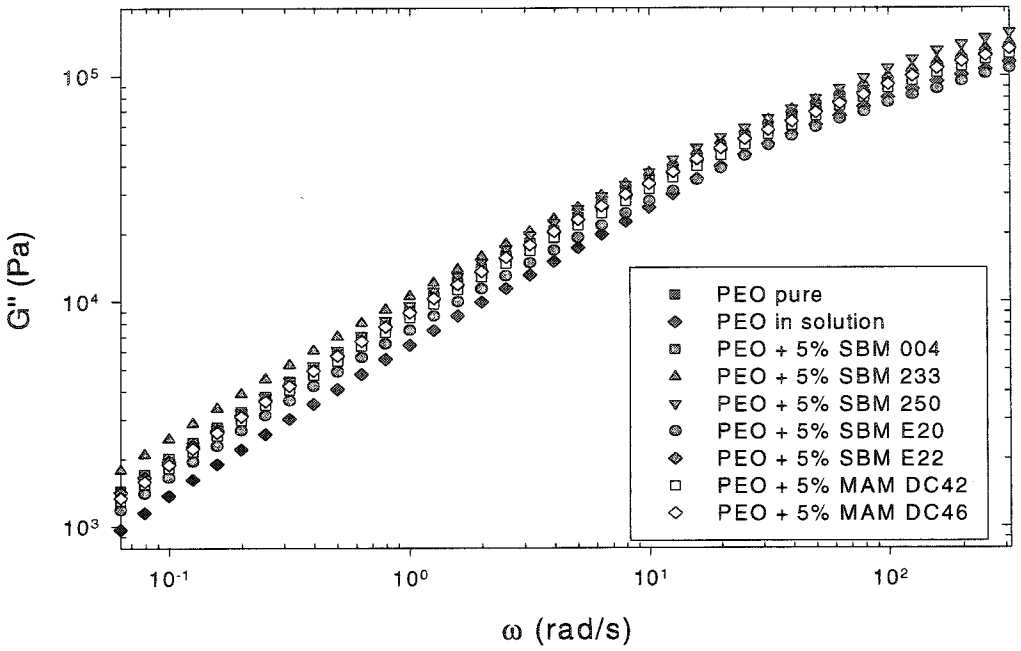

Figure A.27: G" (blend of PEO/5% block copolymer – prepared in solution)