

Property profile of nanostructured blends of amine functionalized elastomer and epoxy

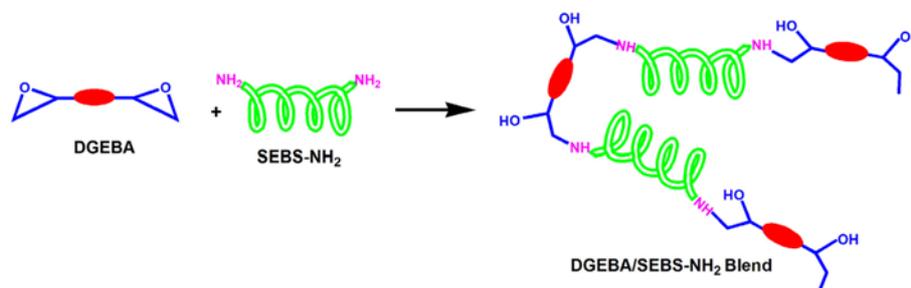
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Abstract—Pure polystyrene-*b*-poly(ethylene-*ran*-butylene)-*b*-polystyrene (SEBS) was functionalized with amine moiety first through nitration, followed by reduction. The resulting amine modified SEBS was blended with various amounts of epoxy via in situ reactive approach. Thin blend films were initially cured at 120 °C for 30 min and post cured at 180 °C for 2 h. These films were then analyzed for their mechanical, thermal and morphological profile. Optimum improvement in tensile strength, modulus and toughness was observed with different epoxy loading in the blends. These blends were found thermally stable up to 300 °C. The morphological studies indicated ample compatibility between the two components of blends.



A prototype of nanoblends from SEBS-NH₂/epoxy

Keywords: Elastomers, Blends, Nanostructures, Electron Microscopy

INTRODUCTION

Designing of new polymeric blends is of special relevance from the viewpoint of both engineering and academia. Polymer blending is a well established, effective and a simple way to tailor the properties of these materials to meet specific requirements. Nano-blends represent superior properties compared to individual components alone, and consequently are widely employed to produce high performance materials [1,2]. Commercial polymer blends have a multiphase morphology with suitable physical and mechanical properties due to the presence of a finely dispersed phase which is resistant to significant phase segregation. Compatibilization involves alteration of the interfacial properties of the blend through block or graft copolymers with segments which display intermolecular attraction and/or chemical reactions with the blend components. These copolymers contemplate at the interface between the blend components and act as emulsifiers, reducing interfacial tension formed in situ, by reactive compatibilization using suitably reactive polymers [3]. It can also provide a degree of control over morphology development in multiphase polymer blends, via manipulation of

the interfacial energies within the system [4-9], which allows the formation of dispersed phases with a core-shell structure [9-11]. SEBS is a triblock copolymer and a thermoplastic elastomer having polystyrene (PS) blocks (hard segments) and polyethylene-polybutylene components (soft segments). The polystyrene components provide strength to the materials, while the rubbery phases give it flexibility to make it less brittle. Moreover, polystyrene blocks tend to clump together and tie the polyethylene and polybutylene blocks together employed as compatibilizer in many polymeric blends. A study of polypropylene (PP)-based blends with 30% by weight of a polyamide-6 (PA6)/SEBS dispersed phase, using both reactive and non-reactive SEBS has been reported. Reaction between the PA6 and SEBS significantly reduces their interfacial energy, which acts both to encourage the SEBS to encapsulate the PA6 and to stabilize the resultant multiphase morphology [8,9]. In addition to the effects of interfacial reaction, the effects on morphology development of varying the ratio of PA6: SEBS in the dispersed phase has been described. A more complete study on polyethylene terephthalate (PET)/PP compatibilized with SEBS, or maleic anhydride grafted SEBS (SEBS-*g*-MA), or glycidyl methacrylate modified SEBS (SEBS-*g*-GMA) at one ternary composition, was reported by Heino et al. covering morphology, mechanical and rheological properties as well [12]. The addition of pure SEBS (5-wt%) stabilized the blend morphology with improved impact strength. Moreover, this effect

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became more prominent with functionalized SEBS. High toughness and stiffness were achieved with SEBS-*g*-GMA for the PET-rich composition. Incorporation of functionalized SEBS copolymers gave a finer dispersion of the minor phase with improved interfacial adhesion. Increase in the glass transition temperature of the PET phase and melt viscosity of the compatibilized blends indicated better interactions between the discrete PET and PP phases induced by SEBS-*g*-GMA. Effectiveness of compatibilizers on mechanical, thermal and morphological profile of PET/PP blends has been reported [13]. Various compatibilizers based on maleic anhydride modified, PP (PP-*g*-MA), maleic anhydride grafted linear low density polyethylene (LLDPE-*g*-MA) and hydrogenated SBS block copolymer (SEBS-*g*-MA) were used. Large deformation behavior of blends denoted the excellent performance of SEBS-*g*-MA. However, addition of a thermoplastic polyolefin alloy (TPO), PP/ethylene-propylene copolymer, augmented the compatibilizing efficiency of PP-*g*-MA comparable to that of SEBS-*g*-MA. Superior effectiveness of SEBS-*g*-MA and PP-*g*-MA plus TPO relative to PP-*g*-MA or LLDPE-*g*-MA is ascribed to better emulsification of the former at the interface, reduced migration of PP-*g*-MA into the PP phase and retardation of PET crystallization in the presence of the elastomeric additive. Additionally, the elastomeric compatibilizers absorb more efficiently, the stresses developed at the PET/PP interface. Previously, we have reported PS/SEBS-*g*-MA and amine functionalized polystyrene (APS)/SEBS-*g*-MA blends [14]. During the blending process, amine functionality introduced on PS serves as a compatibilizer forming in situ amide linkage between APS and anhydride groups on SEBS-*g*-MA. Chemical modification of PS successfully improved interfacial interaction, and the compatibility between the blend components was significantly improved. Thus, the mechanical robust PS-based blends were obtained. Improvement in morphology, thermal and mechanical profile has been followed for APS blends in contrast with PS blends.

Epoxy resins are high performance thermosetting polymers that are particularly important for their low cost, superior mechanical and thermal properties, exceptional adhesion to various substrates, chemical resistance and easy processability. Thus, they are widely used in coatings, adhesives, electronic encapsulants and matrices for composites [15-18]. When cured, epoxy polymers are amorphous and form a highly cross-linked network structure using cross-linking agents or hardeners such as amines, acids and anhydrides with well known curing mechanisms [17]. These distinguishing features stem from their cross-linked chemical structure. Moreover, the low fracture toughness relative to other thermoplastic polymers needs to be toughened for engineering applications. Block copolymers have the ability to self-assemble themselves and possess nano-phase structures, and therefore, when blended with epoxies can control phase separation at nanoscale [19,20]. Various triblock copolymers have been synthesized as modifiers for epoxy resins to give nano-phase structures [21-24]. We blended and tried to chemically link the amine functionalized SEBS with epoxy, and then explored the compatibilization effect in terms of morphological, thermal, and mechanical profile of nano-blends.

In this attempt, the polystyrene-*b*-poly(ethylene-*ran*-butylene)-*b*-polystyrene (SEBS) elastomer was blended with epoxy by solution mixing approach. For this purpose, SEBS was modified via

nitration and then subsequent reduction yielding amine functionalized SEBS. Blends of varying concentrations were prepared using diglycidyl ether of bisphenol A (DGEBA) and amine modified SEBS. The amine functionality introduced on the SEBS chains was exploited to react with epoxide groups of DGEBA through reactive blending in order to produce compatibilized and chemically linked nano-blends. Epoxy/amine modified SEBS blends were characterized for their structural, morphological, mechanical and thermal analyses using FTIR spectroscopy, field emission scanning electron microscopy (FESEM), tensile testing and thermogravimetric analysis (TGA).

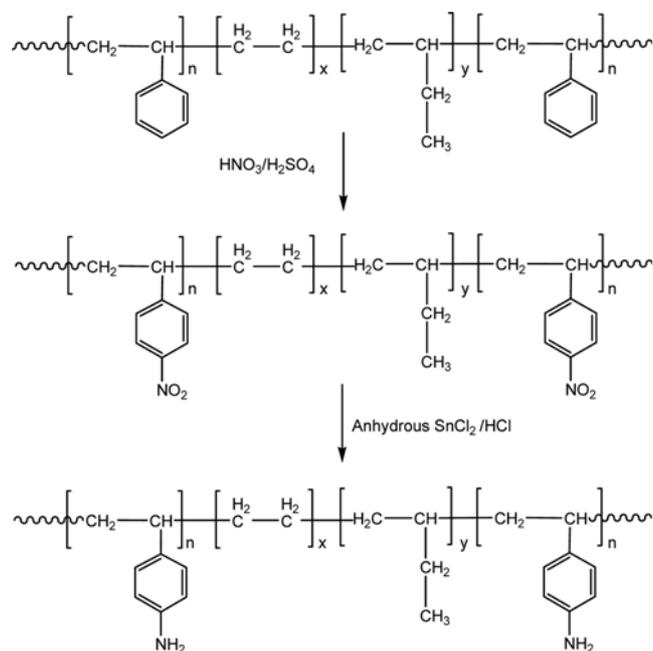
EXPERIMENTAL

1. Materials

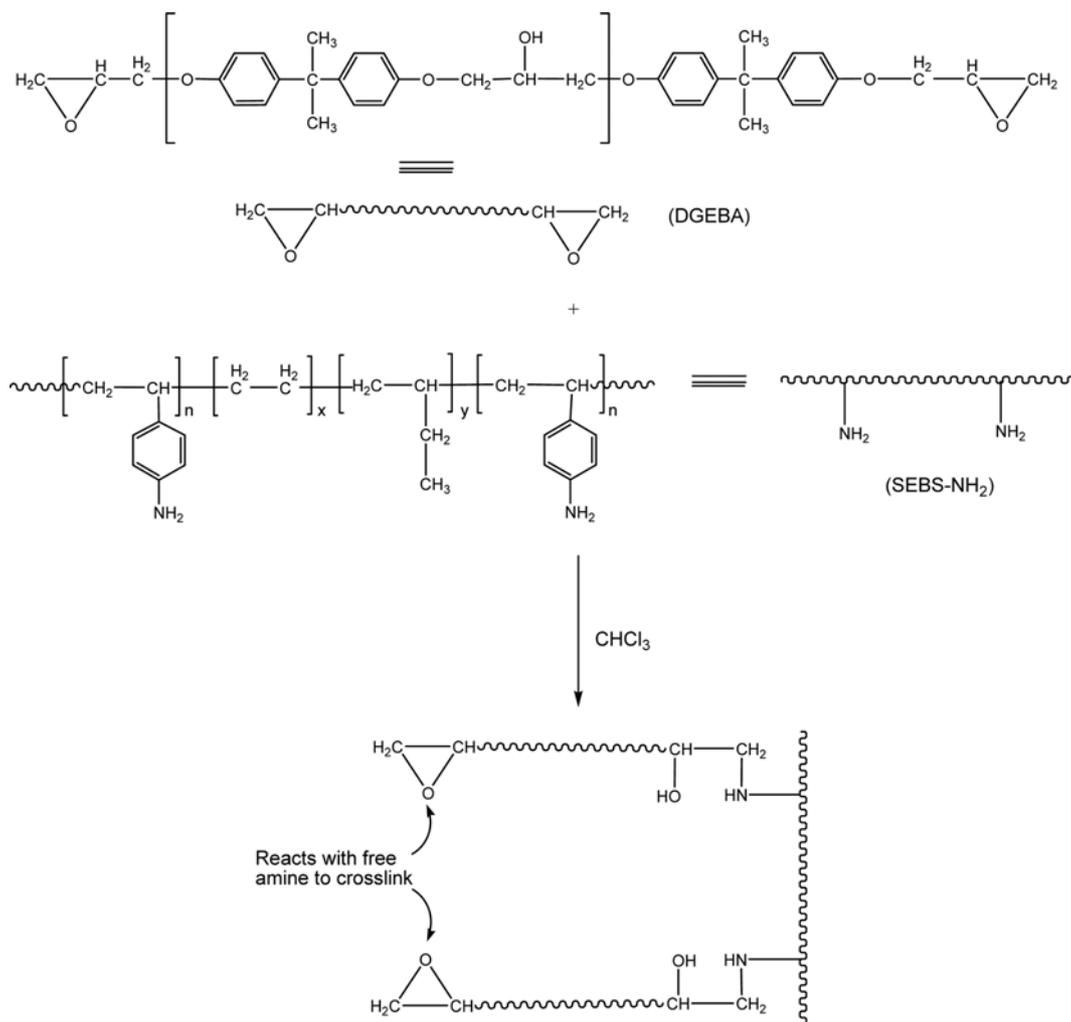
SEBS elastomer (M.W=118,000) with 28% styrene content, anhydrous calcium chloride (99%), anhydrous calcium oxide (99%) and anhydrous stannous chloride (99%) were procured from Aldrich and used as received. Diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight of 172-176 purchased from Sigma was used. Benzophenone (99%), sodium metal (stored in kerosene), ethanol (99%) and hydrochloric acid (99%) were supplied by Fluka. Sodium hydroxide (98%), methanol (99%), nitric acid (65%) and sulfuric acid (98%) obtained by the courtesy of Merck were used as such. Tetrahydrofuran (99%) provided by Merck and anhydrous chloroform ($\geq 99\%$) purchased from Aldrich were used after drying.

2. Functionalization of SEBS Elastomer

SEBS elastomer was functionalized using a two-step strategy (Scheme 1). The primary step involved the nitration of SEBS, thus yielding nitro-functionalized SEBS followed by the reduction of nitro modified SEBS producing amine functionalized SEBS. The synthesis and characterization of this modified polymer has been described elsewhere [25]. The resulting amine modified SEBS was blended with DGEBA through reactive compatibilization approach



Scheme 1. Modification of SEBS with amine functional groups [25].



Scheme 2. Formation of amine modified SEBS/epoxy nanoblends.

yielding nanostructured blends.

3. Amine Modified SEBS/Epoxy Blends

Various compositions of blends were prepared by mixing the amine modified SEBS with DGEBA using chloroform as a solvent. For a particular composition, the required amount of amine functionalized SEBS was placed in conical flask and then dissolved in the chloroform with continuous stirring for 24 h to obtain a homogeneous solution. To this solution, a known quantity of the epoxy resin dissolved in chloroform was added and the stirring was continued for 24 h yielding polymer blend (Scheme 2). Different concentrations of the blends were prepared in the same fashion. Thin blend films were cast by first transferring the contents of the flask into preheated Teflon molds, followed by evaporating the solvent overnight at ambient temperature. These blend films were initially cured at 120°C for 30 min and post cured at 180°C for 2 h to obtain amine modified SEBS/epoxy blend films. After completion of the curing, transparent blend films were peeled off from the Teflon molds. These films were then characterized for their morphological, mechanical and thermal properties.

4. Characterization

The structural determination of amine modified SEBS/epoxy

nanostructured blends was carried out using an Excalibur series Thermo Scientific Nicolet 6700 FTIR spectrometer, over the range $4,000\text{--}550\text{ cm}^{-1}$. Tensile properties of the nanostructures blend samples were measured according to DIN Procedure 53455 having a crosshead speed of 5 mm min^{-1} at 25°C using a Testometric Universal Testing Machine M500-30, and an average value obtained from five to seven different measurements in each case has been reported. For phase morphological studies, blend samples were cryogenically fractured in liquid nitrogen and the morphology was investigated by FEI Nova 230 field emission scanning electron microscope (FESEM). Thermal stability of the blends was determined using NETZSCH TG 209 F3 thermogravimetric analyzer by using 1-5 mg of the sample in Al_2O_3 crucible heated from 30 to 900°C at a heating rate of 10°C/min under nitrogen atmosphere with a gas flow rate of 20 mL/min .

RESULTS AND DISCUSSION

Neat SEBS has very poor film forming property and did not give smooth film. Upon modification of SEBS, the film forming property was improved and amine modified SEBS/epoxy blends pro-

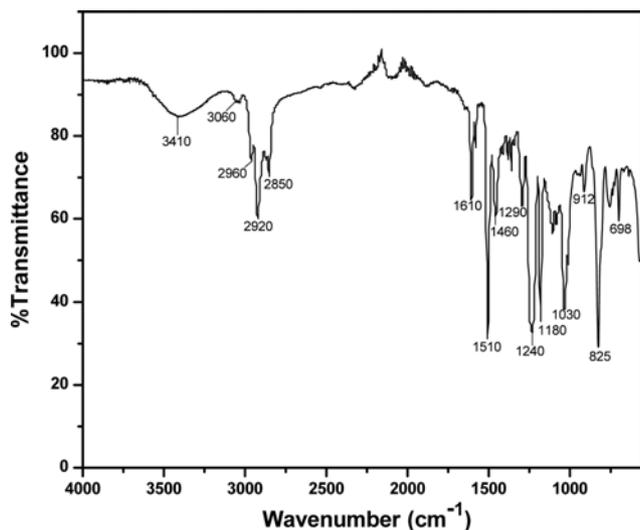


Fig. 1. FTIR spectrum of amine modified SEBS/epoxy nanoblends.

duced very smooth and well textured film. Thin blend films obtained after curing were found to be transparent and light yellow to whitish. The transparency of the blend films decreased by the addition of epoxy and the films became semitransparent and brittle at high epoxy content. The structure elucidation of the blends was carried out by IR spectroscopy. Different analyses performed to characterize these materials are explained below.

1. FTIR Spectroscopy

IR spectrum of the blend film was recorded and the data is represented in Fig. 1. A broad band was observed for O-H and N-H stretching vibrations around $3,410\text{ cm}^{-1}$. Various other bands appeared for N-H bending vibration at $1,610\text{ cm}^{-1}$, aromatic C-H at $3,060\text{ cm}^{-1}$, aromatic C=C stretching at $1,510$ and $1,460\text{ cm}^{-1}$, aliphatic C-H asymmetric and symmetric stretching at $2,920$ and $2,850\text{ cm}^{-1}$. The band for 1, 4-disubstitution on aromatic ring appeared at 825 cm^{-1} . The appearance of OH band is a clear evidence for the formation of linkages between the amine groups on elastomer backbone with epoxide ring, thus yielding compatibilized blend. The FTIR analysis of the blend film confirmed in situ cross linking at the polymer-polymer interface generating stronger interfacial interactions between blend components.

2. Mechanical Properties

Mechanical profile of amine modified SEBS/epoxy blends was

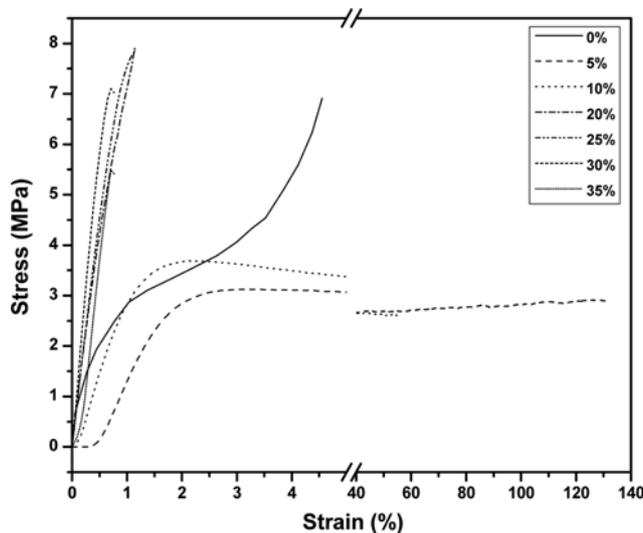


Fig. 2. Stress-strain curves of amine modified SEBS/epoxy nanoblends.

measured by stretching the rectangular thin strip using tensile testing, and the stress-strain curves of the blends are given in Fig. 2. The related data of the mechanical properties are summarized in Table 1. The results indicated an increase in the tensile properties of blend materials. Tensile modulus of elastomer increased with the addition of epoxy. Amine modified SEBS/epoxy blend containing 25-wt% epoxy gave a maximum value of tensile modulus 1.16 GPa. The maximum stress decreased initially and then increased with the addition of epoxy content up to 20-wt%. Beyond 30-wt% it decreased again relative to the amine modified SEBS. The elongation at break decreased with increase in epoxy loading in the blend. Toughness of nanoblend with 5-wt% epoxy showed a maximum value, and then a decreasing trend was observed in this property. The overall mechanical properties of this blend system improved. The modulus of thermosets resins varies in the range 2-6 GPa and can withstand tensile strength in the order of 35-90 MPa. However, they are stiffer and stronger but more brittle when added into elastomeric matrix improving the mechanical profile of the resulting blend. In this particular system, the modulus increased up to 25-wt% epoxy loading and maximum stress showed increase up to 20-wt% epoxy content due to the strong interfacial interactions among the phases. Further increase in epoxy content up to 25-wt%

Table 1. Mechanical data of amine modified SEBS/epoxy nanoblends

DGEBA (%)	Maximum stress (MPa) ± 0.1	Maximum strain (%) ± 0.02	Toughness ($\times 10^6\text{ Jm}^{-3}$) ± 0.02	Tensile modulus (GPa) ± 0.02
0	6.89	4.47	10.93	0.043
5	2.89	130.6	360	0.29
10	2.57	56.0	155	0.31
20	7.92	1.15	5.08	0.88
25	7.85	1.14	5.40	1.16
30	7.02	0.77	3.34	0.88
35	5.41	0.76	2.00	0.83

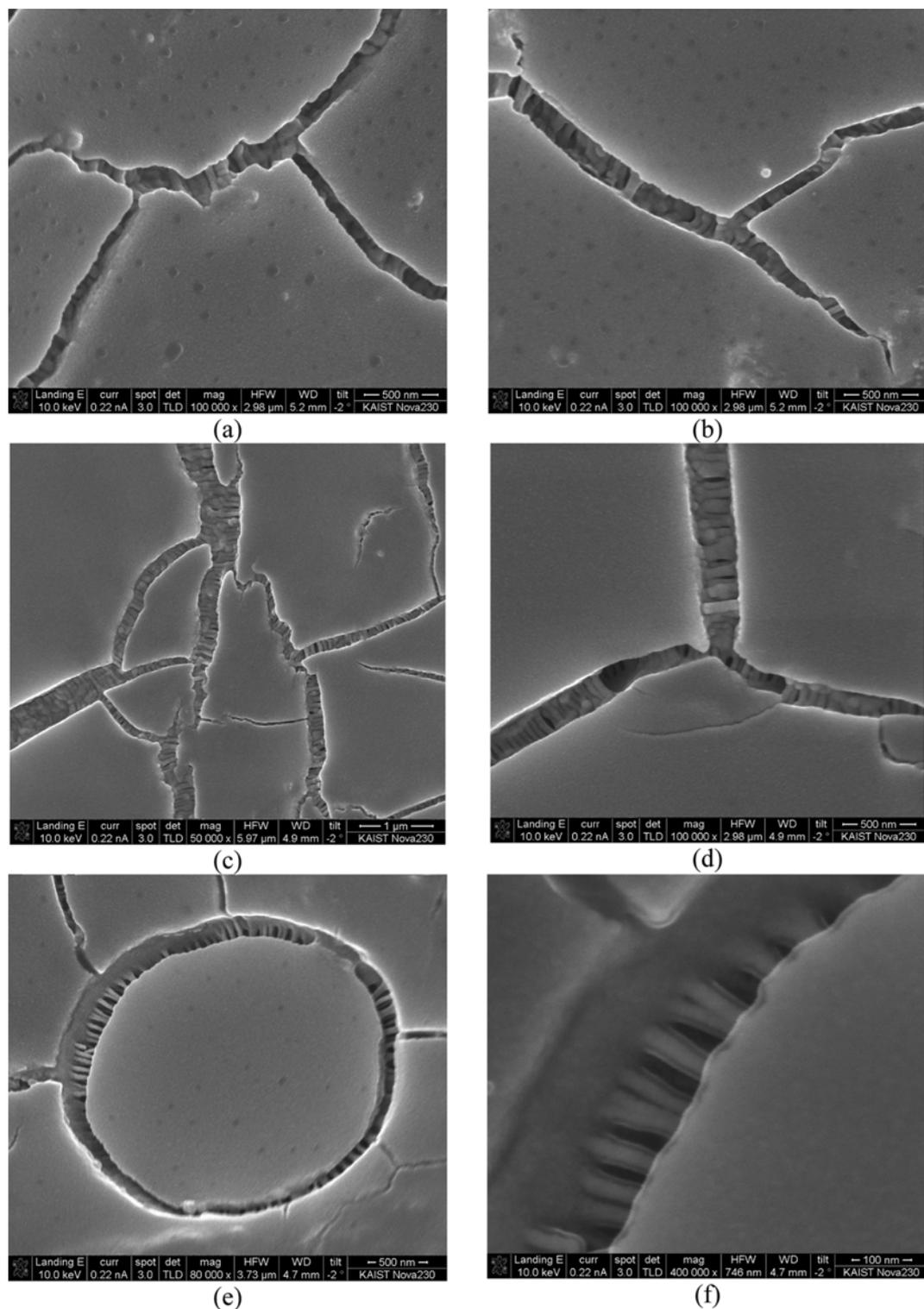


Fig. 3. FESEM micrographs of amine modified SEBS/epoxy nanoblends ((a) & (b)) 5%, ((c) & (d)) 10% ((e) & (f)) 25% ((g) & (h)) 35% ((i) & (j)) 40%.

resulted in a decreased amount of amine modified SEBS in the blend giving a circular morphology (Fig. 3(e) and (f)) with rounded arrangement between matrix and epoxy linked through interlinks/fibrils. In micrograph 3(f), these linking fibrils became more visible and prominent, showing interfacial interactions between the two phases.

The phase morphology of a blend is not only dependent on interfacial tension but also on the combination of interfacial tension and interfacial areas. The introduction of epoxy in the amine-modified SEBS appreciably increased interfacial interactions and improved the mechanical profile of the elastomer. Moreover, this improve-

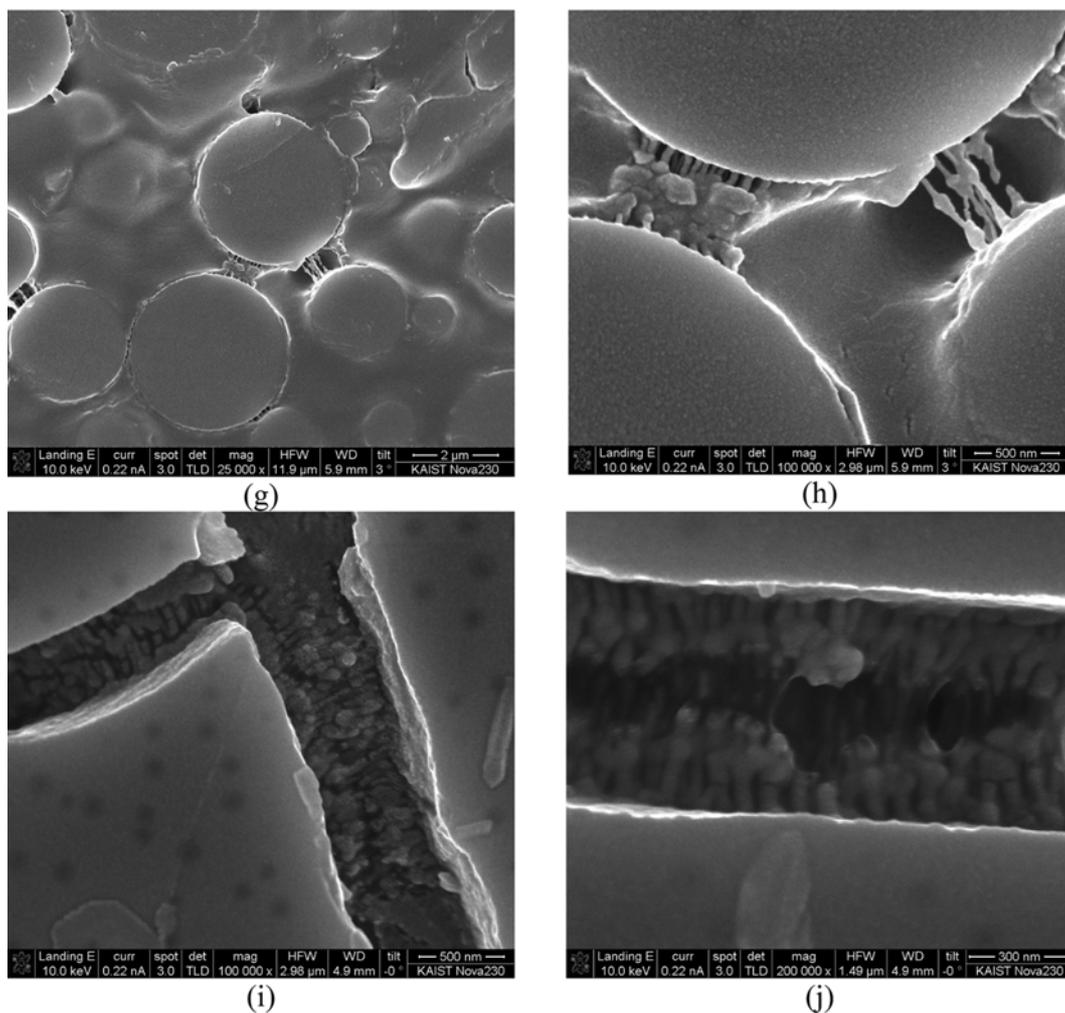


Fig. 3. Continued.

ment in properties was limited only to low concentration of epoxy. Increase in epoxy content up to 35-wt% decreased the amount of amine-modified SEBS in the blend acquiring a globular morphology, which is a typical property of elastomer. Micrographs given in Fig. 3(g) and h showed circular and rounded globules isolated and grew bigger but still bridged through epoxy as indicated in Fig. 3(g) and (h). At 40-wt% epoxy loading, these interlinks became broad and widened the space between matrix and epoxy due to the increased amounts of epoxy that might not be linked with amine modified SEBS (Fig. 3(i) and (j)). Therefore, low epoxy content provided good interfacial interactions with the matrix, giving uniform morphology and homogeneous networks formed in the nanoblends. At higher epoxy loading, amine-modified SEBS/epoxy blends showed weak compatibility between the two phases, thus reducing toughness and increasing brittleness in the blends, as evident from mechanical data.

The interfacial interactions play an imperative role in the improvement of tensile properties of nanoblends. Such interactions produced mechanically robust and tough blends at lower percentage of epoxy loading. At high epoxy loading, all the epoxy molecules may not be linked with elastomer, resulting in poor interfacial interac-

tions between the blend components, leading to brittleness and reduction in toughness of the blend materials. The spectral and morphological analyses depicted chemical reaction between amine-modified SEBS and epoxy rendering interfacial interactions and finer blending of two components. Owing to this chemical reaction, the nanostructured blends showed homogeneous network structures of the two components connected through fibrils.

3. Morphological Analysis

FESEM performed on amine modified SEBS/epoxy blend system are presented in Fig. 3. The aim of this analysis was to evaluate the morphological changes in the blend samples through reactive compatibilization. Pure SEBS is amorphous polymer; therefore it is immiscible with many other polymers. Thus, to enhance the miscibility of SEBS and to increase its adhesion with epoxy, amine functionality was introduced to reduce interfacial tension between the two components [25]. The fractured surfaces of the nanoblends are characterized by the presence of cracks in the matrix depicting the interfacial interactions between the blend components. SEM images of amine modified SEBS/epoxy film with 5-wt% epoxy loading indicated the cracks and ridge in the fractured samples showing the formation of linkages (Fig. 3(a) and (b)). This observation

clearly demonstrates that fibrils are connecting the epoxy domains to the amine modified SEBS matrix suggesting strong interfacial adhesion between the blend components. With the increase in epoxy content up to 10-wt%, fibrils became more prominent (Fig. 3(c) and (d)). Further increase in epoxy content up to 25-wt% resulted in a decreased amine-modified SEBS amount in the blend and at low concentration; it acquired a globular morphology, which is a typical property of elastomer. SEM images (Fig. 3(e) and (f)) indicated circular and rounded arrangement between matrix and epoxy linked through fibrils. At high magnification these linking fibrils became more visible and prominent showing interfacial interactions (Fig. 3(f)). Besides, phase morphology of a blend system is not merely dependent on interfacial tension; rather, it is a combination of interfacial tension and interfacial areas [26,27]. The insertion of epoxy in the amine-functionalized SEBS significantly increased the number of linkages and improved the mechanical profile of the elastomer. Upon 35-wt% epoxy loading in the blend system, the globules segregated and grew larger but still bridged through epoxy as indicated in Fig. 3(g) and (h). At 40-wt% epoxy loading, these interlinks became broad and widened the space between matrix and epoxy due to the increased amounts of epoxy that might not be linked with amine-modified SEBS (Fig. 3(i) and (j)). Therefore, low epoxy content provided good interfacial interactions with the matrix, giving uniform morphology and homogeneous networks formed in the nanoblends. At higher epoxy loading, amine-modified SEBS/epoxy blends showed weak compatibility between the two phases, thus reducing toughness and increasing brittleness in the blends, as is evident from the mechanical data (see Table 1).

4. Thermogravimetric Analysis

Thermal stability of blend films was monitored under nitrogen atmosphere, and the thermograms of the nanoblends are given in Fig. 4. SEBS is a thermoplastic elastomer possessing good thermal stability [28]. Introduction of epoxy reduced the thermal decomposition temperature of the elastomer because of the aliphatic moiety of the epoxy decomposing at low temperature. Thermal decomposition in blend containing 5-wt% epoxy started earlier due to less cross-linked network produced relative to the higher percent-

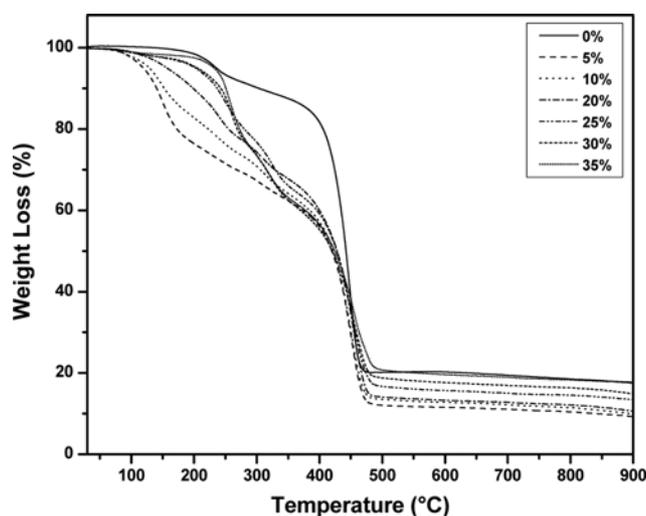


Fig. 4. Thermograms of amine modified SEBS/epoxy nanoblends.

ages of the epoxy. Blends containing higher amounts of epoxy yielded more cross links in the elastomer and subsequent increase in thermal stability. In addition, the residual weight retentions at 800 °C for different concentrations of the blends were found to be 10-20%. This implies that blend systems possess good thermal stability.

CONCLUSIONS

Thermoplastic elastomer was successfully modified to produce nitro-functionalized and amine functionalized SEBS. Various compositions of polymeric blends were prepared by combination of amine modified SEBS and epoxy via solution blending method. Enhancement of mechanical properties in amine modified SEBS/epoxy blends was also observed with good compatibility; improved toughness of amine modified SEBS/epoxy blends made them a good candidate for hybrid materials. FESEM images of the cured epoxy films showed good compatibility of amine modified SEBS with epoxy; no phase separation was observed. Striking morphology was obtained showing interfacial linkages in nanoblends. Thermogravimetric analysis showed that amine modified SEBS/epoxy films exhibited good thermal stability. We expect that these blend systems may find applications as thermally stable and easily processable thermoformed packaging materials [29]. However, brittleness of these blends may restrict their use in high impact applications; therefore, rubber toughening of amine modified SEBS with epoxy blends is proposed to yield an ideal combination of tough and processable polymeric materials with synergistic properties of the blend components as well as the rubber [14].

REFERENCES

1. D.R. Paul and C. B. Bucknall, *Polymer blends: Formulation and performance*, Wiley, NY (2000).
2. T. Araki, Q. Tran-Cong and M. Shibayama, *Structure and properties of multiphase polymeric materials*, Marcel Dekker, NY (1998).
3. M. Xanthos, *Reactive extrusion: Principles and practice*, Hanser, NY (1994).
4. S. Y. Hobbs, M. E. J. Dekkers and V. H. Watkins, *Polymer*, **29**, 1598 (1988).
5. W. T. Cheng, H. Keskkula and D. R. Paul, *Polymer*, **33**, 1606 (1992).
6. H. F. Guo, S. Packirisamy, N. V. Gvozdic and D. J. Meier, *Polymer*, **38**, 785 (1997).
7. H. F. Guo, N. V. Gvozdic and D. J. Meier, *Polymer*, **38**, 4915 (1997).
8. A. N. Wilkinson, L. Laugel, M. L. Clemens, V. M. Harding and M. Marin, *Polymer*, **40**, 4971 (1999).
9. J. Rosch and R. Mülhaupt, *Polym. Bull.*, **32**, 697 (1994).
10. S. Horiuchi, N. Matchariyakul, K. Yase and T. Kitano, *Macromolecules*, **30**, 3664 (1997).
11. B. Ballauri, M. Trabuio and F. P. LaMantia, *In: Recycling of PVC and mixed plastics*, F. P. LaMantia (Ed.), Toronto: Chem. Tec., 77 (1996).
12. K. Heino, J. Kirjava, P. Hietaoja and J. Seppala, *J. Appl. Polym. Sci.*, **65**, 241 (1996).
13. C. P. Papadopoulou and N. K. Kalfoglou, *Polymer*, **41**, 2543 (2000).
14. S. Shabbir, S. Zulfqar, I. Lieberwirth, A. Kausar and M. I. Sarwar, *Surf. Interface Anal.*, **40**, 906 (2008).

15. C. A. May, *Epoxy Resins, Chemistry and Technology*, Marcel Dekker, NY (1988).
16. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, NY (1990).
17. B. Ellis, *Chemistry and technology of epoxy resins*, Blackie Academic and Professional, Glasgow (1993).
18. Z. Chen, J. Yang, Q. Ni, S. Fu and Y. Huang, *Polymer*, **50**, 4753 (2009).
19. M. A. Hillmyer, P. M. Lipic, D. A. Hajduk, K. Almdal and F. S. Bates, *J. Am. Chem. Soc.*, **119**, 2749 (1997).
20. P. M. Lipic, F. S. Bates and M. A. Hillmyer, *J. Am. Chem. Soc.*, **120**, 8963 (1998).
21. J. M. Dean, P. M. Lipic, R. B. Grubbs, R. F. Cook and F. S. Bates, *J. Polym. Sci. Part B Polym. Phys.*, **39**, 2996 (2001).
22. J. M. Dean, N. E. Verghese, H. Q. Pham and F. S. Bates, *Macromolecules*, **36**, 9267 (2003).
23. J. M. Dean, R. B. Grubbs, W. Saad, R. F. Cook and F. S. Bates, *J. Polym. Sci. Part B Polym. Phys.*, **41**, 2444 (2003).
24. J. Wu, Y. Thio and F. S. Bates, *J. Polym. Sci. Part B Polym. Phys.*, **43**, 1950 (2005).
25. A. Kausar, S. Zulfiqar, S. Shabbir, M. Ishaq and M. I. Sarwar, *Polym. Bull.*, **59**, 457 (2007).
26. S. Shabbir, S. Zulfiqar, Z. Ahmad and M. I. Sarwar, *Polym. Eng. Sci.*, **48**, 1793 (2008).
27. R. P. Singh, M. Zhang and D. Chan, *J. Mater. Sci.*, **37**, 781 (2002).
28. S. Zulfiqar, Z. Ahmad, M. Ishaq, S. Saeed and M. I. Sarwar, *J. Mater. Sci.*, **42**, 93 (2007).
29. J. R. Wunsch, *Polystyrene: Synthesis, Production and Applications*, iSmithers Rapra Publishing, Shropshire, 31 (2000).