Compatibilization and Properties of SAN/EPDM Blends with the Addition of Coagents

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ABSTRACT: SAN and EPDM are not miscible. In this work, the dry blending of SAN and EPDM using Centrex (acrylonitrile/EPDM/styrene graft copolymer) and EPMMA (EPDM-*g*-Mah) as coagents was studied. Centrex content was used at 6–20 wt %. EPMMA content in the mixture was 20 wt %. The effects of coagent type and content on the mechanical properties and morphology were investigated. SEM micrographs of SAN/EPDM/Centrex and SAN/EPDM/EPMMA blends showed that both Centrex and EPMMA have an effective role in forming a finer morphology. For the ternary blends, the addition of coagent resulted in a significant reduction in the size of the dispersed phase. The mechanical properties of SAN/EPDM/coagent blends were improved significantly in comparison to the simple SAN/EPDM blends. SAN/EPDM/Centrex blends showed higher stress-at-break and SAN/EPDM/EPMMA blends showed higher impact strength. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 753–760, 2008

Key words: SAN; EPDM; compatibilization; blend; coagent

INTRODUCTION

Nowadays, ABS terpolymer is increasingly used in a variety of engineering applications. However, its yellowing and poor aging characteristics during service life, which is accompanied by depletion in mechanical properties, are its main drawbacks. This event arises from the presence of unsaturated double bonds in polybutadiene domains. An alternative way of overcoming the problem is to substitute EPDM, an elastomerics with enhanced weathering resistance property. At the present time, acrylonitrile-EPDM-styrene graft terpolymer is commercially produced by solution polymerization, referred as AES polymer.[1–2] However, problems of selecting a suitable solvent, solvent recovery and extraction of the product, limit AES production by solution method. In this work, we have focused on preparing an alloy of SAN-EPDM through melt processing, with great prospects such as easy processing to make its different grades of highly impact modifier, compatibilizer in plastics products, and modified-SAN grade.

Present industrial approaches toward new polymer-based materials focus on: (1) the modification of existing polymers, (2) the blending of commercially available polymers, and (3) the use of new polymerization catalysts for polymerization of existing monomers to obtain polymers with a new combination of properties. However, most polymer blends are immiscible and need to be compatibilized. Poly (styrene-*co*-acrylonitrile) (SAN) is a thermoplastic polymer with polar repeating units, highly transparent, excellent gloss, high mechanical strength, and good chemical resistance. However, it has a tendency to yellowing and darkening during its processing.[3] EPDM is ethylene–propylene–diene terpolymer with nonpolar properties and low unsaturated content. EPDM has good weather ability and thermal stability.[3]

SAN/EPDM system is a brittle/ductile combination. The blend does not, however, result in a toughened plastic, given that the two components are immiscible at the molecular level and blends have poor mechanical properties compared with those of their net components. Therefore, the introduction of a small amount of coagent has been suggested to obtain more desirable properties.[4]

In this work, we report the compatibilization of immiscible SAN/EPDM blends. It has been done by using two types of coagents: (1) acrylonitrile-EPDM-styrene terpolymer produced by solution polymerization (Centrex 601) and (2) maleic anhydride (MAh) grafted EPDM (EPMMA) produced by reactive blending. Centrex, a commercial name for AES, is identified as a potential coagent for compatibilizing immiscible components such as SAN and EPDM in forming a

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TABLE I
Specifications of EPDM, SAN and Coagents

EPDM	Ethylene (wt %)	ENB (wt %)	Mooney viscosity 125°C
Keltan (2340A) DSM Co.	53	6	25
SAN	AN (wt %)	Reduced viscosity	
APH Tabriz Petrochemical Co.	28	059 ~ 0.63	
Centrex 601	GR	SAN-g-EPDM (wt %)	
Lanxess Co.	50%	80	
EPMMA	MAh (wt%)	MFI (g/10 min) at 190 °C with 21.6 kg	
OPTIM TP-546/p Pluss pol, Co.	1.2	0.63	

homogeneous blend. One of the main reasons for incompatibility of SAN and EPDM is the significant difference in their interaction parameters. Making use of malienated EPDM, as another type of coagent, with close interaction parameter to that of SAN is expected to bring about compatibility between SAN and EPDM to help stabilization of the morphology of the system. The coagents play an important role in bridging between two phases and improving the stress transfer in the blends. They bring about the continuity of the two phases in an interface.

EXPERIMENTAL

Materials

The materials used and their specifications are given in Table I.

Blend preparation

SAN was dried under vacuum at 80°C for at least 12 h before blending. The polymers were blended in an internal mixer at 175°C and 60 rpm for 15 min. Torque-temperature-time rheograms were analyzed for the optimization purpose. Mixing was stopped after torque stabilization. The EPDM contents in the SAN/EPDM blends were 20, 40, 60 and 80 wt %. This wide range of EPDM content was chosen to yield a wide range of rubber toughened plastics with variety of properties. The weight percentage of the added Centrex with respect to the total weight of SAN/EPDM blends was each 6, 8, 10, and 20%. Also, the weight percentage of used EPMMA was 20%.

For the blending of SAN and EPDM, the weight ratio of SAN/EPDM and the amount of coagent were systematically changed according to experimental series 1–6 given in Table II. Other parameters, such as mixing conditions, speed of mixing, and blending temperatures were kept constant.

Characterization

Morphological observations

SEM microscopy was employed to characterize the blends. The morphology of the fractured specimens was observed using a Cambridge S360 stereo scan electron microscope. The cryogenic specimens were dipped in liquid nitrogen for about 5 min and immediately fractured. Samples were coated with gold before viewing to avoid charging.

Mechanical properties

Tensile measurements were carried out on the compression-molded specimens according to ASTM D638. The testing was performed using an Instron tensile testing machine (model 6025) with a crosshead speed of 50 mm/min at room temperature.

The Izod notched impact tests on the specimens were carried out with a pendulum-type impact tester (Zwick, 5102, Germany) at room temperature. At least five runs were made to report the average.

Simultaneous thermal analysis (STA)

TG-DSC curves of the blends were plotted by STA625. All experiments were carried out in the temperature range of 25–600°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSIONS

It is well known that the mechanical properties of blends depend on the degree of dispersion, size of domains, number of phases, and interfacial adhesion.

The compatibilization aims are to[5]:

- reduce the interfacial tension, thus producing finer dispersion,

TABLE II
Different Blends Formulation (the Mixing Sequence was EPDM and the Coagent SAN)

Exp. series	EPDM (wt %)	Type of coagent (wt %)
1	20, 40, 60, 80	Centrex (6)
2	20, 40, 60, 80	Centrex (8)
3	20, 40, 60, 80	Centrex (10)
4	20, 40, 60, 80	Centrex (20)
5	20, 40, 60, 80	EPMMA (20)
6	20, 40, 60, 80	EPMMA (20)

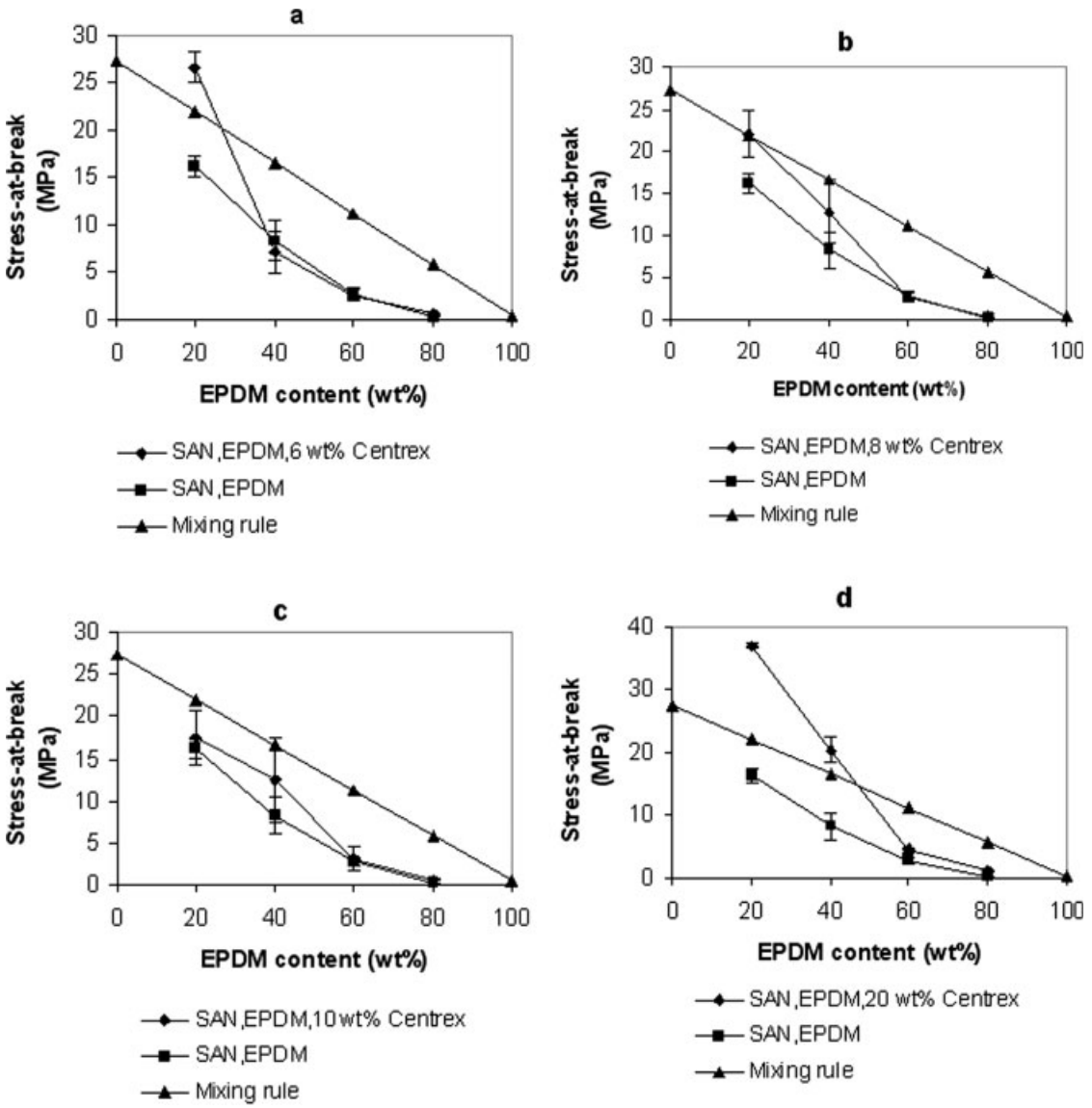

Figure 1 Stress-at-break for the blends at different levels of Centrex; (a) 6 wt %, (b) 8 wt %, (c) 10 wt %, and (d) 20 wt %.

- stabilize the morphology against thermal or shear effects during the processing steps, and
- provide interfacial adhesion in the solid state.

The tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress in most applications.

Figure 1 shows stress-at-break for the blends prepared by various levels of Centrex. In each figure, three curves are depicted, which corresponds to SAN/EPDM/Centrex, simple blend of SAN/EPDM, and the curve obtained based on the mixing rule.

As it is evident, the addition of a small amount of rubber as a dispersed phase into the thermoplastic matrix is more efficient than the addition of a thermoplastic material into the rubber matrix by comparing the result of simple blends with SAN/EPDM/Centrex in high content of EPDM. At 20 wt % of EPDM, SAN/EPDM/Centrex blend shows positive deviation from the mixing rule. In low content of EPDM, Centrex has an effective role in interfacial adhesion between the phases. In high content of SAN, the mechanical properties of the blend are determined by matrix phase. With increasing of EPDM content, there is no difference between the results of simple blends and blends with Centrex. Stress-at-break of the blends containing 6, 8, and 10 wt % Centrex shows an irregular change. This can be explained by the fact that when the amount of Centrex increases, the size of the dispersed phase decreases, and this results in a better dispersion. On the other hand, these amounts of Centrex cannot wet all the dispersed particles. Thus, failure occurs in interfacial places which have not been wet by Centrex.

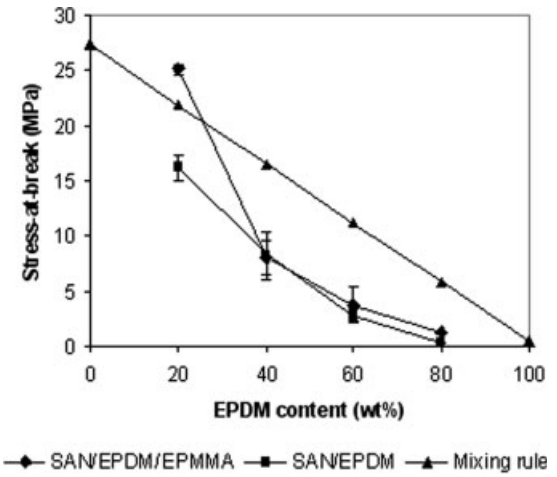

Figure 2 Stress-at-break for the blends prepared with 20 wt % EPMMA.

Figure 2 shows stress-at-break for the blends prepared with 20 wt % of EPMMA. As it can be seen at 20 wt % EPDM, the SAN/EPDM/EPMMA blend shows positive deviation from the mixing rule. This means that EPMMA has a good compatibility with SAN.

When the stress-at-break is low, failure could occur either by debonding or in an EPDM phase. To determine the event, studying the results of strain-at-break can be helpful. Figure 3 shows strain-at-break for the blends prepared with 6, 8, 10, and 20 wt % Centrex. Figure 4 shows strain-at-break for the blends prepared with 20 wt % EPMMA. If the strain-at-break is near the strain-at-break of the neat EPDM, it means that failure occurs in EPDM phase. However, as it can be seen in Figure 3, at high content of EPDM, the strain-at-break of the blend is not near to that of EPDM. Thus, the failure is because of debonding. Figure 4 shows that at high content of EPDM, strain-at-break increases noticeably, which can be attributed to occurrence of good adhesion at the interface of the blend phases. By comparing Figures 3 and 4, it can be found that SAN/EPDM/EPMMA blends show higher strain-at-break than

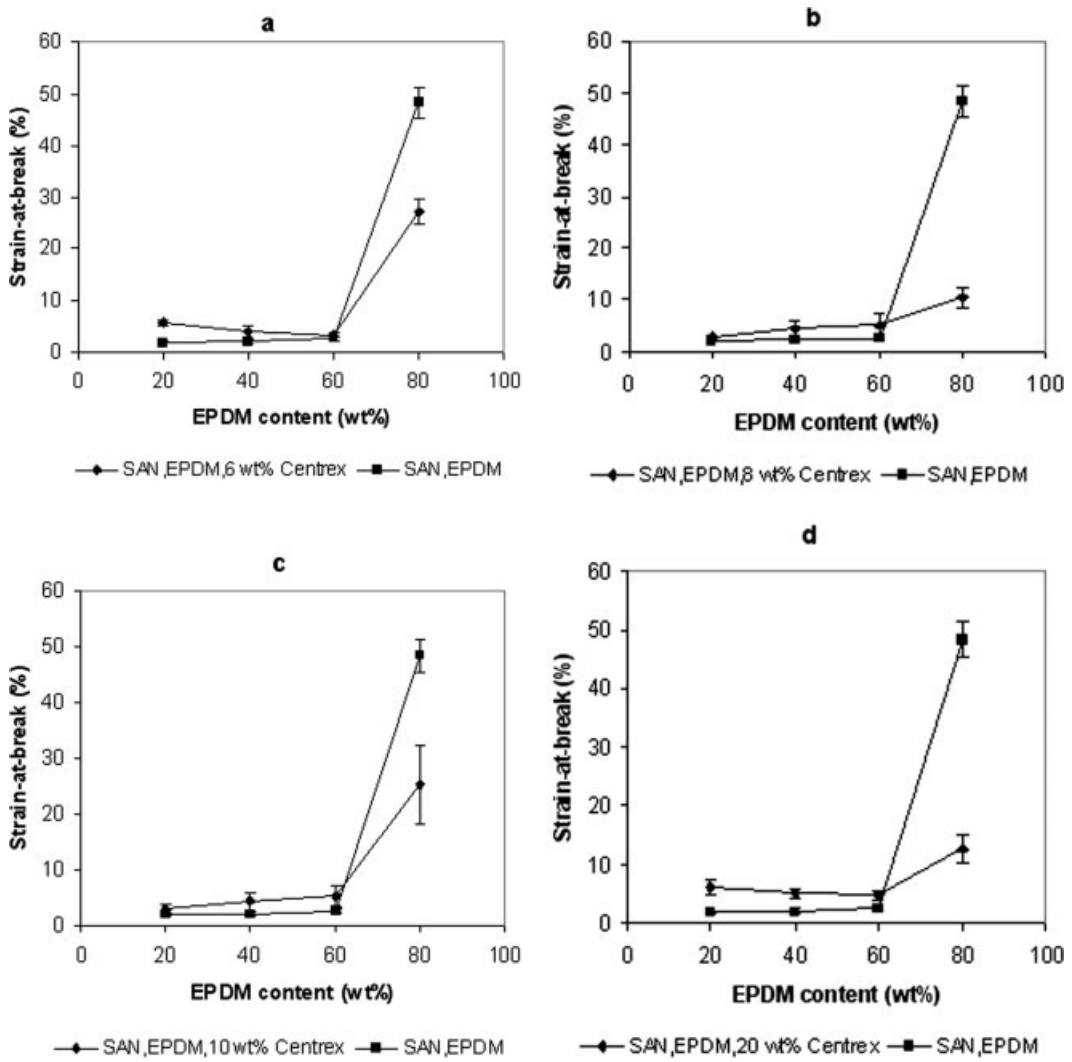

Figure 3 Strain-at-break for the blends at different levels of Centrex; (a) 6 wt %, (b) 8 wt %, (c) 10 wt %, and (d) 20 wt %.

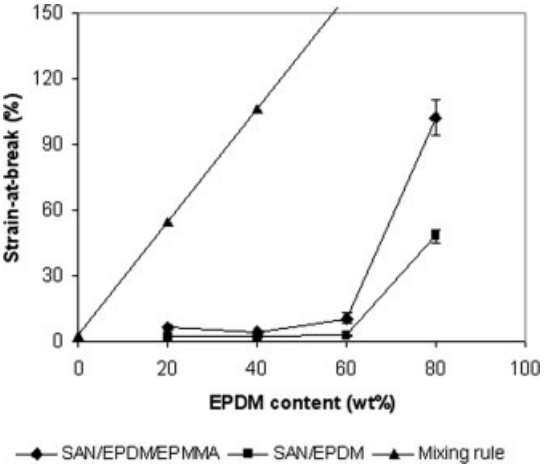

Figure 4 Strain-at-break for the blends prepared with 20 wt % EPMMA.

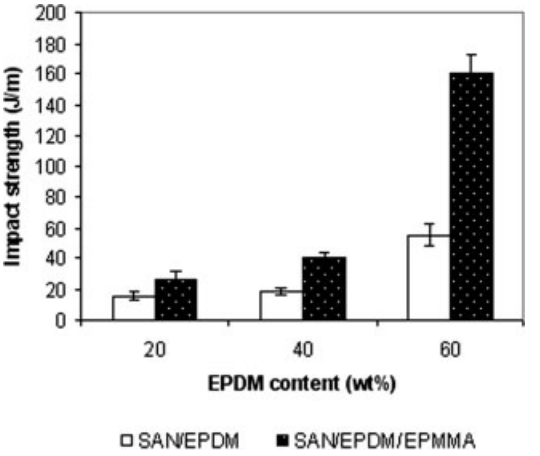

Figure 6 Impact strength of the blends prepared with 20 wt % EPMMA.

that of simple SAN/EPDM blends in all contents of SAN. In Figure 3, however, the strain-at-break at high content of EPDM is less than that of simple SAN/EPDM blend.

The introduction of an elastomer into plastic is a commonly used toughening method. According to the classical theory of elastomer toughening,[6–9] the improvement in the ductility is mainly caused by the brittle-ductile transition of the plastic matrix induced by the elastomer. In fact, the elastomer acts as a stress concentrator in the matrix, and two kinds of plastic deformation are induced. One is craze and the other is formation of shear bands. SAN/EPDM blends tend to fail by crazing or mixed crazing and yielding. Some authors suggested that bimodal-sized (i.e., mixtures of distinctly large and small sizes) rubber particles have a pronounced synergistic toughening effect on SAN.[4] Thus, one can conclude that the mechanism of toughening in crazes may be terminated at shear bands that are initiated by individual small particles or by mutual termination of several crazes where the relative rubber concentration is high. When the EPDM content is high, the rubber-particle network is formed. Thus, this network formation may contribute to the ductility and toughness of blends.

Figure 5 shows the impact strength of the blends containing 6, 8, 10, and 20 wt % Centrex compared to that of the simple blends. It is observed that with the addition of Centrex, the toughness of the blends increases. This clearly indicates that Centrex is able to act as a good coagent to compatibilize SAN and EPDM phases. Figure 6 shows the impact strength of the blends containing 20 wt % of Centrex and EPMMA compared with that of simple blends. As it is observed, with the addition of 20 wt % EPMMA as a coagent, the impact strength of the blend increases higher than that of SAN/EPDM, with 20 wt % Centrex.

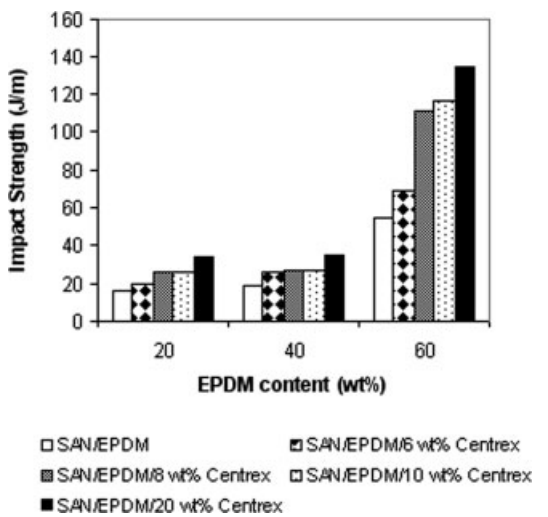

Figure 5 Impact strength of the blends at different levels of Centrex.

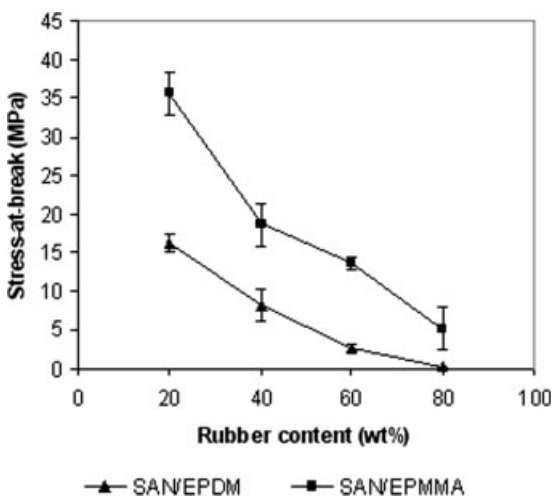

Figure 7 Mechanical properties of SAN/EPMMA (series 6) blends at different levels of rubber content.

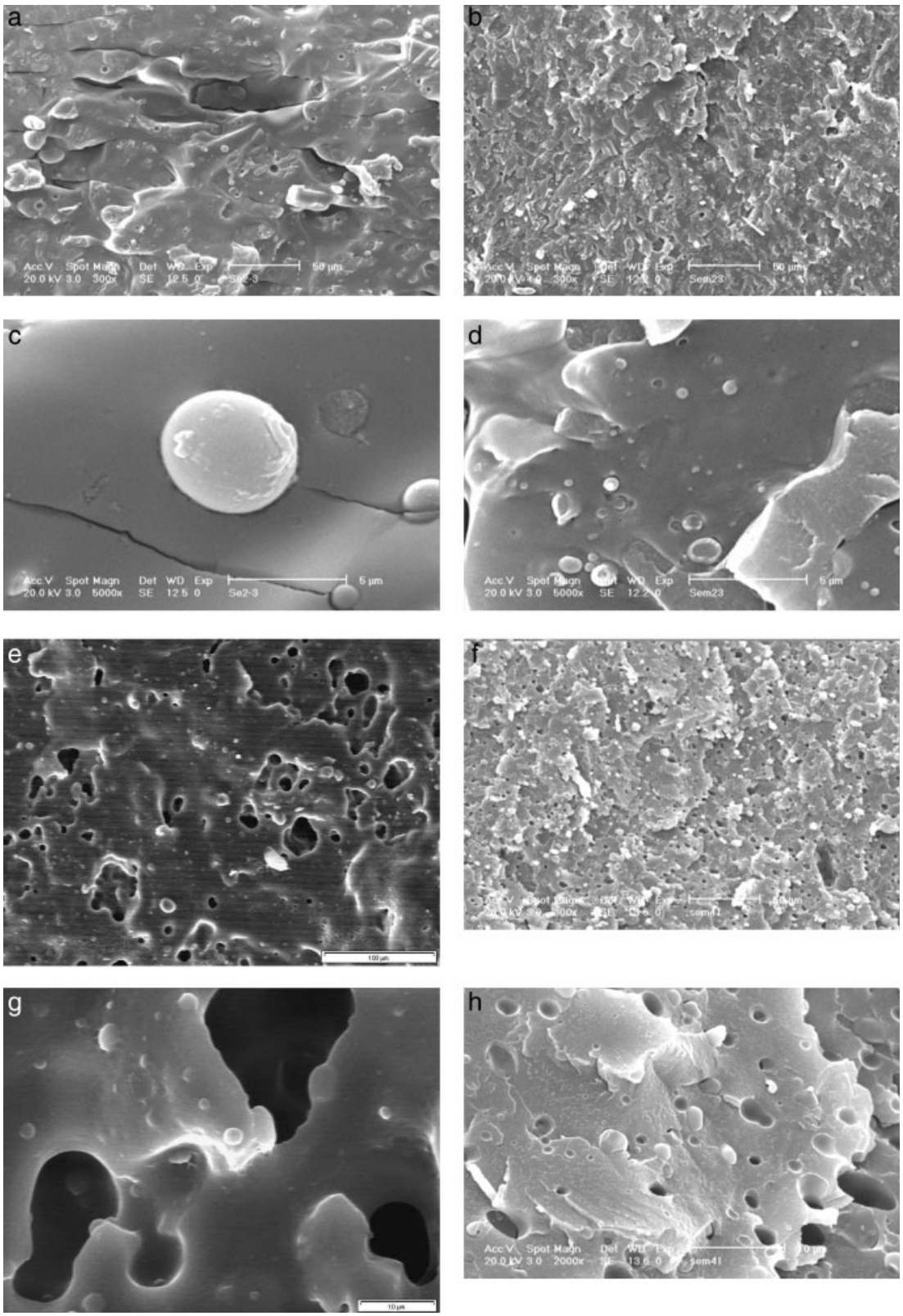

Figure 8 SEM micrographs of SAN/EPDM and SAN/EPMMA blends; (a) with 60 wt % EPDM (magnification ×300), (b) with 60 wt % EPMMA (magnification ×300), (c) with 60 wt % EPDM (magnification ×5000), (d) with 60 wt % EPMMA (magnification ×5000), (e) with 20 wt % EPDM (magnification ×300), (f) with 20 wt % EPMMA (magnification ×300), (g) with 20 wt % EPDM (magnification ×2000), (h) with 20 wt % EPMMA (magnification ×2000).

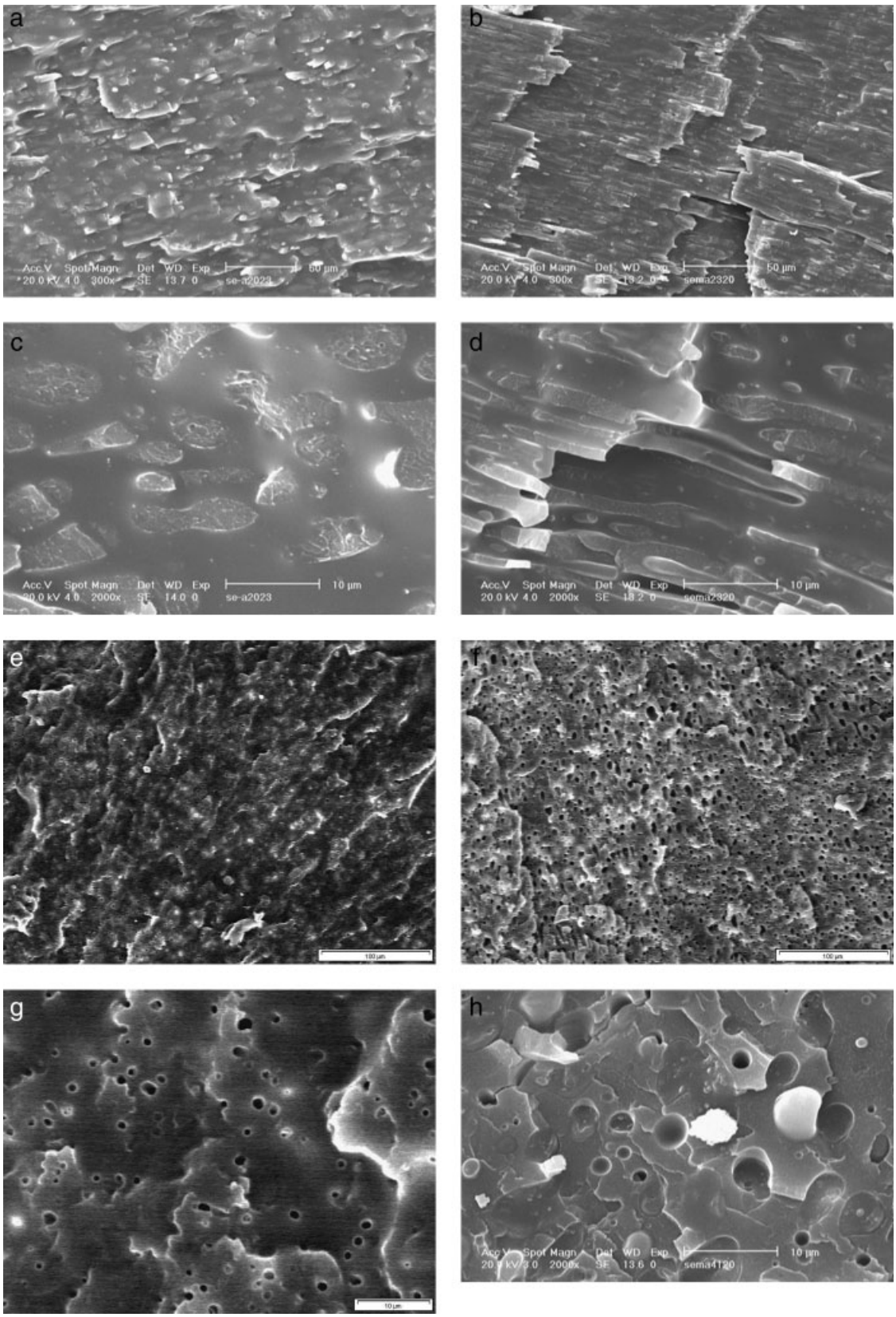

Figure 9 SEM micrographs of SAN/EPDM/Centrex and SAN/EPMMA blends; (a) with 60 wt % Centrex (magnification ×300), (b) with 60 wt % EPMMA (magnification ×300), (c) with 60 wt % Centrex (magnification ×2000), (d) with 60 wt % EPMMA (magnification ×2000), (e) with 20 wt % Centrex (magnification ×300), (f) with 20 wt % EPMMA (magnification ×300), (g) with 20 wt % Centrex (magnification ×2000), (h) with 20 wt % EPMMA (magnification ×2000).

Figure 7 shows the stress and strain-at-break of series 6 in which EPDM is completely replaced by EPMMA. As it can be seen, EPMMA is much more compatible than pure EPDM with SAN. At all levels of SAN, the stress-at-break of SAN/EPMMA is higher than SAN/EPDM blends. At high contents of SAN, the malienated EPDM causes a noticeable increase in an interfacial adhesion between the dispersed rubber phase and thermoplastic matrix. When the rubber content is high, the SAN/EPMMA blend shows a much higher strain-at-break than simple SAN/EPDM blends.

To provide further explanation for the improved mechanical properties of the blend, the blend morphology is characterized by scanning electron microscopy (SEM). A noncompatibilized mechanical EPDM/SAN blend is taken as a reference. The SEM micrographs of simple SAN/EPDM and SAN/EPMMA blends prepared by 60 and 20 wt % rubber contents are shown in Figure 8. Figure 8(a,c,e,g) are related to the simple blends and Figure 8(b,d,f,h) are related to the SAN/EPMMA blends at different magnifications. Note that the micrographs of noncompatibilized simple blend [Fig. 8(a,c,e,g)] exhibit a coarse structure with a large domain sizes. In all micrographs there are microvoids, which are depicted as large dark areas. These microvoids apparently result from EPDM inclusions, which have been pulled out during sample preparation, either during slicing of the sample or staining with OsO_4. The major difference is the quality of phase dispersion. SAN/EPMMA blends show good phase dispersion and a smooth break surface [Fig. 8(b,d,f,h)].

Figure 9 shows the SEM micrographs of SAN/EPDM/Centrex and SAN/EPDM/EPMMA blends prepared by 60 and 20 wt % coagent contents, respectively. As it is seen, both Centrex [Fig. 9(a,c,e,g)] and EPMMA [Fig. 9(b,d,f,h)] have an effective role to reduce the interfacial tension. For the ternary blends, the addition of coagent results in a significant reduction of the dispersed phase. In the absence of coagent, the immiscible phases seek to minimize the extent of interpenetration across the interface by adopting more collapsed conformation in the immiscible vicinity of the interface. This is a cause of interfacial weakness in immiscible blends. The poor interface is attributed to the weak interfacial adhesion between SAN and EPDM. The coagent rests at the interface between the two phases and reduces the interfacial tension, thus enhancing the adhesion between the phases and improving the mechanical properties compared to those of the simple blend.

CONCLUSIONS

In this work, the preparation of SAN/EPDM blends by using coagents by dry blending was investigated. Mechanical properties, impact strength, and SEM micrographs of simple SAN/EPDM, ternary SAN/EPDM/Centrex, and SAN/EPDM/EPMMA blends showed that Centrex and EPMMA can act as a good coagent to compatibilize immiscible SAN and EPDM phases. The addition of coagent reduces the sizes of the dispersed phase, thus imparting better adhesion and mechanical properties. Both EPMMA and Centrex blends have demonstrated ductile behavior with a high elongation prior to break during tensile testing and no failure under impact test. The toughening mechanism is reckoned to be the crazing initiation from rubber particles and shear deformation of the SAN matrix. SAN/EPDM/Centrex blends showed the highest stress-at-break and SAN/EPDM/EPMMA blends showed the highest impact strength.

References

1. Sjanghai kumhosunny plastic Co. Available at: www.Kumhosunny.com (accessed 28 February 2008).
2. Lustran polymers Co. Available at: www.Lustran-polymers.com (accessed 28 February 2008).
3. Hoang, T.; Trung, T.; Yoo, G.; Ahn, J. H.; Zin, W. Bull Korean Chem Soc 2001, 22, 1037.
4. Qu, X.; Shang, S. H.; Liu, G.; Zhang, S. H.; Zhang, Y.; Zhang, L. J Appl Polym Sci 2004, 91, 1685.
5. Qu, X.; Shang, S. H.; Liu, G.; Zhang, L. J Appl Polym Sci 2002, 86, 428.
6. Siegman, A. H. Polym Eng Sci 1984, 24, 877.
7. Newman, S.; Strella, S. J Appl Polym Sci 1956, 9, 2297.
8. Schimitt, J.; Keskula, H. J Appl Polym Sci 1960, 3, 132.
9. Kambour, R. P. Polymer 1964, 5, 143.