Blends of Polyamide 6 and Epichlorohydrin Elastomers. I. Graft Copolymerization in the Melt Blending

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ABSTRACT: With the purpose of improving the mechanical properties of the polyamides, the possibility of combining polyamides with elastomers has been used. The low compatibility of the resulting blends leads to deficient mechanical properties, and therefore, it is necessary to add the compatibilizer to the mixture or to produce the compatibilizer during the melting mixture. Usually, at least one of the components must contain a reactive functional groups. In the present work, blends of polyamide 6 (PA 6) and epichlorohydrin elastomers, polyepichlorohydrin (PEPI), and the equimolar copolymer poly(epichlorohydrin-co-ethylene oxide), ECO, with different compositions were prepared by mechanical mixture using a Banbury-type mixer. The blends were characterized by rheological measurements, the Molau test, elemental analysis, Infrared Spectroscopy by Diffuse Reflectance, Transmission Electron Microscopy, and X-ray Diffractometry. The blends of PA 6 with PEPI and ECO are heterogeneous, showing a morphology of elastomer particles dispersed in the polyamide matrix. The results of rheological measurements and the Molau test indicate a graft copolymerization in the interface between the polyamide and the elastomer, PA 6-g-elastomer, whose concentration decreases with the elastomer content. It was found that the grafting of PEPI and PA 6 changed the diffraction pattern of PA 6. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1827-1833, 1999

Key words: polyamides; epichlorohydrin elastomers; reactive blending; compatibilization

INTRODUCTION

Presently, 50% of the plastics available in the market are polymeric blends. There has been considerable interest in the development of polymeric blends in recent years, motivated by potential opportunities for combining the attractive features of each material while reducing their deficient characteristics.

Polyamides are crystalline polymers that have excellent properties, such as toughness, rigidity, wear resistance, corrosion resistance, and so on, for common applications. The deficiencies include low heat-deflection temperature, poor dimensional stability, and lower impact strength. The impact property of polyamides can be improved by blending them with an elastomer as a dispersed phase. Recent reports¹⁻⁷ of polyamiderubber systems showed that, although these systems are usually immiscible, the mechanical properties of the materials can be improved greatly by compatibilization. Koulouri and coworkers⁸ concluded that nylon 6 may be reactively compatibilized with poly(ethylene-co-ethyl acrylate), PEEA, at elevated temperatures and prolonged mixing time, as a result of the aminolysis reaction between the amine end groups of

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nylon 6 and the pendent ester groups of PEEA. The significant grafting efficiency of the blends with low (up to 25 wt %) PEEA content was proven by tensile testing. Additionally, Fourier transform infrared spectroscopy analysis shows that PEEA is present even after extraction with toluene, which leads to the conclusion that PEEA is chemically attached to the nylon 6 matrix. Oshinski and et al.⁹ investigated the effect of polyamide end-group configurations on the morphology and toughness of blends with maleated elastomers. The difunctional polyamide, polyamide 6,6, was compared to the monofunctional, polyamide 6, of equivalent molecular weight and melt viscosity. The authors used as elastomers styrene-butadiene-styrene block copolymers with a hydrogenated midblock, SEBS, and their versions with X% grafted maleic anhydride, SEBS-g-MA-X%, and a maleated ethylene/propylene random copolymer, EPR-g-MA. Measurements of the extent of the graft reaction between the amine end groups and the grafted maleic anhydride revealed that a larger number of amine groups are consumed by the difunctional polyamides than by monofunctional control, their resulting in crosslinking-type effects. The room-temperature Izod impact strength of blends with the difunctional polyamides is greater than the corresponding blends with the control. Blends of the polyamide 6 and poly(2,6-dimethyl-1,4-phenylene oxide), PPO, were compatibilized in situ for the poly(styrene-co-glycidyl methacrylate), SGMA The epoxy group of the SGMA can react with the amine and carboxyl group of the polyamide, forming a copolymer in the interface, which acts as a compatibilizer.¹⁰

A compatibilizer is designed to (1) reduce the interfacial energy between the phases, (2) permit a finer dispersion during mixing, (3) provide morphology stability against segregation or agglutination, and (4) improve the interfacial adhesion.¹¹ Usually the same elastomer functionalized (grafted) is used with a reactive group (such as maleic anhydride).

The purpose of this work is the preparation and characterization of blends of polyamide 6 with epichlorohydrin elastomers by mixture in the melting. PEPI and ECO exhibit excellent elastomer properties, as well as solvent resistance and environmental stability. A chemical reaction between polyamide and epichlorohydrin elastomers can take place during the mixture in the melting state, resulting in a graft copolymer in the interface that can act as a compatibilizer. Furthermore, intermolecular interaction such as dipole–dipole and hydrogen bonding could also occur between the polymers.⁷

EXPERIMENTAL

Materials and Blends Preparation

All the materials used in this work were industrial products and were used without further purification. Polyamide 6 was obtained from the Petronyl Ind. Com. PEPI (Hydrin H-55) and ECO (Hydrin C-75, equimolar copolymer) elastomers were produced by Zeon Chem. Inc., with an M_w of 627,000 and 605,000 g/mol (determined by gel permeation chromatography, g.p.c.), respectively. Before blending, the PA 6 was carefully dried in a vacuum oven at 100°C for at least 24 h to prevent any hydrolytic scission of polyamide 6.

PA 6/elastomer blends were obtained in a Haake Rheomix 600 equipped with rotor roller, at 200°C, rotational speed of 60 rpm, and residence time of 10 min. The mixing chamber occupied volume was 52 cm³. Then, the melt-blending samples were quenched by water at room temperature, triturated, and dried at 80°C under reduced pressure for 24 h. Sheets of 1.5-mm thickness were prepared by compression molding in an evacuated press at 220°C at 5 ton. During mixture about 0.4 wt % stabilizer triethyleneglicolbis-3(3-tert-butyl-4-hydroxy-5-methylphenyl) (Irganox 245-Ciba Geigy AG), and 0.2 wt % zinc stearate were added. Compositions of the PA 6/elastomer blends varied from 3 to 40 wt % of the elastomer.

Rheological Characterization

The torque was recorded as a function of the time in the blending conditions.

Molau Test

The Molau test¹² has been used to qualitatively investigate a graft copolymerization during the blending process. In our investigation, we conducted the test by dispersion of about 2.5 g of the blends with 25 mL of 80% formic acid. The optical aspect of the dispersion was observed. The polyamide phase is, in principle, soluble in formic acid, whereas the elastomer is insoluble. The Molau test is positive when the formation of a milky, colloidal suspension is observed, indicating that a grafting reaction has taken place. The soluble and insoluble fractions in formic acid are separated by centrifugation. The liquid phase containing polyamide at the bottom of the vessel is removed. The elastomeric residue is suspended again in formic acid and separated by centrifugation, and this procedure is repeated four times. At the last time no polyamide could be isolated by addition of a nonsolvent (water) in the solution. The residual solid is washed with water and dried overnight at 90°C in a vacuum oven, and then characterized by Elemental Analysis, Infrared Spectroscopy, and X-ray Diffractometry.

Elemental Analysis

The grafting degree (α) was determined by elemental analysis of the elastomeric residue obtained from the Molau test with an Elemental Analyzer Perkin-Elmer 2400 CHN. The nitrogen content in the elastomeric residue was measured, from which the polyamide weight percentage could be calculated. The grafting degree is defined as:

 $\alpha = \frac{\text{weight of polyamide coupled to the elastomer}}{\text{elastomer weight}}$

Infrared Spectroscopy by Diffuse Reflectance

An infrared spectrum of the elastomeric residue Molau test was obtained in the range of $400-4000 \text{ cm}^{-1}$ on a 1600 Perkin-Elmer FTIR spectrometer. Samples were analyzed as plates of about 1-mm tickness, using a reflectance accessory. Two hundred scans at a resolution of 1 cm⁻¹ were signal averaged.

Morphology

Blend morphology was assessed via transmission electron microscopy in the equipment MET Zeiss EM 902 using ultrathin sections cryogenically microtomed. An Laica microtome cooled to -100° C and equipped with a diamond knife was used to obtain the ultrathin sections (about 70-nm tickness).

X-ray Diffractometry

The crystalline phase of the pure PA 6, in the blends and in the graft copolymer (isolated from Molau test), were analyzed using a XD-3A Shimadzu X-ray diffractometer. Nickel-filtered CuK α radiation was applied at 30 kV and 20 mA.



Figure 1 Torque as a function of the time at 200°C and 60 rpm for: (**■**) PA 6; (\bigcirc) PEPI, and (**▲**) ECO homopolymers; (\diamondsuit) PA 6/PEPI and (**●**) PA 6/ECO blends containing 20 wt % of the elastomer.

RESULTS AND DISCUSSION

Torque measurements have been used successfully to obtain qualitative information concerning the chemical reactivity and the extension of grafting reaction in the compatibilized blend. Figure 1 illustrates the torque vs. time curves for PA 6, PEPI, and ECO, and for the blends with 20 wt % recorded during processing. The torque for pure polymers do not change with time, and assumes values around 16 Nm for epichlorohydrin elastomers and ca. 4 Nm for PA 6 at 60 rpm and 200°C. It is important to emphasize that melt blending was carried out at 200°C, considering the occurrence of an increase of the temperature during the process due to shear conditions. Higher temperatures lead to degradation of the elastomers, whose processing temperature is around 160°C. In the melt blending, the viscosity ratio of the two components is important. The component with the lower viscosity tends to encapsulate the more viscous (or more elastic) component during mixing, because this reduces the rate of energy dissipation, forming a matrix with a dispersed phase of the other components. The characteristics of this dispersed phase have been investigated. In general, when the dispersed phase has a lower viscosity, it is in the form of long filaments. When the dispersed phase has a higher viscosity, it is in the form of discrete droplets.¹³ Then, it is expected that PA 6 will tend to form the continuous phase while the elastomer will tend to form dispersed domains.

Elastomer	wt % Elastomer	α (%)
PEPI	20	12.4
	40	5.6
ECO	20 40	$\begin{array}{c} 24.1 \\ 11.8 \end{array}$

Table IGrafting Degree (α) for BlendsObtained by Elemental Analysis

For blends, the torque values were situated between the values of the pure components, but it increases with time, probably due to changes in the morphology associated with chemical reactions during melt blending between the chlorine from the elastomer and the amino groups from the polyamide with the formation of graft copolymer in the interface. The torque for blends with ECO is higher in comparison to the PEPI blends, following the behavior observed for the corresponding pure elastomers.

Earlier, Molau¹² and Illing¹⁴ conducted experiments of the selectivity solubility (Molau test) to investigate the occurrence of the graft copolymer in PA/polyolefin blends.

In our case, blends were dispersed in formic acid, which is a solvent for PA 6 and a nonsolvent for elastomers. If there is no graft copolymer present to act as an emulsifier, the elastomer phase will separate and float in the solution. Then, the test result is called negative. On the other hand, if a graft copolymer emulsifier is the nonsoluble component, a white, colloidal suspension will rise, which means that the Molau test is positive. All the PA 6–epichlorohydrin elastomers blends presented turbidity when dispersed in formic acid, indicating that chemical reactions had taken place during the melt blending.

The grafting degree (α) determined by elemental analysis is listed in Table I.

The grafting degree is high, but decreases with an increase of the elastomer in the blends. This can be understood as a decrease of the interfacial area, and hence, of the area for occurrence of the grafting reaction. A lower interfacial area is associated with larger domains and a poor dispersion, which can be due to the higher melt viscosity of the mixture by the increase of the elastomers concentration in the blend.

The grafting reaction was confirmed by Infrared Spectroscopy. A typical spectrum of the residue of the Molau test for the blends containing 20 wt % of PEPI is shown in Figure 2. The presence of a polyamide in the residue is demonstrated by appearance of absorption peaks at 3300 (NH stretching), 3060, 1640 (amide I band), and 1540 (amide II band) cm⁻¹, which are all characteristic of PA 6.

The following two mechanisms are suggested for the graft formation:¹⁵

(A) Aminolysis of elastomer by a terminal amine group of polyamide:



(B) Alkylation of polyamide by elastomer:





Figure 2 Infrared spectra by diffuse reflectance for: (A) PEPI and (B) elastomeric residue of the Molau test.



Figure 3 TEM photomicrographs for blends containing: 5 wt % of PEPI (A) or ECO (B), 20 wt % of PEPI (C), or ECO (D) and 40 wt % of PEPI (E) or ECO (F).

Both mechanisms can occur, but there is not any experimental evidence about the predominant reaction. The acid acceptor zinc stearate was used to neutralize eventual HCl evaluated during melt blending. It is known that mixtures of poly(ethylene oxide) and PA 6 result in a block copolymer poly(amide 6-*b*-ethylene oxide), namely PEBAX,[®] whose characteristics have been recently reported.¹⁶ In fact, the grafting degree for blends of ECO is higher than



Figure 4 X-ray diffractograms for PA 6/ECO blends.

for PEPI blends, probably as a result of the additional reaction between ethylene oxide segments of ECO and PA 6.

The TEM micrographs of the blends (Fig. 3) show that PA 6 constitutes the continuous phase while the elastomers form domains, as expected from the rheological considerations. A third phase can still be distinguished in the interface, as gray regions. For all compositions, the domain size and their distribution are not homogeneous. This is probably caused by the poor mixing conditions and by the simultaneous formation of the graft copolymer. The system is constituted basically by three phases with different rheological properties. The mixing conditions may be optimized, but this is not the aim of this work. From the torque measurements it is clear that PEPI exhibits lower viscosity than ECO; then it is expected that blends containing ECO present a more heterogeneous morphology. This hypothesis is confirmed by TEM. Blends of ECO present larger domains size than for the corresponding blends of PEPI. In addition, the interfacial region in the blends of ECO is larger, which is consistent with the higher grafting degree.

The compatibilizer in a semicrystalline polymer blend can also affect the crystalline forms, as well as the crystallinity degree.¹⁷

For the crystalline phase of PA 6, two types of structures are possible: α -form and γ -form, and the formation of these structures basically depend on the thermal history.¹⁸ The X-ray diffractogram of the α -form of PA 6 is characterized by two sharp peaks at $2\theta = 20.5^{\circ}$ and 23.8° , which correspond to (200) and (020) planes, respectively;

whereas the γ -form crystalline structure is identified by the peak at $2\theta = 21.6^{\circ}$, which corresponds to the (200) plane.

Figures 4 and 5 show the X-ray diffractograms of the polymers, the blends with different compositions of elastomers, and the graft copolymer isolated from the Molau test. The diffraction pattern of PA 6 used in the study shows a typical α -form structure. ECO shows peaks at $2\theta = 13.5^{\circ}$, 16.5° , and 25.8° (Fig. 4). The graft copolymer presents four characteristic peaks at $2\theta = 13.5^{\circ}$, 16.3° , 17.9°, and 25°, but peaks characteristic of PA 6 did not appear, probably due to the lowering quantity, or the hindering of crystallization of short segments of PA 6 between the grafting points. The second hypothesis is more consistent with the observed high grafting degree. The peak at 17.9° indicates the presence of other crystalline forms, which can be associated with the modification of the polymer. The diffractograms for the PA 6-ECO blends are just a superposition of the characteristic peaks of PA 6 and the grafting copolymer.

The elastomer PEPI is amorphous (Fig. 5), but their blends with PA 6 and the grafting copolymer present peaks in the X-ray diffractograms at the same angles as observed for the ECO-grafting copolymer and PA 6/ECO blends. There are two hypotheses to explain this behavior. One is the PEPI crystallization induced by mechanical degradation of the polymer chains during the blending process or by the presence of crystallizable PA 6. Another hypothesis is that only the PEPI-PA 6 graft copolymer is crystalline. In this case, the graft copolymer fraction is high enough to be ob-



Figure 5 X-ray diffractograms for PA 6/PEPI blends.

served by the corresponding peaks in the X-ray diffractogram, as suggested by the Molau test and Elemental Analysis.

The peaks intensity is higher for the blends of PA 6/ECO, probably due to the overlap of elastomers and graft copolymer peaks.

It is important to emphasize that the diffractograms of the blends and of the graft copolymer do not present the diffraction pattern of the PE-BAX.¹⁹ Therefore, the peaks observed cannot be attributed to the chemical reaction between the PA 6 and poly(ethylene oxide) segments.

CONCLUSIONS

A graft copolymer is formed during the mechanical blending of polyamide 6 and epichlorohydrin elastomers. The grafting degree depends on the blend composition and the elastomer type. The morphology of the blends reflects the mixture conditions, rheological behavior of each pure component, and the grafting degree.

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