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BLOG
Acrylonitrile/Styrene/Acrylate Structural Rubber Latex Particles as Impact Modifier for SAN Copolymer

Mohammad Reza Moghbeli* and Shima Tolue

School of Chemical Engineering, Iran University of Science and Technology (IUST), P.O. Box: 16844/13114, Tehran-16846/13114, Iran

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ABSTRACT

Rubber modification of styrene/acrylonitrile (SAN) copolymer has been carried out using acrylonitrile/styrene/acrylate (ASA) structural rubber latex copolymer particles with a rubbery acrylate core and a rigid SAN (30 wt% acrylonitrile, AN) graft shell. The melt flow and toughness of SAN copolymer have been investigated in relation to core composition and particle morphology. The results showed that incorporation of rubber particles increases the torque equilibrium of the SAN copolymer during the melt blending process. The lowest and highest torque values were obtained for the blend samples containing large core-shell and small hemispheric rubber particles, respectively. On the other hand, the highest impact toughness was observed for the blend sample containing ASA core-shell structured particles with P(BA-co-2EHA) core composition due to its lowest glass-rubber transition temperature (T_g). The TEM micrographs were indications of good dispersibility for the particles with raspberry and core-shell structures within the SAN matrix. Whereas, large particle agglomerates were observed for the blends containing hemispheric structural particles. Dynamic mechanical thermal analysis (DMTA) results showed that the blends with core-shell particles possess a higher maximum tan δ and lower tan δ-curve broadening when compared to blends containing rubber particles with other morphologies. A good dispersion state of core-shell rubber particles in the copolymer matrix resulted in a more homogeneous structure and a narrower tan δ curve.

INTRODUCTION

Rubber modification of glassy thermoplastic polymers such as poly(methyl methacrylate) (PMMA) [1,2], poly(vinyl chloride) (PVC) [3,4], poly(butylene terephthalate) (PBT) [5], and styrene/acrylonitrile (SAN) copolymers [6,7] with preformed core-shell rubber latex particles have been developed for many decades. These structural rubber particles with a rubbery core and a rigid thermoplastic shell have been synthesized via a two-stage emulsion polymerization process [8-10]. Most rubber-toughened SAN copolymers or acrylonitrile-butadiene-styrene (ABS) thermoplastic materials consist of a SAN copolymer matrix containing small discrete poly(butadiene)/poly(styrene-co-acrylonitrile) (PB/PSAN) core/shell particles which have a good interaction with the matrix [11-13]. These structural rubber latex particles, namely...
grafted ABS (g-ABS), considerably increase the toughness of SAN matrix even at very low temperatures. Many parameters, such as particle size and size distribution [13], core and shell chemical compositions [14-16], and particle grafting degree and efficiency [17,18] substantially influence the melt rheology and toughness of SAN copolymers. It has been found that the toughening of SAN can be improved using core-shell rubber particles with larger sizes varied in the range of 300-600 nm as compared with other above glassy polymers toughened effectively with smaller rubber particles, 60-100 nm in diameter. On the other hand, when AN content in the matrix was slightly higher than that of the SAN graft shell, the best mechanical properties was obtained for the blend samples [13]. All-acrylic impact modifiers (AIMs) are other types of rubber materials mainly consist of a soft poly(butyl acrylate) (PBA) core and a rigid poly(methyl methacrylate) (PMMA) shell [19,20]. Recently, Steenbrink et al. [7] used acrylic impact modifiers with various rubber particle sizes ranging from 0.1 to 0.6 μm for toughening of SAN copolymer. In most cases, the large core-shell rubber particles show a good dispersion state inside SAN copolymer matrix while small rubber particles tend to agglomerate [14,21]. Although ABS impact modifiers are excellent composite rubber particles with higher performance even at lower temperatures compared to the AIM rubber modifiers, they have poor weatherability against UV and heat in order to be used in automotive and outdoor applications. ASA structural rubber materials are other types of grafted rubber latex particles in which the acrylic rubber cores are covered, in efficient interaction, with a layer of SAN copolymer [12,22]. The absence of double bonds in the core structure improves the heat resistance of the grafted particles as compared to ABS grafted rubber materials.

In spite of a large number of papers published on toughening the SAN copolymers with g-ABS and AIM rubber materials, less attention has been paid to the rubber-modification of SAN copolymers with ASA composite rubber particles. Up to authors' findings, there is no publication on ASA composite rubber particles used in various core compositions and morphologies as impact modifier for SAN copolymer. In the present work, the effects of ASA particle composition and morphology on melt flow behaviour, toughness, and dynamic mechanical properties of the SAN copolymer have been investigated.

**EXPERIMENTAL**

**Materials**

SAN copolymer (30 wt% AN) and g-ABS impact modifier with a mean particle size of 296 nm were purchased from Tabriz Petrochemical Co., Iran. Ethylene bis-stearamide (Bayer, Germany) was used as lubricant.

**Preparation of ASA Emulsion Particles**

Acrylonitrile/styrene/acrylate (ASA) structural latex copolymer particles with various particle morphologies were prepared via a two-stage emulsion polymerization process as reported before [22]. Table 1 shows the characteristics of ASA rubber particles.

<table>
<thead>
<tr>
<th>Code</th>
<th>Core/shell structure</th>
<th>CS particle morphology</th>
<th>Gel content (%)</th>
<th>Dia. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASA1</td>
<td>PBA/SAN</td>
<td>Hemisphere</td>
<td>77</td>
<td>150</td>
</tr>
<tr>
<td>ASA2</td>
<td>PBA/SAN</td>
<td>Raspberry</td>
<td>73</td>
<td>476</td>
</tr>
<tr>
<td>ASA3</td>
<td>PBA/SAN</td>
<td>Core-shell</td>
<td>73</td>
<td>446</td>
</tr>
<tr>
<td>ASA4</td>
<td>P(BA/2EHA)/SAN</td>
<td>Raspberry</td>
<td>69</td>
<td>591</td>
</tr>
<tr>
<td>ASA5</td>
<td>P(BA/2EHA)/SAN</td>
<td>Core-shell</td>
<td>69</td>
<td>585</td>
</tr>
<tr>
<td>g-ABS</td>
<td>PB/SAN</td>
<td>Core-shell</td>
<td>-</td>
<td>295</td>
</tr>
</tbody>
</table>

(*) The core to shell polymer weight ratio for all the samples was close to 50/50; (**) For preparation of the P(BA/2EHA) rubber core, the BA/2EHA ratio was fixed at 75/25 (w/w%).
particles used to rubber-modify the SAN copolymer. In this case, partially cross-linked acrylic rubber cores were first synthesized, and then a hard SAN copolymer (30 wt% AN) was grafted onto the rubbery cores via a second-stage emulsion polymerization.

Particle and Blend Morphology
The morphology of ASA latex particles has been studied through transmission electron microscopy (TEM) (Zeiss EM900, Germany). One drop of diluted latex was transferred onto a 200 mesh copper grid, and dried in open air and finally stained by osmium tetroxide vapor (OsO₄) before microscopy. The average size of ASA particles was determined based on the microscopy images of 300 particles. To investigate the dispersion state of ASA particles inside SAN matrix, the blend samples were cut by an ultramicrotome cryogenically at -40°C and then stained by OsO₄ vapour for 24 h before microscopy.

Blend Fracture Surface
Scanning electron microscopy (SEM) was conducted to study the topographical features of the fracture surface of the blend samples. The fracture surfaces were gold-sputtered before microscopy and observed using a Leo 435 VP SEM (Leo Elektronenmikroskopie, Germany) at an accelerating voltage of 10 kV.

Preparation of Blends
SAN copolymer (from Tabriz Petrochemical Co., Iran) and its blends with ASA rubber particles were prepared in a Brabender batch mixer (EHT50W, Germany) equipped with a co-rotating twin screw. The torque values of the polymer blends were recorded automatically at 2 s intervals by control system of the mixer. The melt blending process was carried out at 190°C and 60 rpm. The ASA rubber content of the blends was fixed at 20% in all cases.

Glass-transition Temperature
The glass transition temperature \( T_g \) and viscoelastic properties of the specimens compression-moulded at 190°C were measured with a dynamic mechanical analysis (DMA 983 DuPont), in fixed frequency mode of 1 Hz. All the experiments on the rectangular test specimens (50×12×1.5 mm) were carried out at a heating rate of 5°C/min over the same temperature range of -100°C to 180°C.

Mechanical Tests
The SAN and its blends were prepared by a melt-mixing tool and cooled at room temperature to be cut into small pieces. The pieces were placed into rectangular cavities of the mould (3×12.7×63.5 mm) preheated at 190°C for 5 min and then compression moulded under 20 MPa at the same temperature for 15 min. Hereafter, the melted samples were cooled down to room temperature under the same applied load. A 2-mm-deep notch with a notch radius of 0.25 mm was applied into the specimen. The notched Izod impact toughness of the samples was measured using an Izod impact tester (Zwick 5102, Germany). The notched samples were tested at room temperature according to the procedure outlined in ASTM D256 protocol. Before testing, the samples were conditioned at 45% relative humidity under room temperature for 48 h. Each reported value is determined by averaging six test specimens.

RESULTS AND DISCUSSION
The details of preparation and characterization of the structural ASA rubber latex particles are explained elsewhere [22]. Figure 1 shows the morphology of ASA particles prepared with various core compositions and different shell monomer addition modes in the second-stage of emulsion polymerization. As shown, the dark and bright regions of the stained structural particles show the acrylic rubber core and rigid SAN copolymer shell, respectively. The existence of unreacted double bonds of residual cross-linker i.e., allyl methacrylate (ALMA), inside the rubbery core gels may cause OsO₄ to stain the acrylic core phase [22]. A series of structured rubber particles consisting of an acrylic rubber core and a rigid SAN copolymer shell with hemisphere, raspberry, and core-shell morphologies are presented in Table 1. Figure 1a shows a hemispheric structure containing an incomplete coverage of the core polymer with the shell copolymer. For the composite particles with raspberry morphology (Figure 1b) rigid bright shells as isolated islands cover the whole surface of the dark rubber cores while, bright uniform
shell rings round the soft rubbery cores exhibit the real core-shell structure (Figures 1c and 1d).

**Melt Blending Behaviour**
The torque values of melt SAN copolymer containing ASA rubber particles having various morphologies, as approximate viscosity characteristic of the blends were measured during melt blending process. Figure 2 shows the variation of torque value versus time for the SAN copolymer and its blends with different ASA rubber modifiers at 190°C.

For the SAN copolymer, the amount of torque first increased to a maximum, and then dropped gradually to an equilibrium value in the so-called plateau region. Finally, adding lubricant to SAN copolymer melt restricted torque value to some extent because of the melt slippage over the screws. By dissolving the lubricant into the melt, the torque value increased again to reach a constant level where the mixing process stopped. By addition of ASA rubber particles to SAN copolymer system the melt rheological behaviour was changed (Figure 2).

As shown in Figure 2, incorporation of ASA rubber particles into the melt matrix increased the viscosity, and consequently, the torque equilibrium of the melt SAN to some extent. Using ASA rubber materials of various particle morphologies, possibly with higher melt viscosity, increased the melt

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**Figure 1.** TEM Micrographs of ASA structured latex particles: (a) ASA1 (hemisphere), (b) ASA2 (raspberry), (c) ASA3 (core-shell), and (d) ASA5 (core-shell). The particles were stained by OsO₄ vapour.
viscosity of the blends in comparison with the neat copolymer. Therefore, a higher and steady value of torque is obtained in the plateau region for all the blend samples as compared SAN copolymer itself. The effect of acrylic and poly(butadiene) based core-shell rubber materials on viscosity enhancement of SAN copolymer has been reported in literature [17,23]. For the ASA blends, a balance between the rate of re-agglomeration and agglomerate breakdown of the ASA rubber particles results in constant degree of torque equilibrium. After lubrication of the melt blends, a rather similar rheological behaviour like that of the SAN melt was observed. Adding the lubricant to the melt blend immediately lowered the amount of torque due to the melt slippage over the screws. The distribution of the lubricant into the melt blend afforded the torque value increasing again to reach a lower constant level, which was an indication of a homogeneous mixing condition suitable for easy material discharge.

As shown in Figure 2, the blends containing various ASA rubber materials under applied shear mixing conditions demonstrate melt viscosity changes rather similar and close to that of the neat copolymer. Nevertheless, the ASA particles with various morphologies and properties showed different torque equilibria in the plateau region. Table 2 indicates the equilibrium time and torque of the ASA blend samples in the plateau region for comparison purposes. As indicated, higher torque equilibrium was obtained for the blend samples containing the ASA particles with hemispheric particle morphology and smaller particle size (Table 2). This behaviour can be attributed to weak interfacial adhesion between rubber particles and matrix which leads to particle aggregate formation and subsequent rising in torque value. The lowest torque value was obtained for the blend with largest ASA5 core-shell rubber particles. The large ASA core-shell particles seemed to have a very efficient plasticizing effect to facilitate the melt flow of the blend when compared to other ASA rubber materials (Figure 2 and Table 2). A good interaction between the grafted SAN shell of core-shell particles and copolymer matrix prevents particle agglomeration and reduces the torque equilibrium.

**Impact Toughness**

A relative poor toughness of 15.7 J/m for impact strength was obtained for the SAN copolymer by notched Izod test. Depending on the size and morphology of ASA rubber particles, the impact strength of SAN/ASA the blends varied in the range of 23.8-52.4 J/m (Table 3). For the rubber-modified SAN copolymer with ASA rubber particles having hemispheric morphology and lowest particle size, the impact strength increased up to 23.8 J/m as compared with neat copolymer. Incorporation of...
larger ASA rubber particles with raspberry or core-shell structures considerably increased the impact toughness of the blend samples.

A commercial g-ABS impact modifier comprised of a PB core and SAN grafted shell was used to modify the SAN copolymer for evaluation purposes. The results showed that applying larger ASA rubber latex particles, close to 500 nm, is more useful than smaller g-ABS particles in enhancing the toughness of SAN copolymer. However, the highest toughness was observed for the blend sample containing greater ASA core-shell particles whose rubber cores consisted of partially cross-linked BA/2EHA (75/25 by weight) copolymer. In fact, the presence of 2EHA units in the core structure would decrease its glass transition temperature and effectively decrease the impact energy.

For those ASA particles with the same large particle size, the toughness of the blends with ASA core-shell structured particles is higher than that of the particles with raspberry morphology. This result can be related to efficient interfacial adhesion and dispersion state of the core-shell particles dispersed inside copolymer matrix. Figure 3 is a good

Table 3. Effect of various ASA rubber particles on the impact toughness of SAN copolymer.

<table>
<thead>
<tr>
<th>Code</th>
<th>Modifier</th>
<th>Impact (J/m)</th>
<th>Tg (°C)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Lower</td>
</tr>
<tr>
<td>SAN</td>
<td>-</td>
<td>15.7</td>
<td></td>
</tr>
<tr>
<td>BL1</td>
<td>ASA1</td>
<td>25.6</td>
<td>124.9</td>
</tr>
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<td>BL2</td>
<td>ASA2</td>
<td>46.4</td>
<td>121.5</td>
</tr>
<tr>
<td>BL3</td>
<td>ASA3</td>
<td>45.3</td>
<td>123.3</td>
</tr>
<tr>
<td>BL4</td>
<td>ASA4</td>
<td>21.2</td>
<td>126.6</td>
</tr>
<tr>
<td>BL5</td>
<td>ASA5</td>
<td>52.4</td>
<td>122.3</td>
</tr>
<tr>
<td>BL6</td>
<td>g-ABS</td>
<td>46.2</td>
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<td></td>
<td></td>
<td>Upper</td>
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<td></td>
<td></td>
<td>124.9</td>
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</table>

Figure 3. TEM Micrographs of blend samples containing ASA rubber materials: (a) no ASA (SAN copolymer), (b) ASA1, (c) ASA2, and (d) ASA5. The ultrathin section of the blend specimens was stained by OsO4 vapour.
indication of the dispersion state of ASA particles for the selected blends with major differences in toughness when compared with neat copolymer.

As shown (Figure 3), for the blend samples containing particles with hemispheric raspberry morphologies, there are some rubber particle aggregates observed (Figures 3b and 3c). In contrast, a rather good dispersion state of rubber particles is observed for the blends containing rubber particles with core-shell structure (Figure 3d). These differences can be attributed to the grafting level of polymer shell which engulfs the rubbery cores. In fact, the lowest and highest grafting levels was obtained for the ASA particles having hemispheric and core-shell structures, respectively [22].

Fracture Surface
SEM Micrographs with the same magnification show fracture surface of SAN copolymer and blend samples after impact tests (Figure 4). A very smooth fracture surface is observed for the brittle SAN copolymer (Figure 4a and Table 3). The surface features of the blends seem to be dependent upon the morphology of the constituted rubber composite particles. As shown, a low ductile behaviour with no significant plastic flow is observed for the blend containing rubber particles with hemispheric morphology (Figure 4b). In contrast, a more coarse-fracture surface with higher plasticizing effect is observed for blends containing raspberry or core-shell structured rubber particles (Figures 4c and 4d). These low-modulus rubber particles of large size can...
deviate the direction of crack propagation within the matrix and cause rough fracture surface with increased impact toughness (Table 3).

**Dynamic Mechanical Properties**
The incorporation of structural rubbery particles (20 wt%) inside the copolymer matrix has had no significant effect on the storage modulus of SAN copolymer (Figure 5). The tan δ curves of neat SAN copolymer and its blends with ASA particles versus temperature are indicated in Figure 6. Due to thin rubbery phase in the blends and large difference in the maximum height of damping peak of the rubber and copolymer matrix, the tan δ curves are shown on two temperature ranges (Figures 6a and 6b).

As shown (Figures 6a and 6b), the heterogeneity is to be confirmed by two tan δ peaks. The lower glass transition temperature (T_g) corresponds to the rubber phase T_g, while the higher temperature is the glass transition temperature of the copolymer phase.

**Figure 5.** Temperature dependence of storage modulus of SAN copolymer and SAN/ASA blend samples with various ASA impact modifiers.

**Figure 6.** The tan δ-temperature curves of SAN copolymer and SAN/ASA blend samples.
Figure 6b shows that the SAN copolymer has a high $T_g$ at about 124°C with a broad and lowest value of tan $\delta$. By addition of ASA rubber particles with different morphologies and characteristics, various sizes of interfacial area between the SAN shell and matrix in the blends are developed which affect the high temperature tan $\delta$ curves.

Addition of rubbery particles has increased the maximum tan $\delta$ height to some extent (Figure 6). In this case, the blends with core-shell particles have shown a higher maximum tan $\delta$ and lower tan $\delta$ curve broadness when compared to blends containing ASA rubber particles with other morphologies. In fact, the maximum tan $\delta$ height and width may be related to the matrix/particle interfacial adhesion and consequent dispersion state of the particles within copolymer matrix [13,24].

A good dispersive state of core-shell particles in the copolymer matrix resulted in a more homogeneous structure with higher tan $\delta$ height and lower curve broadness. In contrast, using hemispheric and raspberry-shaped particles has reduced the interfacial area between the SAN shell and copolymer matrix due to formation of larger particle aggregates. This behaviour may have induced a new motional component to the dynamic response of the sample which leads to local heterogeneity and curve broadening. Therefore, it seems that higher interfacial area between the components in the blend induces more homogeneous motions, while its reduction favours heterogeneous molecular motions.

CONCLUSION

The toughening effect of ASA structural rubber materials with various core compositions and particle morphologies has been investigated using SAN copolymer as a matrix. The mean size of particles, with rather similar gel contents of approximately 70%, was in the range of 150-550 nm in diameter. Incorporation of ASA rubber particles in the melt matrix impart elasticity, and consequently the torque equilibrium of the SAN melt increases to some extent. Nevertheless, the core-shell structured particles exhibit the lowest torque equilibrium because of the highly efficient particle dispersion within the melt matrix. Depending on the size and morphology of ASA rubber particles, the impact strength of SAN/ASA blend samples vary within the range of 23.8-52.4 J/m. Incorporation of larger ASA core-shell particles with 2EHA/BA copolymer core composition considerably increases the impact toughness of the blend samples by comparison to hemispheric structured particles which indicated the lowest toughening efficiency. The DMTA results show that adding rubber particles with various morphologies have no significant effect on the elastic modulus of the SAN copolymer, while increasing the maximum tan $\delta$ to some extent, especially for the blend samples containing ASA core-shell particles.

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