# Blends of Polyamide 6 and Epichlorohydrin Elastomers. II. Thermal, Dynamic Mechanical, and Mechanical Properties

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**ABSTRACT:** The mechanical blending of polyamide 6 and epichlorohydrin elastomers, polyepichlorohydrin, PEPI, and poly(epichlorohydrin-*co*-ethylene oxide), ECO, is accompanied by grafting copolymerization. In this work the influence of the graft copolymer on the thermal and mechanical properties of the blends is investigated. The blends are immiscible and the crystallinity degree normalized to the polyamide 6 contents in the blends is higher than expected. The X-ray diffraction results show that the grafting copolymer is also crystalline; hence, the presence of crystalline phase of copolymer can be responsible for the apparent enhancement of crystallinity. The DMA analysis reveals the presence of a shoulder in the peak corresponding to the PA 6 glass transition, as observed by loss modulus curves, which was assigned to relaxations of the grafting copolymer. Tensile tests show that the blends are more fragile than the PA 6, despite the graft copolymer. These results were attributed to the mechanical fragile interface constituted by a network type structure of the graft copolymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1835–1841, 1999

**Keywords:** polyamide; epichlorohydrin elastomers; reactive blending; thermal and mechanical properties

## INTRODUCTION

The physical blending of two or more polymers to obtain new products has a great technical and commercial importance, particularly when the development of new polymers becomes cost ineffective and is environmentally unfavorable.

There are some heterogeneous polymer blends systems that have commercial success; for example, impact polystyrene and poly(acrylonitrilebutadiene-styrene) (ABS).<sup>1</sup>

Most of the articles concerning this subject indicate that the presence of the third component acting as a compatibilizer can stabilize the second phase and induce changes in both rheological and mechanical properties. These effects were attributed to the reaction during melt mixing between the pure polymers and the functional groups present in the compatibilizer, giving rise to copolymers that bridge the phases<sup>2</sup> or to the specific interactions between the components.

Presently, an attractive alternative to compatibilize blends is the formation of the block or graft copolymer *in situ* during blend preparation through an interfacial reaction of functionalized polymer components. Examples of *in situ* compatibilization have concentrated mainly in blends of different polyamides and maleic anhydride (MA)-grafted polyolefins, where the reaction between anhydride and the  $-NH_2$  end groups of polyamides is possible.<sup>3</sup>

Chiang and et al.<sup>4</sup> studied polymer blends of polyamide 6 (PA 6) and poly(phenylene oxide), PPO, compatibilized by the poly(styrene-*co*-glycidyl methacrylate), (SG). PS is miscible with PPO,

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Figure 1 DSC curves for PA 6/PEPI blends.

and the epoxy groups of the SG copolymers can react with the amine group and carboxylic end groups of PA 6 in the interface to form a graft copolymer, SG-g-PA 6, which tends to anchor along the interface acting as a compatibilizer of the blends. The optimum glycidyl methacrylate content in SG copolymer for PA 6/PPO compatibilization is about 5%. In this case, smaller domains, higher viscosity in the melting, and improved mechanical properties are observed. Further, an increase of GMA content results in numerous grafts points per chain, forming typepinning structures with small styrene segments penetrating into the PPO phase, which results in less interfacial adhesion.

Cho and colleagues<sup>5</sup> have studied blends of linear low-density polyethylene (ethylene–octene-1 copolymer) and ethylene–propylene– butene-1 terpolymer (ter-PP) mixed mechanically. Although these blend systems are immiscible in the solid and in the melt states, addition of ter-PP up to 20 wt % in the blend is viable for engineering applications with the advantages of improved processibility and mechanical properties. This is attributed to interfacial interaction between the components.

In a previous article<sup>6</sup> we described the melt blending of Polyamide 6 (PA 6) with polyepicholorohydrin (PEPI) and with equimolar copolymer poly(epichlorohydrin-*co*-ethylene oxide) (ECO), accompanied by chemical reactions between the components with the formation of the graft copolymer, PA 6-*g*-elastomer.

The aim of the present work is to determine the thermal and mechanical properties of the PA

6/epichlorohydrin elastomers blends, and to analyze the influence of the graft copolymer on these properties.

## **EXPERIMENTAL**

#### **Materials and Blends Preparation**

The blends preparation was described in our previous article.  $^{\rm 6}$ 

#### Differential Scanning Calorimetry (DSC)

DSC measurements were carried out in an inert atmosphere using a DSC 2910 equipment (TA Instruments). Sample weights were about 10 mg, and the heating rate was  $20^{\circ}$ C · min<sup>-1</sup>. The samples were quenched to  $-80^{\circ}$ C, heated to  $260^{\circ}$ C, and kept at this temperature for 2 min, quenched again to  $-80^{\circ}$ C, followed by heating to  $260^{\circ}$ C. The second heating scan was recorded.

#### **Dynamic Mechanical Analysis (DMA)**

The DMA were carried out by using a DMA Model 983 from TA Instruments, in the temperature range from -60-300°C under nitrogen atmosphere, at 1-Hz frequency, and 0.2-mm amplitude sinusoidal. The dimensions of the specimens used were  $8.0 \times 1.5 \times 5.0$  mm. The samples were heated in steps of 3°C, remaining at each temperature for ca. 1 min to achieve thermal equilibrium.



Figure 2 DSC curves for PA 6/ECO blends.

PEPI (wt %)	$T_g$ PEPI Rich Phase (°C)	$T_g$ PA 6 Rich Phase (°C)	$T_m \; (^{\rm o}{\rm C})$	$\Delta H_m~(\rm J/g)$	$\Delta H_{mN}({\rm J/g}_{\rm PA~6})$
0	_	57	224	52	52
5	-16	57	224	51	54
10	-22	59	223	58	64
20	-24	55	225	46	58
30	-20	61	224	43	61
40	-20	59	223	28	47
100	-18	—	_		—

Table I Data Obtained from DSC Curves for PA 6/PEPI Blends

#### **Mechanical Properties**

The mechanical properties of the blends were evaluated by tensile tests according to the ASTM D1708-66 using an EMIC-2000 universal testing machine. The crosshead speed was 5 mm  $\cdot$  min<sup>-1</sup>. The results were averaged with at least seven measurements.

#### **RESULTS AND DISCUSSION**

Figures 1 and 2 show DSC curves for blends of PA 6 with PEPI and ECO elastomers, respectively.

The PA 6 is a semicrystalline polymer presenting glass transition at  $57^{\circ}$ C and melting point at 224°C. PEPI is an amorphous polymer, exhibiting glass transition at  $-18^{\circ}$ C (Fig. 1). ECO is a semicrystalline polymer, with glass transition at  $-36^{\circ}$ C and melting point at 107°C (Fig. 2). DSC curves of the polyamide/elastomers blends reveal two glass transitions at temperatures corresponding to the transitions of the pure polymers, and an endothermic peak due to melting of the PA 6 crystalline phase. This indicates immiscibility in the whole range of compositions studied. The glass transition temperature  $(T_g)$ , melting point  $(T_m)$ , fusion enthalpy  $(\Delta H_m)$ , and the fusion enthalpy normalized with respect to the perceptual of polyamide in the mixture,  $\Delta H_{mN}$ , are shown in Tables I and II for blends of PA 6/PEPI and PA 6/ECO, respectively.

The  $\Delta H_{mN}$  increases with a decrease of polyamide concentration in the mixture. Apparently this result is unexpected, because the polyamide is the principal crystalline component in the blends. The melting temperature is practically independent of the blend composition. Xray diffractometry showed that the presence of epichlorohydrin elastomers changes the diffractogram pattern of PA 6, and that the PA 6-gelastomer copolymer is also crystalline.<sup>6</sup> Therefore, the DSC results can also reflect the presence of the graft copolymer or the crystallization of PA 6 induced by the presence of graft copolymer, or both effects.

The loss modulus vs. temperature curves (Log E'' vs. T) obtained from DMA experiments of the homopolymers and PA 6/elastomers blends containing 5, 20, and 40 wt % in elastomers are illustrated in Figures 3 and 4. PA 6 shows three peaks: the most intense peak with maximum at 57°C is attributed to the glass

ECO (wt %)	$T_g$ ECO Rich Phase (°C)	$T_g$ PA 6 Rich Phase (°C)	$T_m \; (^{\circ}\mathrm{C})$	$\Delta H_m~({\rm J/g})$	$\Delta H_{mN}(\mathrm{J/g}_{\mathrm{PA}~6})$
0	_	57	224	52	52
5	-41	55	227	53	56
10	-41	60	226	54	60
20	-40	56	225	41	51
30	-39	62	224	37	53
40	-38	55	224	33	55
100	-36	—	107	0.98	—

Table II Data Obtained from DSC Curves for PA 6/ECO Blends



**Figure 3** Loss modulus as a function of the temperature for PA 6/PEPI blends:  $\triangle -0$ ;  $\bigcirc -5$ ;  $\cdots -20$ ;  $\bullet -40$ ; and -100 wt % PEPI.

transition; the  $\beta$  relaxation at about  $-55^{\circ}$ C corresponds to the relaxations of hydrogen bonded amide groups; and the melting is observed at

224°C. PEPI and ECO elastomers exhibit peaks with maximal at -29 and -44°C, respectively, attributed to glass transition. Two glass transi-



**Figure 4** Loss modulus as a function of the temperature for PA 6/ECO blends:  $\triangle -0$ ;  $\bigcirc -5$ ;  $\cdots -20$ ;  $\bigcirc -40$ ; and -100 wt % ECO.



**Figure 5** Loss modulus as a function of the temperature for (- - -) PA 6/PEPI or (—) PA 6/ECO blends containing: (A) 5, (B) 20, and (C) 40 elastomer (wt %).

tions were observed for the blends, as expect from the DSC data.

The glass transition of PA 6 becomes broad with the addition of the elastomers, and a shoulder appears at around  $25^{\circ}$ C. This shoulder can be associated with the presence of the graft co-



**Figure 6** Stress-strain curves: (A) PA 6/PEPI blends, (B) PA 6/ECO blends.

polymer in the interface.<sup>6</sup> In addition, the  $T_g$  of the PA 6-rich phase shifts slightly to the lower temperature. This fact was not observed in the DSC data because of the poor definition of the glass transition of PA 6. DMA technique is more

Table IIITensile Properties of the PA 6/PEPIBlends

PEPI	Stress at	Strain at	Young's Modulus
(wt %)	Break (MPa)	Break (%)	(MPa)
$0 \\ 5 \\ 10 \\ 20 \\ 30 \\ 40$	$40 \pm 18 \\ 45 \pm 8 \\ 57 \pm 4 \\ 40 \pm 6 \\ 23 \pm 3 \\ 18 \pm 1$	$\begin{array}{c} 73 \pm 4 \\ 11 \pm 4 \\ 17 \pm 5 \\ 16 \pm 5 \\ 14 \pm 3 \\ 18 \pm 6 \end{array}$	$\begin{array}{c} 1293 \pm 111 \\ 1159 \pm 243 \\ 701 \pm 171 \\ 660 \pm 32 \\ 640 \pm 75 \\ 581 \pm 87 \end{array}$

ECO (wt %)	Stress at Break (MPa)	Strain at Break (%)	Young's Modulus (MPa)
0	$40\pm18$	$73\pm~4$	$1293 \pm 111$
5	$46 \pm 17$	$38\pm12$	$1127\pm318$
10	$43 \pm 10$	$34\pm~7$	$742\pm154$
20	$38\pm13$	$10\pm~5$	$1270\pm316$
30	$18 \pm 8$	$8\pm4$	$788 \pm 175$
40	$17 \pm 2$	$6 \pm 1$	$573 \pm 121$

Table IV Tensile Properties of the PA 6/ECO Blends

sensitive to detection of transitions and disturbances caused by chemical reactions and interactions.

Loss modulus curves for blends with the same compositions but different elastomers are shown in Figure 5. The glass transition of the PA 6 in the blends containing ECO shifts to lower temperatures and the shoulder at 25°C becomes more intense in comparison to PEPI blends. This result is expected because the grafting degree is higher for the ECO blends.<sup>6</sup>

The mechanical properties of the mixtures were evaluated by tensile tests. The stress-strain curves are shown in Figure 6 and the dates obtained from them were recorded in Tables III and IV.

The results of the tensile tests for the blends reveal that Young's modulus were reduced in relation to the PA 6 pure. The elongation at break and tensile strength of the blends were significantly lower in comparison with PA 6, indicating that the addition of elastomers do not improve the tensile mechanical properties of PA 6.

The copolymer PA 6-g-elastomer should contribute to the interfacial adhesion, but its efficiency to promote compatibilization in the PA 6-epichlorohydrin elastomers blends depends on the chemical structure, temperature, mixing conditions, and the concentration of polymers and reactive groups. The graft copolymer concentration in the PA 6/epichlorohydrin elastomers blends is relatively high (ca. 6% for blends containing 20% of PEPI, for example),<sup>6</sup> and its structure should be very complex, because the reactive group chloromethylene is present in each epichlorohydrin segment and can participate in the graft reaction, forming a network-type structure. High reactive group concentrations induce high crosslinking density. As a consequence of this structure, the elastomer segments lost flexibility and the ability to dissipate mechanical energy.



Network type structure Pa 6-g-elastomer

The graft copolymerization in the interface is desired to promote adhesion and compatibilization in blends, but the extension of the grafting reaction and the structure of the copolymer are decisive to improve the blend properties. High concentration of graft copolymer brings processing difficulties, because of their rheology. The TEM micrographs for PA 6/epichlorohydrin elastomers blends reported previously<sup>6</sup> reveal a heterogeneous morphology, with elastomers domains of different dimensions and forms and a poorly defined interface. This morphology is a result of the complex rheological behavior of the mixture, whose composition changes strongly during the blending. In addition, copolymers exhibiting network structures can act as a rigid shell around the elastomer particle, hindering the transference of mechanical energy between the matrix and the dispersed phase observed by tensile tests. Oshinski and colleagues<sup>7</sup> observed a similar behavior for PA 6,6/SEBS-g-MA blends.

## CONCLUSIONS

The PA 6-epichlorohydrin elastomers blends show a lower tensile strength in comparison to pure polyamide, despite the presence of graft copolymer PA 6-g-elastomer to promote interfacial adhesion. It is suggested that the mechanical properties of the blends are strongly influenced by the interface, apparently more fragile. The performance of the graft copolymer for compatibilization is determined by their concentration and structure.

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