

# Structure and Properties of Polyamides-Epoxidized Elastomers Blends

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**ABSTRACT:** Blends of aliphatic polyamides (PA6, PA66, and PA12), containing 0–15 wt % nonepoxidized or epoxidized elastomers (statistical copolymer butadiene–styrene BS/EBS or linear block copolymer styrene–butadiene–styrene SBS/ESBS) were investigated. For PA6–elastomer blends, taken as an example, it was shown that with increasing blending time, mechanical properties of blends increase, especially, if ESBS copolymer is used. It can be treated as an indirect sign of reactions between components. It was also found that in blends considerable changes of glass temperatures of components occur. Polyamides in blends with elastomers have smaller heats of fusion in comparison with virgin polyamides. It testifies to hindering of PA crystalliza-

tion by elastomers. In some cases, significant shifts of melting points are also observed. Measurements of water contact angle show that all blends have very similar values of contact angles, which are lower than those of virgin polyamides. Elastomer content does not also affect the blend water uptake. However, it depends on the polyamide and elastomer type contrary to contact angle. Highest water uptake changes are observed in blends of PA66, especially for epoxidized elastomers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1872–1879, 2006

**Key words:** reactive processing; epoxidized elastomers; polyamides; phase behavior

## INTRODUCTION

Blending processes of two or more polymers are potentially a huge source of new polymeric materials. Very wide possibilities of the choice of polymers, their proportions, and blending conditions, which may lead to new materials with precious properties, are reflected by a very great number of papers, books, and patents dealing with polymer blends.<sup>1</sup> A special class of blends comprises polymer components that are capable of mutual reactions during blending, because of the existence of active groups and mechanochemical processes. Aliphatic polyamides (especially PA6) containing amine, amide, and carboxylic groups are frequently components of such reactive systems with different functionalized polymers.<sup>2–4</sup> Functional groups most frequently introduced into polymers are the anhydride, oxazoline, and epoxy (oxiran) groups. Various polymers with oxiran side groups (*e.g.*, of glycidyl methacrylate or obtained by grafting) were so far applied as components in blends with polyamides.<sup>1–8</sup> However, there exists only single data about polyamide systems with polymers having epoxy groups situated directly in the backbone—mainly

with epoxidized diene elastomers. Epoxidized natural rubber (ENR) was used to improve the adhesion of tire rubber to PA12.<sup>9</sup> Properties of PA6 blends with epoxidized ethylene–propylene–diene elastomer (EEPDM) were also studied.<sup>10</sup> EEPDM was used as modifier in blends with other polymers, *e.g.*, PBT<sup>11</sup> and PC.<sup>12</sup> Almost all studies on blends of ENR with various polymers, *e.g.*, PVC, chlorinated polyethylene, and SAN copolymer, were discussed in a review paper.<sup>13</sup> Some properties of PVC blends with epoxidized SBS copolymers were also described.<sup>14</sup>

This article presents the investigation on phase morphology and different properties of blends of three aliphatic polyamides—PA6, PA66, and PA12, with two nonepoxidized and epoxidized elastomers—statistical copolymer butadiene/styrene (BS or EBS) and linear block copolymer styrene/butadiene/styrene (SBS or ESBS). Both copolymers have similar styrene content, but they differ in distribution of styrene and butadiene units along the chain.

## EXPERIMENTAL

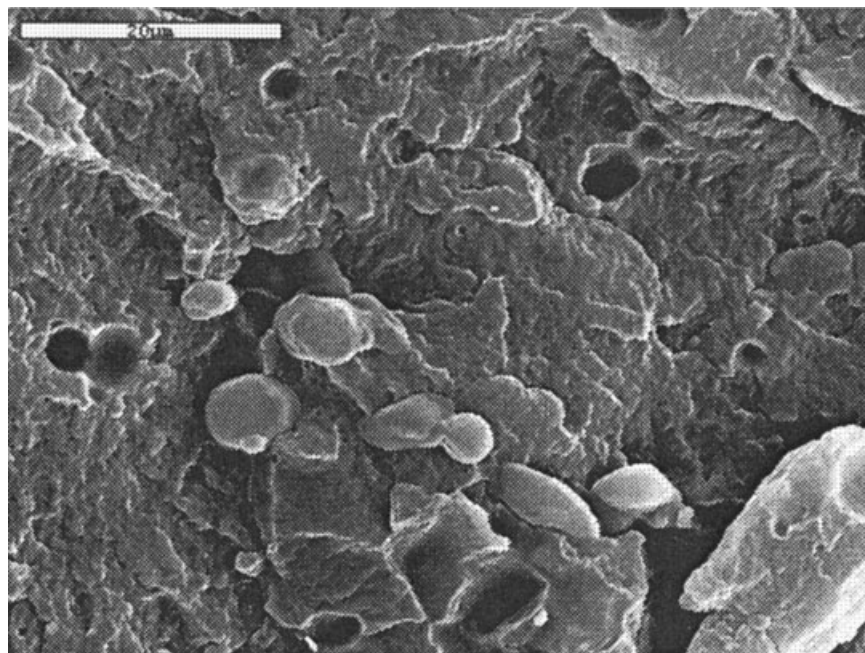
The following polyamides and elastomers were used:

- PA6–Tarnamid T, manufactured by Tarnow S.A. (Poland).
- PA6.6–Durethan A, manufactured by Bayer (Germany).

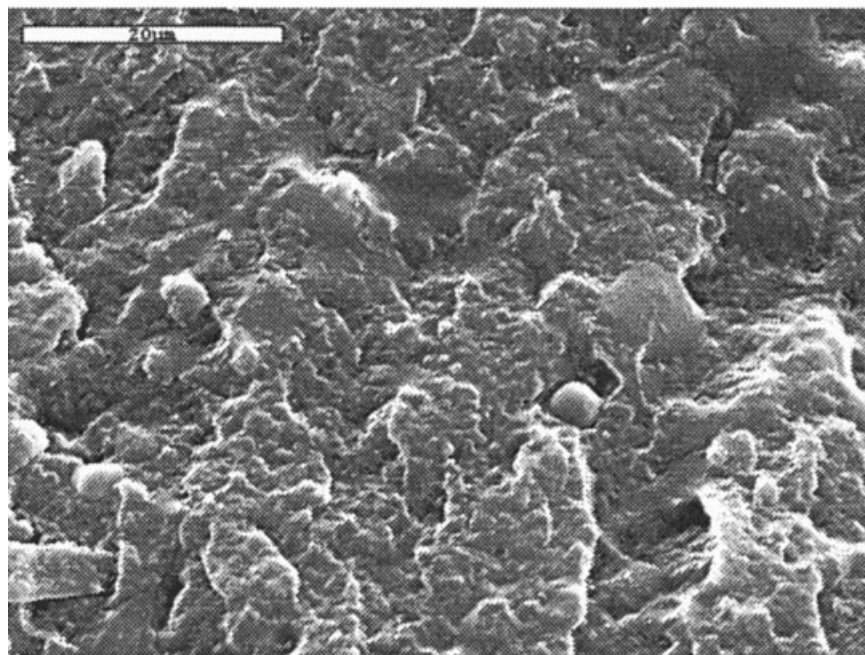
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**TABLE I**  
**Relative Mechanical Properties of PA6 Blends with BS/EBS and SBS/ESBS for Various Elastomer Content and Number of Injection Cycles (Blending Time)**

Property	Elastomer content (%)	BS		EBS		SBS		ESBS	
		1	2	1	2	1	2	1	2
Tensile strength	5	0.95	0.89	0.78	0.78	0.75	0.89	0.88	0.95
	10	0.82	0.82	0.74	0.75	0.75	0.79	0.72	0.86
	15	0.69	0.71	0.63	0.70	0.67	0.72	0.69	0.80
Charpy notched impact strength	5	0.97	1.00	0.69	0.92	0.59	1.06	0.87	2.02
	10	0.76	0.77	0.89	1.00	1.00	1.08	1.28	2.15
	15	1.16	1.21	0.81	0.92	1.16	1.17	1.87	3.24



(a)



(b)

**Figure 1** SEM micrographs of sample fractures of PA6 - SBS/ESBS blends (a) PA6 -SBS blend, (b) PA6 -ESBS blend.

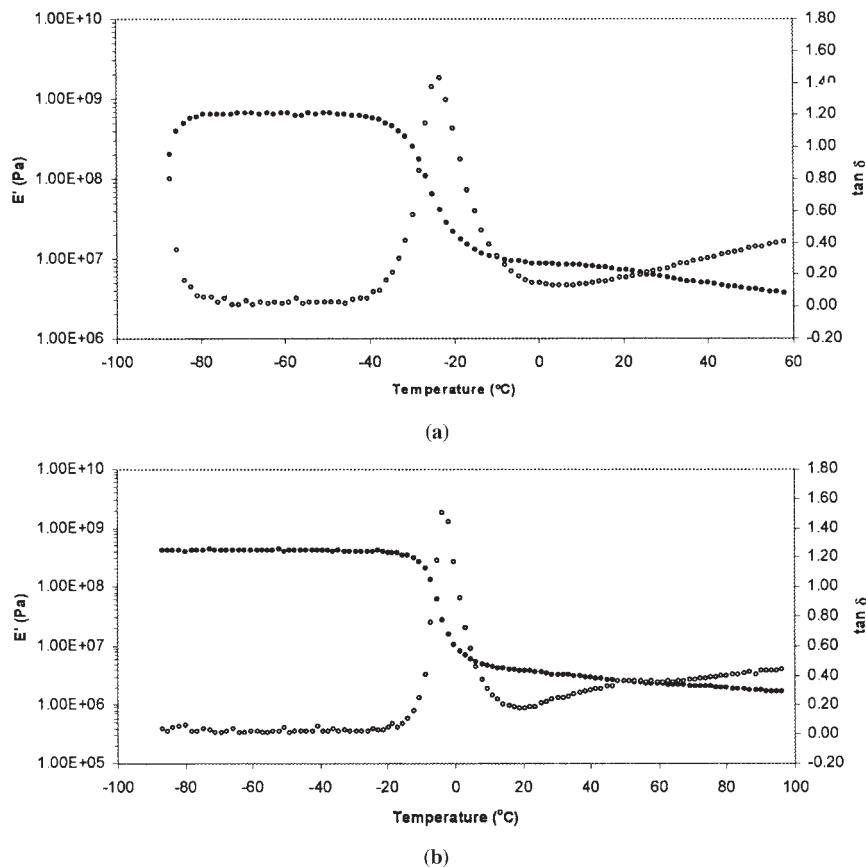


Figure 2 DMTA spectra of nonexoxidized (a) and epoxidized (b) BS copolymer.

- PA12–Grilamid, manufactured by Emser (Germany).
- SBS–Kraton D1102TR, manufactured by Shell (styrene content 28%).
- BS–KER 1500, manufactured by Dwory S.A. (Poland) (styrene content 26%).

EBS and ESBS elastomers were obtained by the method consisting in oxidation of double bonds with formic peracid created *in situ* from formic acid and hydrogen peroxide. The reaction was carried out in hot toluene solution.<sup>15</sup> The epoxy groups content was equal to 0.25–0.30 mol/100 g for both elastomers.

The blends of all polyamides containing 5–15% of elastomer (BS, EBS, SBS, ESBS) were prepared in the plasticating system of a screw injection molding machine. This method makes possible the direct molding of the test samples, without additional water cooling and drying of blends. The blending time was changed by variation of the number of injection cycles.<sup>1–3</sup> To this end, the specimens were ground and repeatedly injected. Other important parameters such as the mean barrel temperature (473 K for PA12, 503 K for PA6, and 543 K for PA6.6), screw rotation speed, and pressure at the end of the rotating screw were chosen to obtain optically homogeneous blends without

symptoms of thermal degradation. The mean residence time of the blend in the barrel was estimated to be ~2 min per injection cycle.

The structure and properties of blends were investigated with mechanical tests, water uptake and contact angle measurements, as well as DSC, SEM, and DMTA methods. DMTA samples (1 mm thick) were additionally prepared by compression molding from previously injected specimens. All measurements were carried out with typical equipment at standard conditions

## RESULTS AND DISCUSSION

One of the most fundamental features of reactive systems is the dependence of their properties on the blending time, which result from the reactions between components. The same phenomenon can also be observed for investigated blends. It will be demonstrated taking as an example the blends of PA6 with BS/EBS and SBS/ESBS elastomers. Table I shows the relative values (with respect to pure PA6) of tensile strength (static property) and impact strength (dynamic property) for different PA6 blends with 5–15% elastomer as the functions of the blending time expressed with the number of injection cycles.

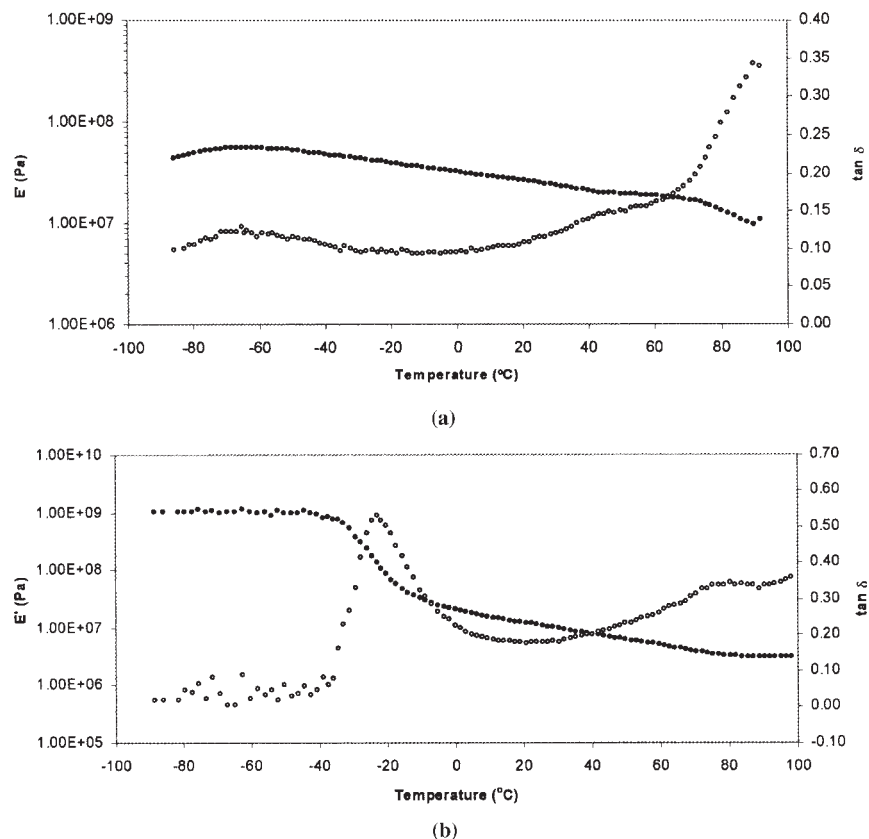


Figure 3 DMTA spectra of nonexoxidized (a) and epoxidized (b) SBS copolymer.

It can be seen that SBS/ESBS elastomer is generally much more efficient PA6 modifier in comparison with BS/EBS, both with respect to static and dynamic properties. An increase of elastomer content in blend lowers, as a rule, the tensile strength at a simultaneous rise of the impact strength. The extension of the blending time improves the properties of all systems. However, in the case of SBS and ESBS, the blending time dependent property changes are much more intensive. This is especially visible for ESBS, where the impact strength increases on average two times for any elastomer concentration, with increasing the blending time. The BS epoxidation leads to quite different effect in comparison with that of SBS. The obtained values of mechanical properties of EBS-based systems seem to be lower than those measured for BS. It is probably due to the fact that EBS elastomer has a much stronger tendency to react within its own phase (crosslinking) than with polyamide molecules in contrast to ESBS elastomer. This behavior will be discussed later.

The visible rise of interfacial adhesion resulting in property improvement for blends containing ESBS follows clearly from the SEM observations. Figure 1(a) and 1b show the liquid nitrogen sample fractures of PA6-SBS and PA6-ESBS blends with 15% elastomer content, respectively. The SBS containing blend is characterized by the sharp boundaries between spher-

ical elastomer particles and polyamide matrix. The visible hollows, which are the imprints of the elastomer phase, testify to a relatively low adhesion between SBS and PA6. Such phenomena are not observed for ESBS based blend. It should be also noted that the ESBS particles have approximately 2–3 times smaller dimensions in comparison with those of SBS. It can also be treated as a sign of better compatibility in the systems containing epoxidized elastomers. The behavior described earlier is also similar for blends with other investigated polyamides.

From the foregoing data, it follows that the elastomer epoxidation and the change of blending time improves the interfacial adhesion and compatibility, resulting in a visible improvement of mechanical properties of polyamide–elastomer blends. For this reason, it should also be expected that the increased interactions between components significantly change their phase properties, such as glass temperature, melting point, and heat of fusion in comparison with those of virgin (unblended) materials.

Figures 2–5 show some examples of DMA spectra (frequency 1 Hz) of pure components and blends with 15% elastomer. From Figures 2 and 3, it can be seen that epoxidation increases significantly the glass temperatures of BS and SBS (polybutadiene block). In the last case, very strong changes of the DMA spectrum

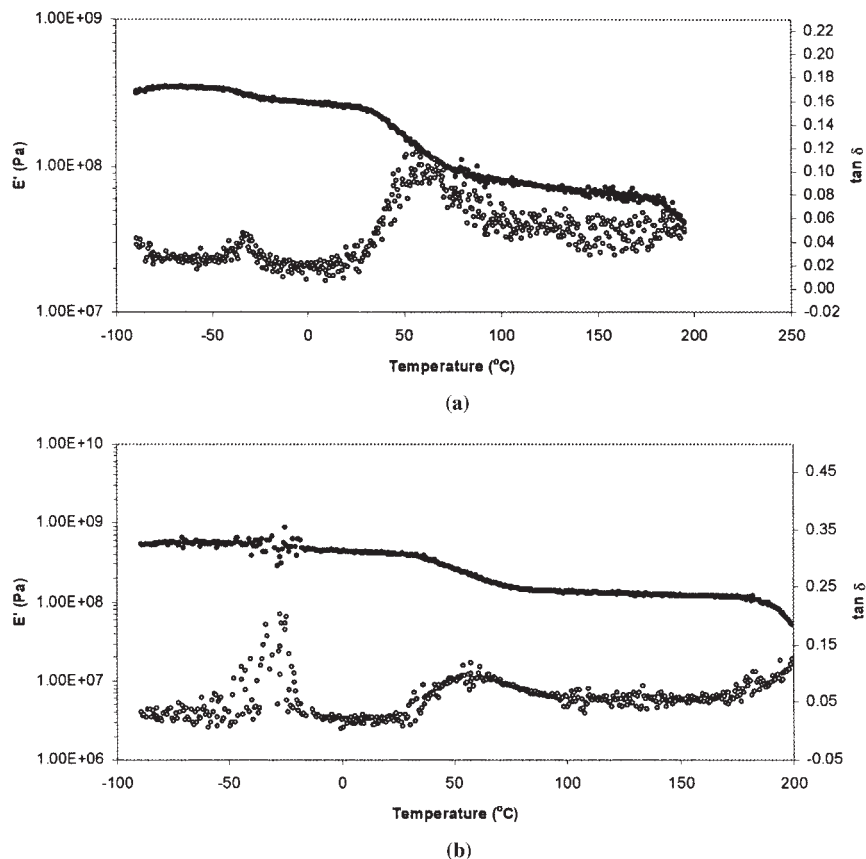


Figure 4 DMTA spectra PA6 –BS/EBS blends (a) PA6 –BS blend, (b) PA6 –EBS blend.

shape are observed. In the blend spectra (Figs. 4 and 5), two maximums of  $\tan\delta$  corresponding to vitrification of the soft elastomer block (lower temperature) and amorphous PA phase (higher temperature) commonly appear. However, in many cases, very strong scattering of measuring points in the transition regions is observed. This behavior is practically independent of sample preparation conditions, *e.g.*, cooling rate, during compression molding. It results prob-

ably from the creation of microcracks at the phase boundary, which are due to shrinkage stresses during the phase transitions. For this reason, the glass temperatures in blends, which are summarized in Table II, are determined with some errors resulting from the scattering of test data.

The data of Table II show that the blending in some cases leads to significant changes of glass temperatures of components. The observed shifts depend

TABLE II  
Glass Temperatures of Polyamide–Elastomer Blends<sup>a</sup>

Component A	Component B						
	PA12	PA66	PA6	SBS	ESBS	BS	EBS
PA12 <sup>b</sup>	334	—	—	335	332	334	332
PA66 <sup>b</sup>	—	336	—	339	340	340	344
PA6 <sup>b</sup>	—	—	338	330	335	331	332
SBS <sup>c</sup>	229	<sup>d</sup>	218	208	—	—	—
ESBS <sup>c</sup>	<sup>d</sup>	273	233	—	249	—	—
BS	219	235	240	—	—	250	—
EBS	261	270	246	—	—	—	269

<sup>a</sup> Glass temperature (K) of component A in blend with component B.

<sup>b</sup> Amorphous phase.

<sup>c</sup> Elastic (polybutadiene) block.

<sup>d</sup> Invisible.

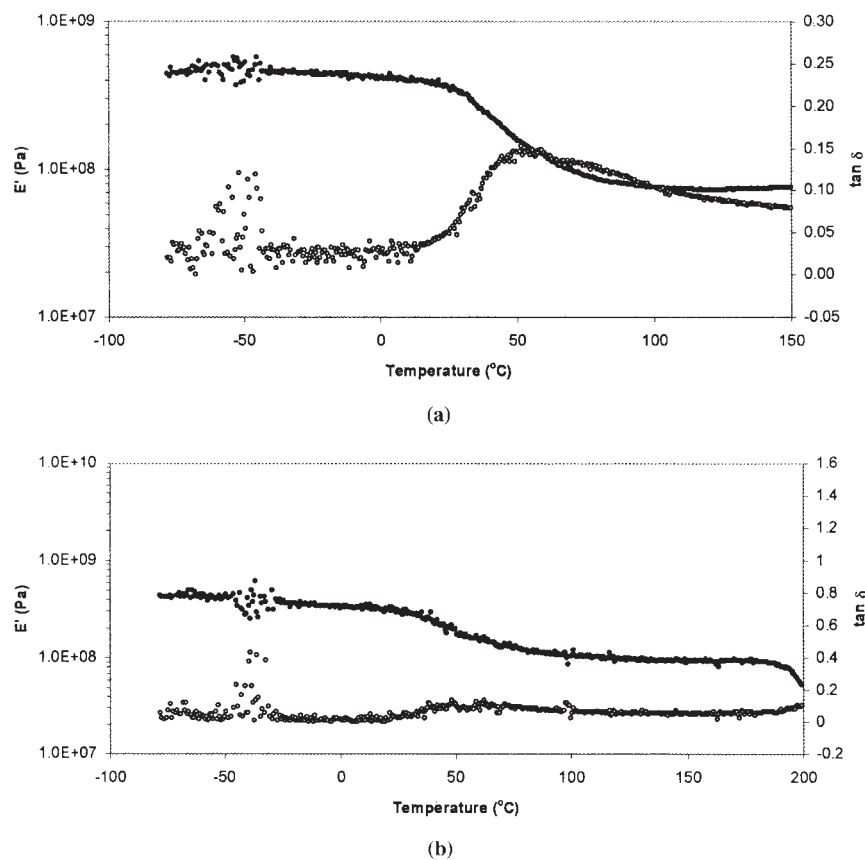


Figure 5 DMTA spectra of PA6-BS/EBS blends (a) PA6-SBS blend, (b) PA6-ESBS blend.

strictly on the blend type. Glass temperatures of elastomers decrease as a rule when blended with polyamides. Only in blends of EBS and ESBS with PA66, positive glass temperature deviations from those of pure elastomers are visible. Simultaneously, PA66 is the only polyamide that shows significant positive deviations of its glass temperature in blend with all elastomers. It should be noted that the absolute (positive or negative) glass temperature changes of all polyamides seem to be somewhat larger in blends with epoxidized elastomers in comparison with their nonepoxidized equivalents. Such behavior results probably not only from specific interactions between components, but it is also dependent on the processing temperature. PA66 blending requires a very high temperature, which intensifies the crosslinking processes in an elastomer leading to the structure stiffening and the rise of glass temperatures. In such case, amorphous PA66 phase with some amount of partially grafted elastomer (polybutadiene or epoxidized polybutadiene) chains should demonstrate a decreased mobility, resulting in a rise of its glass temperature, as it is really observed. At lower processing temperatures required for PA12 and PA6, the crosslinking reactions are probably less intensive. Hence, the amorphous PA phase containing more flexible elastomer chains can have somewhat lower glass temperature.

The earlier mentioned suppositions are partially confirmed by the results of PA's crystallinity measurements with DSC method. Table III shows the melting point ( $T_m$ ) and heat of fusion ( $\Delta H_m$ ) values for polyamides and their blends with 15% elastomer. The measured heat of fusion values for blends were recalculated with respect to polyamide content.

It is evident from Table III that the elastomer addition hinders the crystallization of polyamides, because the heats of fusion for all polyamides in blends are lower in comparison with pure polyamides. It should be noted that PA66 blends exhibit on average the smallest relative heat of fusion lowering, *i.e.*, in this case more crystalline phase and less lattice defects are

TABLE III  
Melting Point and heat of Fusion Values for Polyamides and Polyamide Blends

Elastomer	PA12		PA66		PA6	
	$T_m$ (K)	$\Delta H_m$ (J/g)	$T_m$ (K)	$\Delta H_m$ (J/g)	$T_m$ (K)	$\Delta H_m$ (J/g)
—	452.8	61.0	537.6	69.6	495.7	95.2
SBS	452.6	42.5	537.8	65.1	495.7	66.1
ESBS	453.3	52.9	537.7	67.6	495.1	68.6
BS	453.2	46.2	540.8	57.7	494.4	61.0
EBS	452.0	47.7	539.8	58.1	496.3	83.6

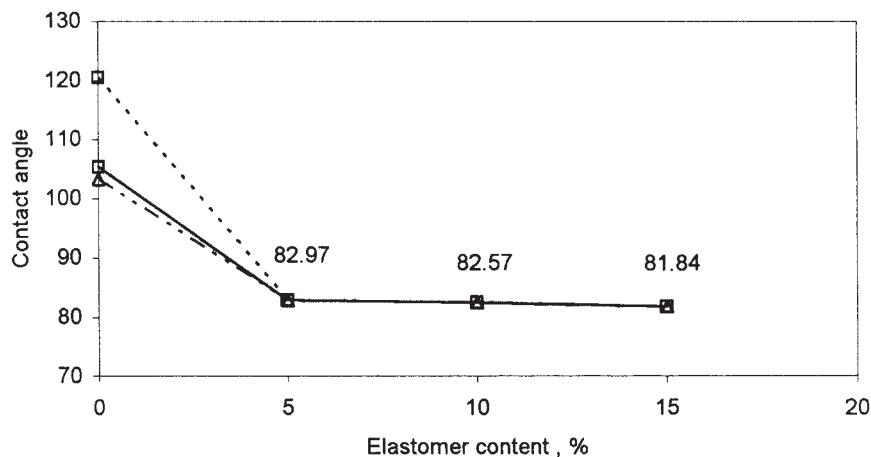


Figure 6 Mean contact angle for blends of PA6, PA66, and PA12, with various elastomers.

created. It is supported by the fact that the PA66 melting points in all blends are higher in comparison with those of pure polyamide. Such behavior can also be treated as an indirect evidence of a weaker disturbance of PA66 crystallization by more strongly crosslinked, *i.e.*, less mobile elastomer molecules. The next interesting observation resulting from data in Table III is that all heats of fusion for blends containing epoxidized elastomers are somewhat higher than those measured for the nonepoxidized forms. Such behavior is difficult to explain unequivocally. It may be due to the fact that epoxidized elastomers show generally a stronger tendency to crosslink than their nonepoxidized equivalents. In such case, the PA crystallization course is less disturbed in comparison with unmodified elastomers. It is also possible that the discussed behavior is attributed to a better nucleation ability of epoxidized elastomers resulting from their polar structure and improved miscibility with polyamides.

Polyamides, especially those containing short aliphatic chains in monomer units, are polymers characterized by a relatively good wettability and high water uptake. It could be *a priori* expected that the addition of nonpolar or weak-polar elastomer should change visibly this behavior, which is also important from the practical point of view. For this reason, contact angle and water uptake measurements were performed for all investigated systems.

The contact angle was determined with the method that relays on measurements of the base diameter and height of a very small drop (spherical cap) placed on the sample surface. The obtained results for PA6, PA66, and PA12 and their blends with SBS, ESBS, BS, and EBS in amount 5–15% are shown in Figure 6. It is evident from these data that significant contact angle differences are observed only for pure polyamides. Surprisingly, PA blends exhibit no considerable contact angle changes, both with respect to polyamide or

elastomer type and elastomer content. It was found that with increasing elastomer content in the range 5–15%, the mean contact angle decreases only  $\sim 1^\circ$ . This value is smaller than the error of contact angle measurements. Quantitatively similar effects ( $\sim 1^\circ$ ) are connected with the use of epoxidized elastomers instead of their nonepoxidized equivalents, or with replacement of PA12 (the highest contact angle) with PA6 or PA66 (lower and similar contact angles). This somewhat surprising behavior can be probably attributed either to the specific properties of sample surface, *e.g.*, surface oxidation during preparation of samples, or more probably to structure changes of polyamide phase caused by a very small elastomer addition.

The water uptake measurements were carried out after 24-h long immersion of test samples in distilled water, at room temperature. It was found that no significant relationship between water uptake and elastomer content (5–15%) exists, *i.e.*, the blends consisting of the same polyamide and elastomer but in different proportions have as a rule very similar water uptake. However, the water uptake depends on the type of polyamide and elastomer. Figure 7 shows the relative water uptake (with respect to pure polyamide) for various PA–elastomer blends. The water uptake for all blends is defined as the mean value for the same elastomer–polyamide systems with different elastomer contents. It can be seen that the water uptake in blends containing epoxidized elastomers is generally higher in comparison with similar blends based on the nonepoxidized forms. It is presumably due to the higher polarity of epoxidized elastomers. Moreover, the use of SBS and ESBS leads to blends with smaller water uptake as for BS and EBS, respectively. Such behavior can be attributed to differences in molecular structures of both elastomer types. The PA66 based blends demonstrate very high water uptake changes caused by the presence of elastomer. For PA12 and PA6 the corresponding changes are much

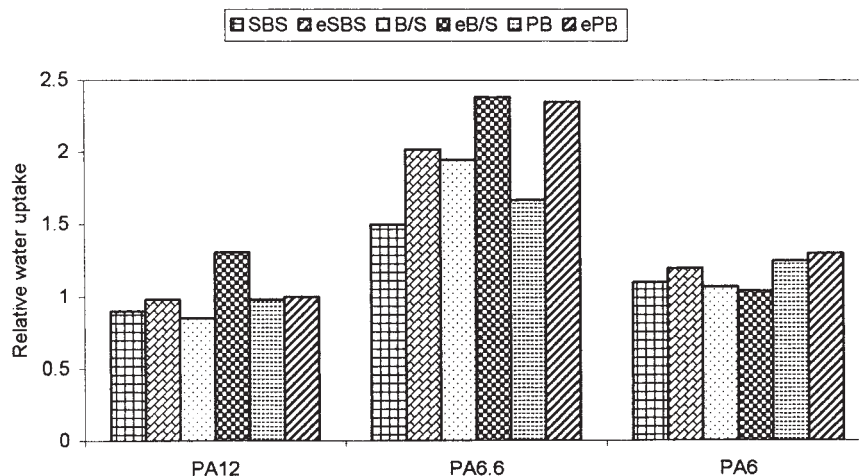


Figure 7 Relative water uptake for various polyamide –elastomer blends.

smaller. This fact can also be interpreted as a result of the high processing temperature of the PA66 based systems, which show on average the lowest toughening efficiency with nonepoxidized or epoxidized elastomers compared with PA6 and PA12. The elastomer crosslinking processes, which lower the interfacial adhesion, make it easier to penetrate water molecules into the system.

### CONCLUSIONS

The experimental studies of blends of aliphatic polyamides with nonepoxidized and epoxidized elastomers have shown that the mechanical properties of blends significantly depend on the blending time, especially, if epoxidized elastomers are used. This can be treated as an indirect sign of reactions between components. The highest toughening efficiency was observed for the epoxidized SBS copolymer. Significant changes of glass temperatures of components, which depend on the polyamide–elastomer system, also confirm the interactions between blend components. Elastomer addition hinders as a rule the polyamide crystallization resulting in some lowering of the heat of fusion of the polyamide phase, especially, if nonepoxidized elastomers are used. Elastomer addition lowers also the water contact angle at simultaneous rise of

the water uptake. The quantitative changes are strongly dependent on the types of polyamide and elastomer used as the blend components.

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