Morphology and thermal behaviour of SAN/EPDM blends

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Received 20 March 2007; accepted in revised form 9 May 2007

Abstract. Blends of styrene-acrylonitrile (SAN) with ethylene-propylene-diene (EPDM) with and without high impact polystyrene (HIPS) as a compatibilizer were studied. One series of blends was prepared in composition 95/5, 90/10, 85/15, 80/20 and 60/40; and the second series of blends was prepared with the addition of 5 wt% of HIPS. Their morphology and thermal behaviour were inspected by scanning electronic microscopy (SEM) and dynamic mechanic analysis (DMA), respectively. Further on, blends were separated to their components by Soxhlet extraction in selective solvent and characterized by Fourier Transform Infrared Spectroscopy (FTIR) and gel permeation chromatography (GPC), respectively. The results of morphological observations revealed that the addition of a small percentage of compatibilizer decreases the domain size of the dispersed phase and the compatibility of the blends was enhanced. The shifts of values of glass temperatures (T_g) in the examined blends also indicate that with addition of compatibilizer HIPS miscibility between SAN and EPDM is improved.

Keywords: polymer blends and alloys, thermal properties, morphology

1. Introduction

Blending of styrene-acrylonitrile and ethylene-propylene-diene rubber may provide an efficient way with tailored properties. Styrene-acrylonitrile/ethylene-propylene-diene rubber (SAN/EPDM) system is a brittle/ductile combination but the blend does not result in a toughened plastic, given that two components are immiscible at the molecular level because of their difference in polarity and blends have poor mechanical properties compared to those of their neat components. The ability of rubber to improve the mechanical properties of glassy polymers depends mostly on the dispersed rubber particle size that implies compatibility of the rubber phase with the matrix [1]. Therefore, the introduction of a small amount of compatibilizer has been investigated to obtain more desirable properties. A compatibilizer can be made either

separately and then added to a polymer blend or created *in situ* during the blending process [2, 3]. The first method has the advantage of better controlling the molecular architecture of the compatibilizer. The second method, often called reactive extrusion or reactive compatibilization, allows us to generate the compatibilizer *in situ* at the interfaces directly during blending [4, 5]. System called acrylonitrile-ethylene/propylene/diene elastomer-styrene (AES), which is formed by EPDM rubber dispersed into a glassy matrix of a SAN copolymer, containing also SAN molecules grafted onto the EPDM rubber (EPDM-g-SAN) which act as compatibilizing agents between the two immiscible components [6, 7]. Generally, the rubbery particles are grafted by a brittle polymer which is the same as the matrix. These grafted chains enhance the interfacial bonding between the rubbery particles and the brittle matrix, and also make the rubbery particles dis-

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perse throughout in the matrix polymer to match the thermodynamic parameters. Elastomer-modified thermoplastic high impact polystyrene (HIPS) is one of the oldest styrenic polymers and provides a good balance between rigidity and elasticity and it is often used as a compatibilizer. Many authors have observed that some of the most important factors in controlling the mechanical properties of various styrene copolymers (like SAN and acrylonitrile-butadiene-styrene, ABS) and HIPS are rubber particle size [8, 9] and the volume fraction of the rubbery phase [10, 11]. In this study, we investigate the effect of high impact polystyrene as compatibilizer and *in situ* formed graft copolymer on the morphology and thermal properties of blends. SAN/EPDM and SAN/EPDM/HIPS blends with different fractions of the elastomer component were processed by extrusion resulting in polymer materials of different microstructures.

2. Experimental

2.1. Materials

Studied blends were prepared with ethylene-propylene-diene (EPDM, Keltan 312, DSM), containing 55 wt% ethylene and 4 wt% ethylidene norbornene, Mooney viscosity 36 MU and styrene-acrylonitrile (SAN, Tyril 790, The Dow Chemical Company) with 24 wt% AN, the melt flow rate (MFR, 220°C, 10 kg) was 27 g/10 min. The interfacial agent was high-impact polystyrene (PS-HI 417) supplied by DIOKI, (Croatia), with 8 wt% polybutadiene.

2.2. Preparation of samples

The extrusion process was carried out on a Haake Rheocord System 9000 twin-screw extruder (Haake, Karlsruhe, Germany), a co-rotating extruder with standard, non-intensive screw characteristics. Following temperatures have been chosen for the four heating zones (from hopper to die): 170/190/200/210°C and the screws rotation speed has been set to 60 rpm. Blends were injection moulded according to ISO 294 and dumbbell specimens were formed

according to ISO 3167. Compositions of the studied blends are listed in Table 1.

2.3. Polymer blend separation

The prepared SAN/EPDM blends were separated to components by successive extraction in selective solvent for eight hours using Soxhlet method. To check the extraction efficiency, preliminary extractions have been made for 8, 24 and 48 hours. The styrene-acrylonitrile polymer is extracted in mixture of methanol/acetone (ratio 55:45 vol%), the EPDM polymer in hexane and the graft polymer is extracted in tetrahydrofuran (THF). The remaining part of the blend was considered as the gel content.

2.4. Gel permeation chromatography (GPC)

The molecular masses and their distributions ($\bar{M}_n$, $\bar{M}_w$) of extracted polymers were determined by the gel permeation chromatography (GPC) carried out on the PL-GPC 20 Polymer Laboratories instrument fitted with RI detector. Tetrahydrofuran was used as a solvent ($c = 10$ mg/5 ml). Molecular masses were calculated as polystyrene equivalents.

2.5. FTIR measurements

FTIR spectra of extracted polymers were recorded on Perkin Elmer Spectrum One in the range of 4000 to 500 cm^{-1} , with a resolution of 4 cm^{-1} . All samples were prepared as thin films (0.1 mm) cast from 6 wt% toluene solution.

2.6. Scanning electron microscopy (SEM)

Morphologies of the studied blends were characterised from a cross-section of cryogenically fractured surfaces of injection moulded samples (2 mm thick) using a Philips XL 30 Scanning Electron Microscope. Samples were immersed in liquid nitrogen for more than 15 min to cool down and then fractured immediately. The dried samples were sputter-coated with gold prior to scanning electron microscopy (SEM) examination.

2.7. DMA measurements

Dynamical mechanical properties of the blends were analyzed using a DMA Q 800 TA Instruments. Specimens for the dynamic mechanical test

Table 1. Composition of SAN/EPDM and SAN/EPDM/HIPS blends

Samples	SAN/EPDM					SAN/EPDM/HIPS				
	95	90	85	80	60	95	90	85	80	60
SAN	95	90	85	80	60	95	90	85	80	60
EPDM	5	10	15	20	40	5	10	15	20	40
HIPS	–	–	–	–	–	5	5	5	5	5

were cut into 50×10×1 mm. The glass transition temperatures (T_{g1} and T_{g2}) of the samples were measured at a frequency of 1 Hz with the temperature ranging from –100 to +150°C and a temperature rate of 10°C/min. After the testing at a particular temperature the samples were cooled to –100°C in nitrogen atmosphere.

3. Results and discussion

3.1. Analysis of polymer fractions in blends

To elucidate the extrusion process, reactions and interactions that are established [12–16], the separation of SAN/EPDM blends on its components was carried out by selective solvent extraction and the results are presented in Figure 1. Significant differences in the fractions of graft copolymer (EPDM-g-SAN), SAN polymer, EPDM polymer and gel were observed. The most significant component formed during extrusion is the graft copoly-

mer, Figure 2, and it is expected to improve compatibility of two polymer phases in SAN/EPDM blends. The increase of the ratio of formed graft copolymer in blends can be explained by the fact that increasing reaction temperature favours the

Figure 1. Fraction of extracted components: SAN, EPDM, graft polymer and gel from extruded SAN/EPDM blends processed without and with HIPS compatibilizer

Figure 2. Grafting reaction of SAN radicals onto EPDM polymer chain: a) on double bonds of ethylidene norbornene, b) on tertiary C-atom

formation of polymer radicals and increases their mobility. Such chemical bonding improved compatibility in the blends and prevented further degradation of the polymer during the extrusion process [17]. Significantly higher concentration of graft copolymers is observed when the compatibilizer HIPS is present in the blends. From the results, Figure 1, it is observed that fraction of formed graft is in the interval of 45–68 wt% for samples prepared without compatibilizer while the fraction of formed grafts for samples with compatibilizer is 58–80 wt%. It is assumed that the high concentration of polymer radicals is present due to presence of double bonds of butadiene. Low concentration of SAN polymer obtained after extraction confirms that the most of SAN radicals participate in grafting or in crosslinking reaction. Formation of polymer radicals is also confirmed by the changes of molecular masses of blends components, see Figure 3. Molecular masses (M_n , M_w) of SAN polymer obtained after extrusion process are slightly increased, which indicates chemical bonding of SAN radicals between themselves. Changes of molecular masses of SAN matrix can significantly affect compatibility of blends, i. e. higher molecular masses would increase viscosity of matrix and that leads to finer morphology and better compatibility in blends [18]. The molecular masses of extracted EPDM from blends samples are slightly changed showing higher stability under process conditions, Figure 3. It is also known from the literature, EPDM rubber is more stable than SAN copolymer at higher temperatures (200°C) [19]. Further on, the values of molecular masses of the formed graft copolymers are approximately the same as those as SAN polymer because the high

Figure 3. Number molecular masses, and weight molecular masses, of extracted SAN, EPDM and graft polymer from extruded SAN/EPDM blends and molecular masses of commercial SAN polymer and EPDM polymer

fraction of SAN polymer is present. On the other hand, crosslinking reaction results in the formation of a gel, which is present in higher concentration in blends prepared without HIPS and it will contribute to incompatibility of polymers in the blends.

Results of distribution of molecular masses of extracted SAN and EPDM-g-SAN components are shown in Figures 4 and 5. Comparing the differential curves of SAN polymer extracted from blend composition 95/5, Figure 4a, and curves of SAN extracted from blend composition 95/5/5, Figure 4b, it can be seen that there are significant changes in the distribution of molecular masses. Broad distribution of molecular masses indicates presence of newly formed SAN polymer chains of lower molecular masses denoting higher polydispersity of the system. On the other hand, narrow distribution of molecular masses means participating of SAN polymer in grafting reactions, which is supported by the results of higher fraction of graft copolymer, Figure 1. The similar behaviour of distribution of molecular masses of the extracted EPDM-g-SAN graft copolymer in the considered samples is observed, Figure 5.

Figure 4. Integral and differential curves for the SAN polymer: a) SAN polymer extracted from SAN/EPDM blend composition 95/5, b) SAN polymer extracted from SAN/EPDM/HIPS blend composition 95/5/5

Figure 5. Integral and differential curves for the EPDM-g-SAN graft copolymer: a) graft copolymer extracted from SAN/EPDM blend composition 95/5, b) graft copolymer extracted from SAN/EPDM/HIPS blend composition 95/5/5

3.2. FTIR analysis

The structure of the EPDM-g-SAN graft copolymer was determined from FTIR spectra, as is shown in Figure 6. The characteristic absorption bands of EPDM rubber appeared at 722 cm^{-1} corresponding $-(\text{CH}_2)-$ stretching and at 1374 cm^{-1} due to $-\text{C}-\text{CH}_3$ stretching; for SAN copolymer vibrations at 2237 cm^{-1} due to $-\text{CN}$ groups and the vibrations at 1453 and 1493 cm^{-1} corresponding to aromatic

ring were observed. On the other hand, graft copolymer, reveals characteristic vibrations of both SAN and EPDM polymers which indicate grafting reaction that appear during processing [20].

3.3. Dynamical mechanical analysis

Measurement of the glass transition temperatures T_g , were used to study miscibility of SAN/EPDM systems because the difference in the T_g values of EPDM and SAN was sufficiently large. There are two distinct glass transitions for all blends, in our case the lower glass transition is due to the EPDM phase (-50°C) and the higher glass transition (109°C) is due to the SAN phase (21–23). Table 2 contains the T_g values for EPDM, SAN and their blends with and without HIPS as a compatibilizer. From inspection of Table 2 it can be seen that with adding HIPS to the SAN/EPDM blends, the T_g values of EPDM phase shifts to -40°C , significantly higher values after addition of 5% HIPS, whereas that of the SAN phase moves to 104°C , a lower temperature, at HIPS content of also 5%. For the blends prepared with compatibilizer and with higher fraction of elastomer, slight shift of T_g values is observed. Meanwhile, the results do not reveal a new peak which would correspond to the HIPS phase. This means that a new isolated phase in SAN/EPDM blend was not formed and it is assumed that HIPS is located at the boundaries between SAN and EPDM [24]. From these results it can be concluded that by adding HIPS in SAN/EPDM blends glass transition becomes less distinct, indicating better interaction and the increasing compatibility between the SAN and EPDM polymers.

Figure 6. FTIR spectra of extracted SAN, EPDM and graft copolymer from extruded SAN/EPDM blend

Table 2. Glass transition temperatures (T_{g1} , T_{g2}) obtained for SAN/EPDM, SAN/EPDM/HIPS blends and for pure SAN and EPDM polymers

SAN/EPDM	T_{g1} [°C]	T_{g2} [°C]	SAN/EPDM/HIPS	T_{g1} [°C]	T_{g2} [°C]
95/5	-48.2±0.1	104.6±0.1	95/5/5	-40.0±0.2	104.9±0.1
90/10	-47.2±0.2	105.3±0.2	90/10/5	-43.7±0.1	106.2±0.1
85/15	-50.3±0.1	105.0±0.3	85/15/5	-49.7±0.1	104.9±0.2
80/20	-51.0±0.2	105.0±0.1	80/20/5	-49.2±0.2	104.6±0.1
60/40	-51.3±0.2	106.1±0.1	60/40/5	-49.0±0.1	106.1±0.2
EPDM	-50.0±0.2	—	SAN	—	109.0±0.1

3.4. Morphology of the blends

The micrographs of the cryogenically fractured surfaces of the SAN/EPDM blends compositions 95/5, 85/15, 60/40 are displayed in Figure 7. The inspection of these micrographs indicates two phases with different domain size and shape. As is well known from the literature [25], polymer present in the lower concentration usually forms a discontinuous phase whereas the polymer present in the higher concentration forms continuous phase and such morphology of blends is usually named a particle-in-matrix type. Finer morphology can be observed with lower concentration of EPDM, Figure 7a, in comparison with morphology of blends with higher concentration of EPDM, Figure 7b and 7c. The high interfacial tension between the SAN and EPDM phases leads to a larger size of the dispersed rubber phase (3.4 μm) as is well seen on Figure 7b in comparison with particle size on micrograph

Figure 7a, where the size of dispersed phase is 0.5 μm . If the particle size is greater than the critical value the blends will still be a brittle and incompatible. For example, the effective toughness occurs at an optimum particle size of 0.1–1 μm for SAN [26] and when the optimum particle size of dispersed EPDM is achieved, necessary levels of adhesion with the SAN matrix is provided and effective increase of impact toughness is achieved. However, as the ratio of two polymers in blend progress toward equality, co-continuous phase is formed, Figure 7c. Further, the particle size of dispersed phase on micrograph Figure 7c is significantly higher in comparison with particle size on micrographs Figure 7a and 7b. It can be seen that partial separation of two phases is present because block segments of EPDM do not adhere to SAN phase completely.

Figure 7. SEM micrographs of fractured surface of SAN/EPDM blends of composition: a) 95/5, b) 85/15 and c) 60/40

Figure 8. SEM micrographs of fractured surface of SAN/EPDM/HIPS blend of composition: a) 95/5/5, b) 85/15/5 and c) 60/40/5

The compatibility of the SAN/EPDM system is improved by addition of HIPS as a compatibilizer as can be seen from micrographs in Figure 8. Especially finer morphology is observed for the samples prepared with compatibilizer, micrographs Figures 8b and 8c in comparison with the samples prepared without compatibilizer, micrographs Figures 7b and 7c. It was also seen that the size of the dispersed phase domain (EPDM) decreased with the addition of compatibilizer (2.1 μm), micrograph Figure 8b), no phase separation is present in the blend and the size distribution is more uniform. Such morphology could be also explained as result of the high fraction of the graft copolymer formed during the processing and there was a high degree of compatibility between the graft copolymer with the rubber particles and the matrix. The graft copolymer will be preferentially located at the interface resulting in better adhesion between the phases, thus reducing the interfacial tension and enhancing the adhesion. In other words, compatibilizers improved morphology and the compatibility of the blend due to reduction of the interfacial tension between phases, which comply with the many various theories from the literature [27–31].

4. Conclusions

High impact polystyrene, used as a compatibilizer significantly decreases the particle size of dispersed phase in SAN/EPDM polymer blends resulting in finer morphology and improved compatibility. Presence of compatibilizer was lead to the formation of a graft copolymer in high concentration during the processing of blends and such *in situ* formed graft makes an interphase between the two polymers as well as main component in bulk of blend. From the dynamic mechanic analysis of the blends, the glass transition temperature of the EPDM phase was increased from -50°C to -40°C , whereas that of the SAN phase was decreased from 109°C to 104°C with the addition of 5% of HIPS content indicating better adhesion of the phases.

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