

Reactive Blending of Polyamides with Epoxidized Elastomers

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ABSTRACT: Melt blending of aliphatic polyamides (PA6, PA66, PA12) with epoxidized and nonepoxidized elastomers (SBS, BS, PB) was investigated. IR and rheological studies have shown that epoxidized elastomers can simultaneously react both with polyamides and within their own phases during melt blending. Relative intensity of both processes is the main factor, which determines structure and properties of blends. SEM observations indicated that use of epoxidized elastomers improves blend homogeneity and decreases mean size of dispersed elastomer phase in comparison with nonepoxidized elastomers. Mechanical properties of epoxidized elastomers based

blends are generally better with respect to similar blends with nonepoxidized elastomers. They depend on blend composition and type of polyamide and elastomer. Elastomer addition decreases tensile strength of all systems but in some cases, a considerable rise of impact strength was measured. Epoxidized SBS block copolymer was found to be the most effective modifier, especially with respect to PA6 and PA12. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2992–3000, 2007

Key words: aliphatic polyamides; polybutadiene; butadiene-styrene copolymers; epoxidation; melt blending

INTRODUCTION

Reactive blending is in many cases the most effective way of gaining new polymeric materials with unique properties. This is due to the possibility of reactions between two or more polymeric components with active groups during their melt blending. Most of the aliphatic polyamides are typical thermoplastic polymers with amine, amide, and carboxylic groups, which are potentially capable of reaction during the blending with properly chosen functional polymers. The blends containing polyamides (especially PA6) as one of the components were the subject of different investigations and review works.^{1–3} As the second component or compatibilizer polyolefins,^{4–10} polystyrene and styrene polymers (ABS or SAN)^{11–17} and different elastomers such as natural and nitril rubbers,^{3,18–20} SEBS^{16,21–24} or EPM, and EPDM copolymers^{23–27} were oft used. To improve the blend properties, they were frequently functionalized with the anhydride,^{11,15,18,23,25} oxazoline,^{3,10,12–14,17,20} or epoxy^{4,6,8,9,11,19,24,28,29} groups by grafting (or copolymerization) with maleic anhydride, vinyl oxazoline, or glycidyl methacrylate. The use of glycidyl methacrylate (GMA) leads to functionalized polymers with side epoxy groups. The oxidation of double bonds

makes it possible to introduce the epoxy groups into the main polymer chain. The best examples of such compounds are the epoxidized diene elastomers. The majority of literature data about the blends of polyamides with epoxy groups containing polymers refers to GMA functionalized polymers. Only single works deal with other epoxy polymers, such as epoxidized natural rubber,¹⁹ a dendrimer with oxiran end groups²⁹ or diepoxides.³⁰ The epoxidized diene elastomers were more widely applied in blends with other polymers (including nonepoxidized elastomers), such as poly(butylene terephthalate),³¹ poly(vinyl chloride),^{32–36} poly(methyl methacrylate),³⁷ poly(3-hydroxybutyrate),³⁸ and styrene-butadiene rubber.³⁹

The aim of this study was to examine the reactivity and some properties of blends of three polyamides (PA 6, PA 6.6, and PA 12) with three epoxidized or nonepoxidized elastomers—linear block copolymer styrene-butadiene-styrene (ESBS or SBS), statistical copolymer butadiene/styrene (EBS or BS), and 1,4-*cis*-polybutadiene (EPB or PB).

EXPERIMENTAL

For the investigations, the following polyamides and elastomers were used:

PA6: Tarnamid T, manufactured by Tarnow S.A.
PA6.6: Durethan A, manufactured by Bayer

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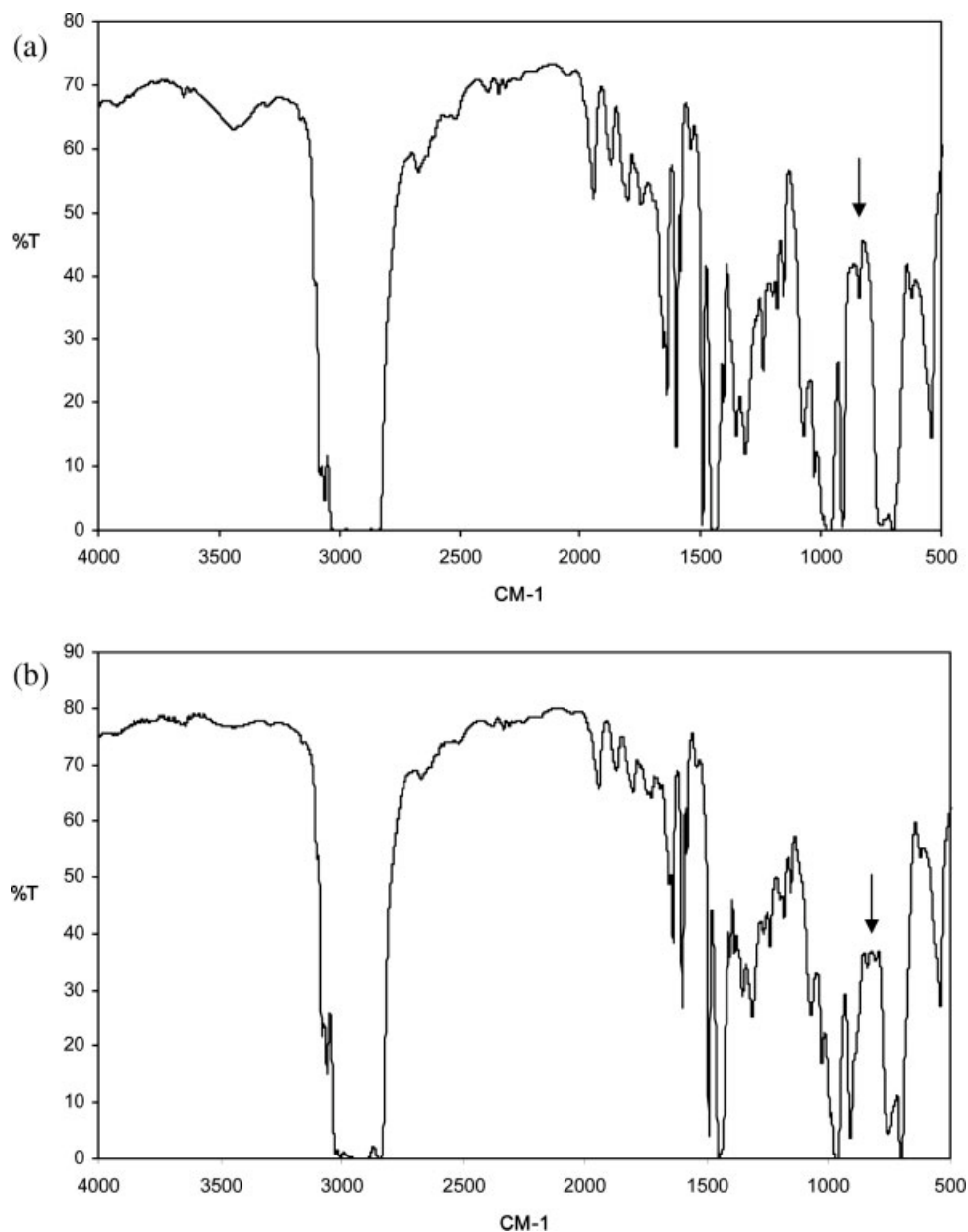


Figure 1 IR-spectra of nonepoxidized (a) and epoxidized (b) SBS copolymer.

PA12: Grilamid manufactured by Emser

SBS: Kraton D1102TR, manufactured by Shell (styrene content 27%)

BS: KER 1500, manufactured by Dwory S.A. (styrene content 25%)

PB: SKD-EF manufactured by Russia Efremov Synthetic Rubber Enterprise (cis-structure content 92%)

Epoxidized elastomers (ESBS, EBS, EPB) were obtained by the method consisting in oxidation of double bonds in an elastomer (dissolved in toluene) with formic peracid created in situ from formic acid and hydrogen peroxide.⁴⁰ The mean content of epoxy

groups in elastomers used for blending was found to be 0.25–0.30 mol/100 g. For reactivity studies, elastomers with a lower content of oxirane groups were also applied.

The blends of all polyamides containing 5, 10, or 15% of epoxidized or nonepoxidized elastomer were prepared in the plasticating system of a screw injection molding machine. The optimal blending conditions, i.e., the mean residence time of the composition in the heated part of the barrel (~ 6 min) and the mean melt temperature (473 K for PA12, 503 K for PA6, and 543 K for PA6.6), were controlled by choice of the number of injection cycles, the mean barrel temperature, and the pressure at the end of the rotating screw. The blends obtained under these

conditions were optically homogeneous, and they did not show any visible thermal degradation. It was especially important for blends with PA6.6, which require high processing temperatures. The applied homogenization method has some advantages over typical blending in extruder or kneader, because it needs no water cooling of the blends, and it makes possible the simultaneous molding of the specimens for testing. The film samples, e.g., for IR studies, were gained by compression molding.

For IR studies of the reactivity, blends containing up to 75% of elastomer and "layer compositions" obtained by coating of PA films with an elastomer solution were also prepared.

The properties of elastomers and polyamide-elastomer blends were studied by means of IR spectroscopy, SEM observations, rheological measurements, and mechanical testing.

RESULTS AND DISCUSSION

The creation of new groups or compounds during reactive melt blending of two or more polymers is usually observed indirectly as some time-dependent changes in structure and properties of a blend. The changes in IR-spectra can be treated as a more direct evidence of reaction between blend components. However, the IR-investigations of the reactive polymer systems are frequently faced with difficulties resulting from very small changes in IR-spectra. This is mainly due to a low content of the reaction products associated with covering of their weak absorption bands by much more intense bands of other groups present in polymers. For instance, the reaction between components during the blending of PA1010 with PP-g-GMA was observed as fine but reproducible changes in the IR-spectrum of the system.⁸ In this case, the reaction can be evidenced as a decay of weak absorption peaks corresponding to the epoxy groups in elastomer. Figures 1(a) and 1(b) present as an example the IR-spectra of nonepoxidized and epoxidized SBS copolymer, respectively. The basic qualitative difference in both IR-spectra appears in the range 800–900 cm^{-1} , which corresponds to the absorption range of oxiran groups.⁴¹ The IR-spectrum of ESBS [Fig. 1(b)] show in this range (denoted by arrow) an additional small peak, which does not appear in SBS spectrum [Fig. 1(a)]. The same behavior was also observed for other elastomers at different epoxidation degrees. This additional peak is also visible in IR-spectra of blends with high elastomer content, while for blends containing less elastomer it disappears. It is shown as an example in Figures 2(a) and 2(b) for blends of PA12 with 75 and 25% ESBS, respectively. To exclude a possible "dilution effect" caused by decreasing elas-

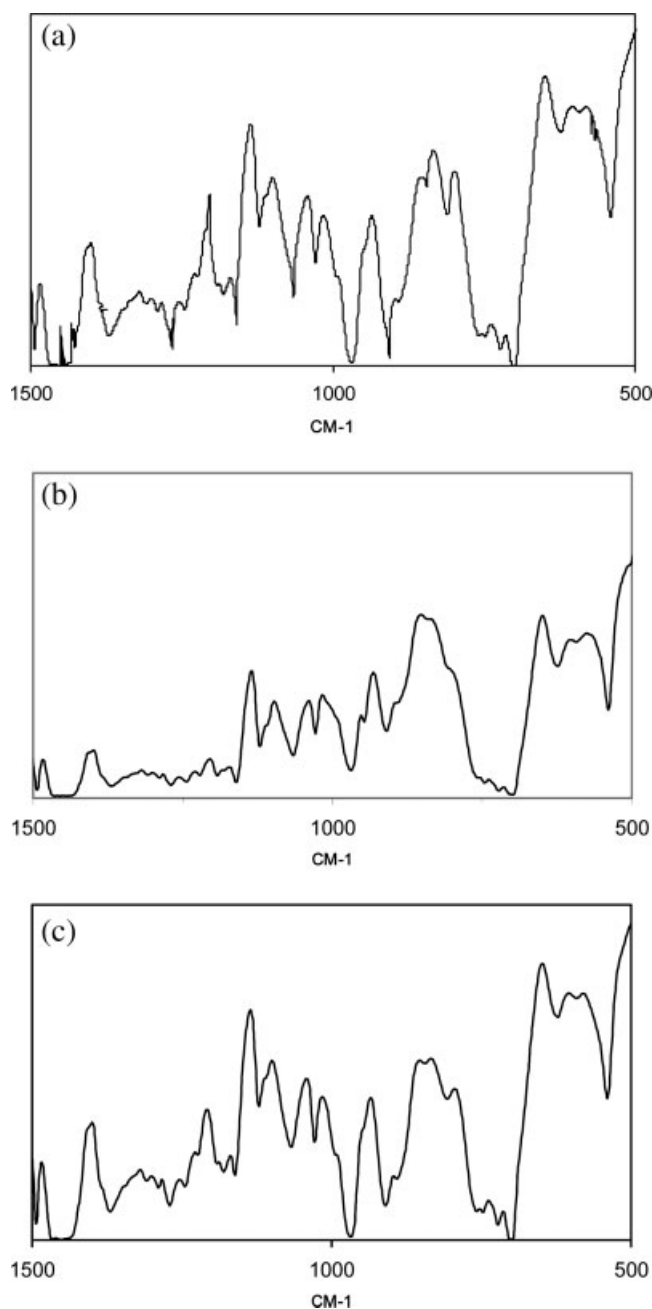


Figure 2 IR-spectra of different PA12–ESBS systems: (a) blend with 75% ESBS, (b) blend with 25% ESBS, (c) layer composition with 25% ESBS.

tomers concentration in blend, which can also lead to the peak decay, a "layer composition" with 25% ESBS was prepared. To this end, a PA12-film was coated with ESBS toluene solution several times and dried under vacuum at a low temperature. The prepared sample was heated in a laboratory press for ~ 10 min at 473 K to initiate the probable reaction between active groups. IR-spectra of the sample before and after heating were measured. From the spectrum after heating shown in Figure 2(c) it follows that the peaks corresponding to epoxy groups are visible, i.e., the

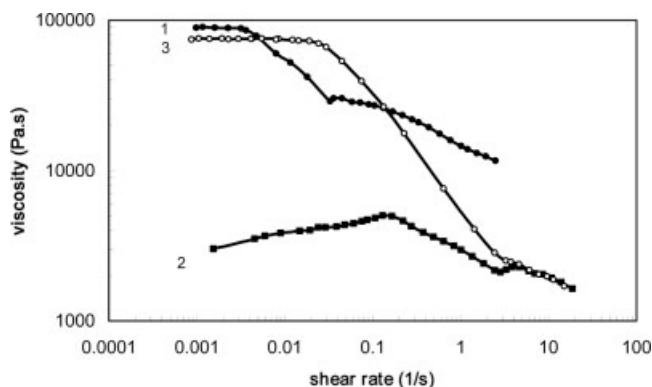


Figure 3 Viscosity curves of SBS and ESBS at different heating times: 1, ESBS (15 min); 2, ESBS (3 min); 3, SBS.

“dilution effect” plays no significant role. Therefore, it can be assumed that the epoxy groups of the elastomer finely dispersed in the excess of PA are used up in the reaction with its end groups. This is probably due to a much larger contact area of blend components in comparison with the “layer composition”. Fine qualitative differences (secondary peaks) in IR-spectrum of the “layer composition” observed in the range $1150\text{--}1250\text{ cm}^{-1}$ before and after heating result probably from the reaction between components at the phase boundary.

The reaction between polyamide and epoxidized elastomer during their melt blending is accompanied by another important competitive process, i.e., the reaction between oxiran groups within elastomer phase leading to its crosslinking. The intensive crosslinking can decrease the elastomer ability to blend and react with polyamide resulting in worsening the blend properties. The elastomer phase changes were studied by viscosity measurements with a stress rheometer (plate and plate geometry). The elastomer sample was placed between plates and its viscosity curve was measured just after the desired temperature had been reached (~ 3 min). The measurement with the use of the same sample was repeated after a longer heating time (e.g., 15 min). Figure 3 presents as an example the results obtained for SBS and ESBS containing $0.16\text{ mol}/100\text{ g}$ of epoxy groups at 473 K . It was found that the nonepoxidized SBS behaves stably because the heating time does not change significantly its viscosity curve with characteristic shape reflecting the shear rate-dependent structural changes (breakdown of domain structure) during the flow of block copolymers.⁴² It was also found that BS and PB behave less stably while heating, and their viscosity was about 10 times higher than that of SBS. Significant viscosity variations with the heating time can be observed for ESBS. The ESBS viscosity measured after a short heating time (~ 3 min) shows a monotonic increase at very low shear rates, which usually correspond to

the Newtonian flow region. Such flow region can be observed on the viscosity curve of the same sample after a longer heating time (~ 15 min). In this case, the ESBS viscosity becomes about 10 times higher and almost independent of the heating time. The above changes can be interpreted as a result of reaction between elastomer molecules, which lead to an increase in molecular weight and viscosity of the system during measurement. It is supported by the fact that the “inflection point” of the viscosity curve (corresponding to the structure breakdown) is shifted toward lower shear rate values with increasing time of thermal treatment, i.e., with an increase of molecular weight. The maximum on the curve for short heating time (Fig. 3) can be interpreted as a result of two competitive processes—viscosity rise caused by reaction and viscosity lowering due to the shear-thinning behavior at higher shear rates.

Contrary to ESBS, the other investigated elastomers (EBS, EPB) demonstrate a much higher crosslinking tendency when heating. After the short (~ 3 min) heating time, their viscosities became so high that the measurements could not be performed. The effect of chemical structure on the crosslinking ability of epoxidized elastomers is especially visible for ESBS and EBS. Both copolymers have a similar epoxy group content and styrene content. They differ only by a distribution of styrene mers (block or statistical) in the chain. It was also stated that the intensity of crosslinking reactions increases with higher epoxy group content for all elastomers. Higher crosslinking susceptibility during thermal treatment demonstrates also the nonepoxidized elastomers BS and PB in comparison with SBS.

Different reactivity of ESBS, EBS, and EPB described above affects the rheological properties of their blends with polyamides. Figure 4 shows as an example the comparison of viscosity curves of PA12 and its blends with 15% addition of various nonepoxidized and epoxidized elastomers. It can be seen

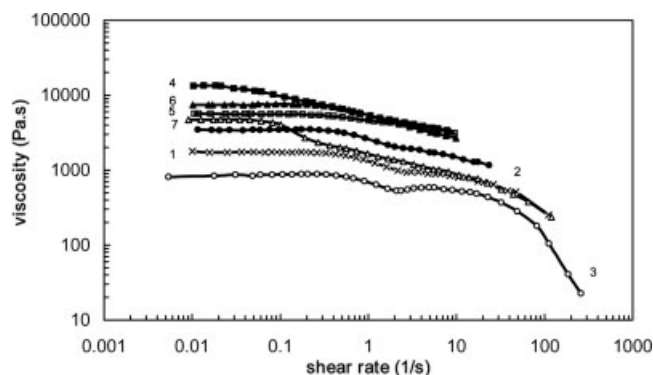
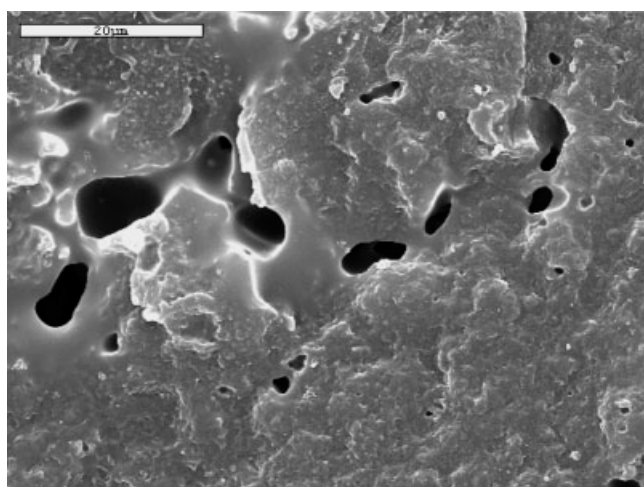
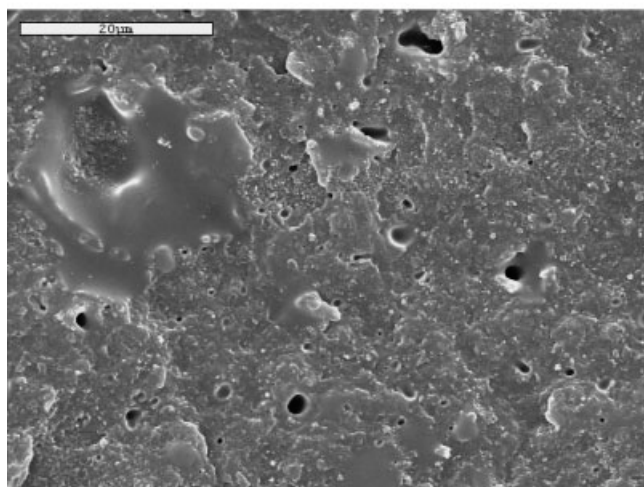


Figure 4 Viscosity curves of PA12 and its blends with different elastomers: 1, PA12, and its blends with, 2, SBS; 3, ESBS; 4, BS; 5, EBS; 6, PB; 7, EPB.



(a)

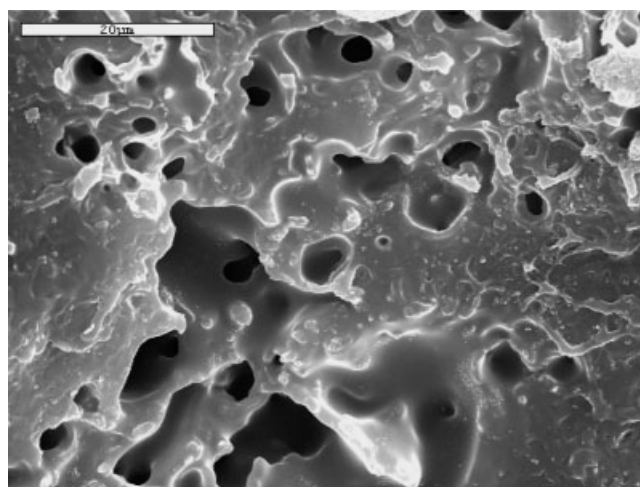


(b)

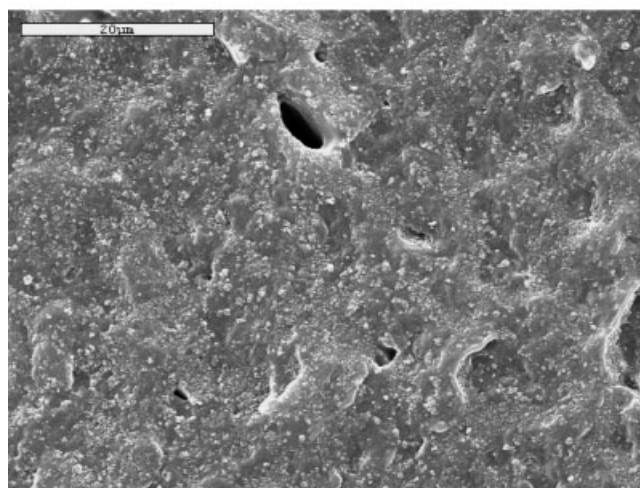
Figure 5 SEM micrographs of PA12 blends with BS (a) and EBS (b).

that the viscosity of blends with epoxidized elastomers is lower in comparison with blends containing the nonepoxidized equivalents. The viscosity of almost all blends is higher than the viscosity of pure polyamide. The only exception is the PA12-ESBS blend. Similar tendency can be also observed for other polyamides. The ESBS elastomer is probably the only one, which lowers the viscosity of blends with polyamides at increasing concentration in blend (within investigated range 0–15%). Such behavior results probably from the specific ESBS properties discussed previously, i.e., its ability to react with polyamides at relatively low viscosity and crosslinking tendency. It seems that ESBS blended with polyamides acts as a “lubricant” in contrast to other elastomers, which in blends with polyamides behave as “rigid fillers”. Some of these features can be also observed in SEM micrographs discussed below.

The existence of chemical reactions between polyamides and epoxidized elastomers leads to a visible improvement of the homogeneity of their blends. This statement follows clearly from the SEM observations of the phase structures of blends with 15% epoxidized elastomers and their nonepoxidized equivalents. The examples of electron micrographs for six polyamide-elastomer systems are presented in Figures 5–10. The blend samples used for SEM observations were fractured after immersion in liquid nitrogen, and then the elastomer phase was removed by extraction with hot toluene. From Figures 5–10, it can be seen that the epoxidized elastomers are as a rule more finely dispersed in the polyamide matrix. This is especially valid for systems containing EBS and EPB elastomers. Besides a better dispergation ability, these elastomers show a higher inclination to cross-link in comparison with ESBS. This behavior is the

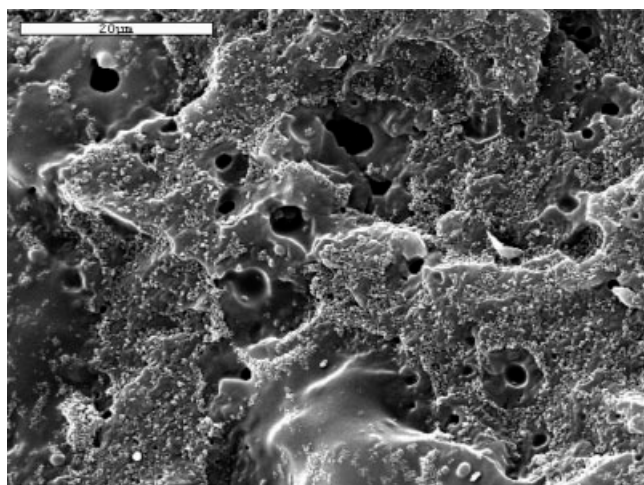


(a)

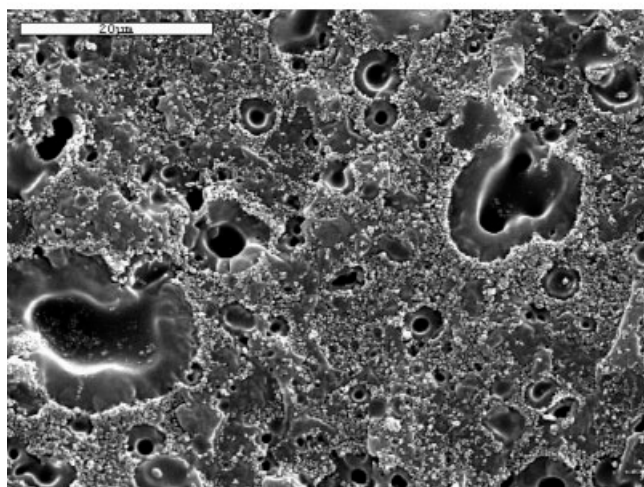


(b)

Figure 6 SEM micrographs of PA12 blends with PB (a) and EPB (b).



(a)



(b)

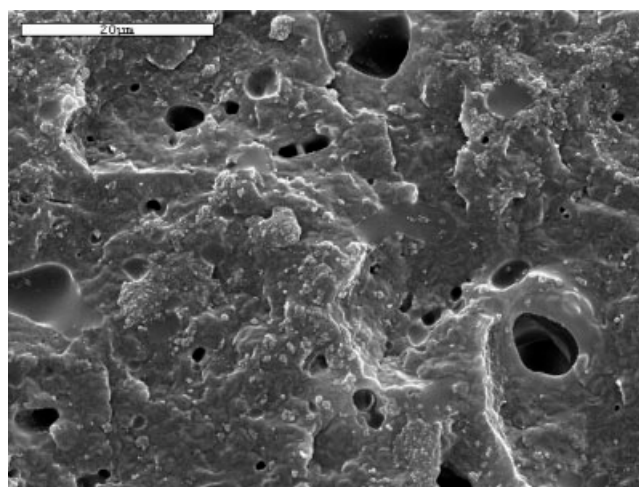
Figure 7 SEM micrographs of PA6 blends with SBS (a) and ESBS (b).

most clearly visible in Figure 10(b) for the system PA66–EPB with the highest processing temperature, where the crosslinking reactions are probably the most intense. Toluene insoluble, i.e., crosslinked, spherical elastomer particles appear at the fracture surface. The SEM observations for other systems lead to the general conclusion that the crosslinking intensity of both epoxidized and nonepoxidized elastomers increases with the rise of the processing temperature, which depends on the polyamide type. It is probably one of the main reasons that the toughening efficiency (discussed later) of polyamides with crosslinking susceptible elastomers (EBS, EPB) is generally lower in comparison with ESBS, and it decreases with increasing processing temperature of polyamide.

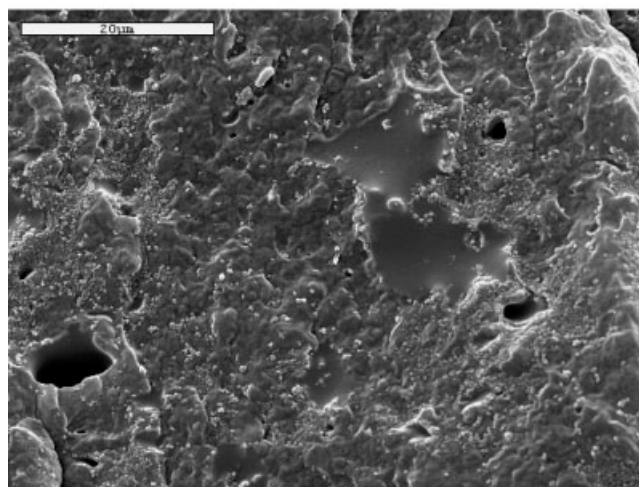
The SEM observations indicate another interesting feature especially in blends containing ESBS [Figs.

7(b) and 9(b)]. Around the holes originating from the extracted elastomer, “the annular structures” can be observed. In blends with nonepoxidized elastomers [Figs. 7(a) and 9(a)], such phenomenon is much less intense. These structures in blends with epoxidized elastomers can be treated as a sign of the existence of an interlayer created from products of the reaction between components. It is not possible to remove the interlayer by extraction because of its strong chemical bounding to the polyamide phase and lower toluene solubility.

The strength properties of blends reflect both their morphological features and the properties of virgin components. Table I presents the relative values (with respect to pure polyamide) of the tensile strength (static property) and notched impact strength (dynamic property) for blends of polyamides with epoxidized elastomers added in amount of 0–15%. It

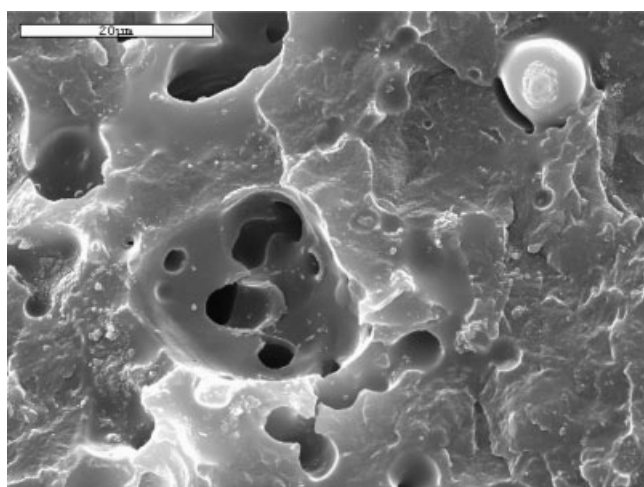


(a)

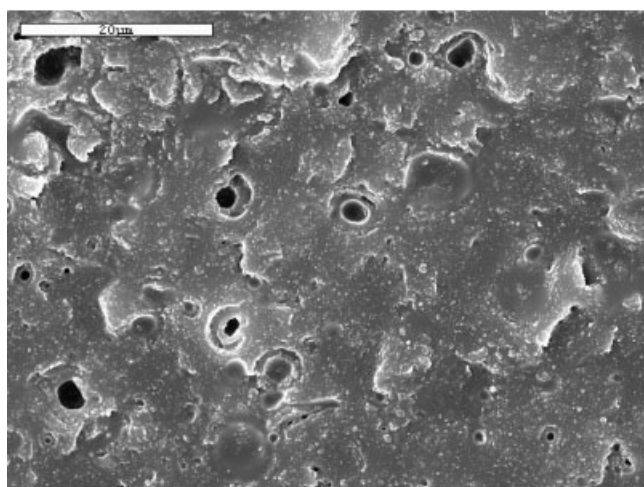


(b)

Figure 8 SEM micrographs of PA6 blends with BS (a) and EBS (b).



(a)



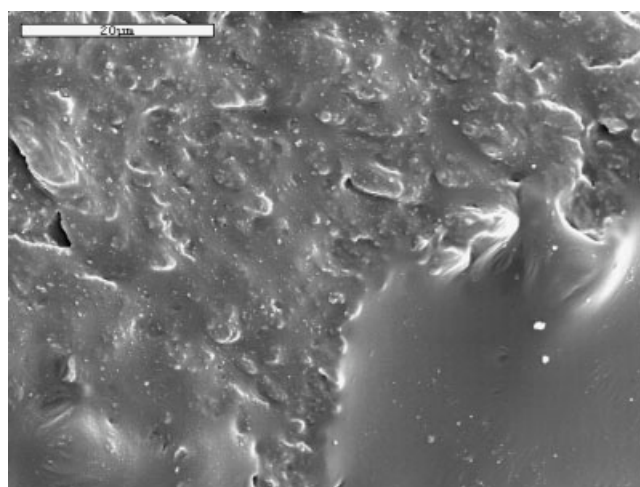
(b)

Figure 9 SEM micrographs of PA66 blends with SBS (a) and ESBS (b).

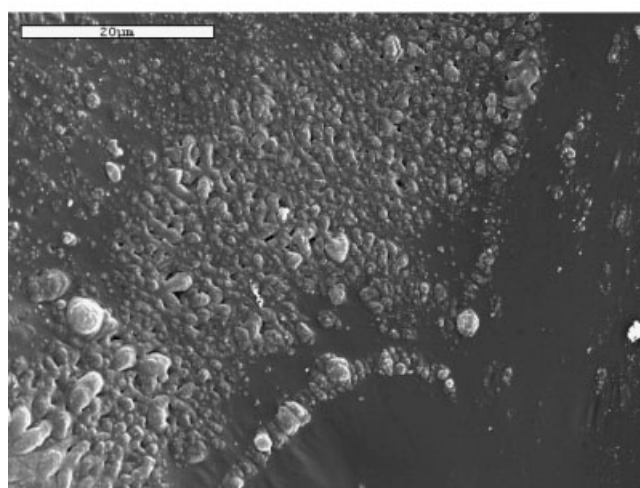
should be noted that these properties for similar blends with nonepoxidized elastomers (not included in the table) are as a rule somewhat lower. It can be treated as a result of better adhesion at the phase boundary due to increased affinity and reactions between components. Generally, the addition of the “softer and weaker” elastomer leads to a monotonic decrease of the tensile strength of all systems in comparison with the initial polyamide. It can be seen that the best results in all cases are obtained for blends based on ESBS. The more crosslinking susceptible EBS and EPB are less efficient. On the basis of the results of other experiments, it can be concluded that the strengthening efficiency of epoxidized elastomers decreases with the rise of their crosslinking susceptibility, which in turn lowers their ability to react with polyamide and to improve the interfacial adhesion between blend components.

Another interesting tendency that follows from the data of Table I is an increase in the relative tensile strength with increasing of the processing temperature, which in turn depends on the polyamide type. It is especially visible for blends containing 5 and 10% of elastomer. More intense elastomer crosslinking and reactions between components resulting in the loss of flexibility and the rise of strength of the elastomer phase can be treated as the probable reasons of such behavior.

This statement is supported by an opposite tendency with respect to the influence of the processing temperature on the relative impact strength. The lowest values of this property are obtained for blends of PA66 (with the highest processing temperature) containing 15% of elastomer. Moreover, EBS and EPB with higher crosslinking susceptibility are less efficient than ESBS. It should be noted that a good tough-



(a)



(b)

Figure 10 SEM micrographs of PA66 blends with PB (a) and EPB (b).

TABLE I
Relative Strength Properties of Various Polyamide–Epoxydized Elastomer Blends

| Elastomer content (wt %) | PA12 | | | PA6 | | | PA66 | | |
|---|------|------|------|------|------|------|------|------|------|
| | ESBS | EBS | EPB | ESBS | EBS | EPB | ESBS | EBS | EPB |
| Relative tensile strength (static property) | | | | | | | | | |
| 5 | 0.85 | 0.77 | 0.73 | 0.88 | 0.80 | 0.74 | 0.95 | 0.92 | 0.87 |
| 10 | 0.78 | 0.67 | 0.63 | 0.75 | 0.74 | 0.68 | 0.80 | 0.78 | 0.75 |
| 15 | 0.77 | 0.59 | 0.55 | 0.68 | 0.65 | 0.63 | 0.74 | 0.72 | 0.62 |
| Relative notched impact strength (dynamic property) | | | | | | | | | |
| 5 | 0.72 | 0.54 | 0.51 | 1.08 | 0.82 | 0.72 | 1.04 | 0.69 | 0.60 |
| 10 | 1.17 | 0.61 | 0.57 | 1.47 | 0.89 | 0.87 | 0.97 | 0.51 | 0.47 |
| 15 | 1.40 | 0.69 | 0.61 | 1.48 | 1.16 | 0.92 | 0.92 | 0.47 | 0.30 |

ening efficiency of ESBS (increasing with its content) is restricted to PA12 and PA66, which require moderate processing temperatures. At very high processing temperature ESBS becomes also too rigid for an efficient toughening. The significant temperature effect on the toughening efficiency is additionally confirmed by the fact that PA6 and PA66, which behave completely different in blends with ESBS, have a very similar chemical structure.

CONCLUSIONS

The investigations have shown that during melt blending of aliphatic polyamides and epoxydized elastomers, chemical reactions between active groups of components take place. Simultaneously, competitive crosslinking processes in elastomers occur. The structure and properties of different polyamides, epoxydized elastomers blends depend on the intensity of both competitive processes. The intensity is in turn a function of the elastomer type dependent crosslinking susceptibility and the polyamide type dependent processing temperature. The use of easily crosslinkable elastomers and very high processing temperatures lead to the lowering of blends impact strength (dynamic property). Simultaneously, the temperature increase is conducive to a less intense decrease of the tensile strength (static property) of blends. The epoxydized linear block copolymer styrene/butadiene/styrene (ESBS) was found to be the most efficient polyamide modifier especially with respect to PA6 and PA12. In comparison with other epoxydized elastomers used in the studies, ESBS shows a relatively low crosslinking tendency at moderate processing temperatures characteristic of PA12 and PA6.

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