Blend of bisphenol-A polycarbonate (PC) and (acrylonitrile-styrene-acrylic rubber) terpolymer (ASA) having excellent balance in the interfacial properties and mechanical strength was developed for the automobile applications. Since interfacial adhesion between PC and styrene-acrylonitrile copolymer (SAN) matrix of ASA is not strong enough, two different types of compatibilizers, i.e., diblock copolymer composed of tetramethyl polycarbonate (TMPC) and SAN (TMPC-b-SAN) and poly(methyl methacrylate) (PMMA) were examined to improve interfacial adhesion between PC and SAN. TMPC-b-SAN was more effective than PMMA in increasing interfacial adhesion between PC and SAN matrix of ASA (or weld-line strength of PC/ASA blend). When blend composition was fixed, PC/ASA blends exhibited similar mechanical properties except impact strength and weld-line strength. Impact strength of PC/ASA blend at low temperature was influenced by rubber particle size and its morphology. PC/ASA blends containing commercially available PMMA as compatibilizer also exhibited excellent balance in mechanical properties and interfacial adhesion.

Keywords: polycarbonate, (acrylonitrile-co-styrene-co-acrylic rubber) terpolymer, interfacial strength, impact strength, morphology

1. Introduction

Even though bisphenol-A polycarbonate (PC) is using in a wide variety of applications because of its excellent balance of properties, application of PC often deterred because of its poor characteristics such as thickness dependence of notched impact strength, poor solvent and hydrolysis resistance, and poor ultraviolet stability (Freitag et al., 1988). To overcome deficient characteristics of PC, acrylonitrile-butadiene-styrene terpolymer (ABS) was blended with PC. Blends of PC with ABS materials is widely used commercially because these blends provide products having improved balance of properties at reduced cost in comparison to PC (Freitag et al., 1988; Guest and Daly, 1989; Keitz et al., 1984; Paul et al., 1988; Quentens et al., 1991). However, application of the typical PC/ABS blends also often limited because of their following drawbacks. Since interfacial adhesion between PC and acrylonitrile-styrene copolymer (SAN) matrix of ABS is not strong enough, PC/ASA blend exhibited poor adhesion at weld (Callaghan et al., 1993; Cheng et al., 1992; Kang et al., 2000; Kim et al., 1992; Kim et al., 2001; Wool, 1989).

Butadiene rubber containing double bond in its repeat unit underwent physical or chemical aging caused by ultraviolet (UV) radiation during the outdoor applications (Cheng et al., 1992). Aging of butadiene rubber resulted in continuous decline in the mechanical strength and color changes of blend. Application of the PC/ABS blends could be broadened by improving interfacial adhesion between PC and SAN matrix as well as by removing aging problems of the butadiene rubber.

Aging problems in the butadiene rubber could be solved by using acrylonitrile-styrene-acrylic rubber terpolymer (ASA) instead of ABS (Works, 1996). Note that acrylic elastomer, i.e., polybutylacrylate does not contain double bond in its repeat unit. Problems of the interfacial adhesion between PC and SAN matrix of ABS could be also solved by adding proper compatibilizer (Kang et al., 2000; Kim et al., 2001; Works, 1996). Even though it was known that ASA exhibited excellent UV stability, properties of PC/ASA blend such as impact strength at low temperature and tensile elongation were poorer than those of PC/ABS blend. In this study, various ASA terpolymers, in which rubber particles are different in size and shape, were examined to solve problems in the mechanical property of PC/ASA blends.

Compatibilizer was added to PC/ASA blends to enhance...
interfacial adhesion between PC and SAN matrix of ASA. In here, TMPC-b-SAN and PMMA were examined as compatibilizer. In the previous researches (Kim et al., 2001), we have explored TMPC-b-SAN for the compatibilizer of the PC/SAN blend. It was known that TMPC-b-SAN was the most effective in improving interfacial properties of PC/SAN blend when AN content of SAN in block copolymer was the same with that of SAN used in PC/SAN blend. Based on the knowledge related to the miscibility of PMMA with SAN (or PC), commercially available PMMA was also examined as compatibilizer of PC/ASA blend. Note that PMMA is miscible with SAN containing AN from 8 wt% to 33 wt% (Fowler et al., 1987; Suess et al., 1987) and PMMA blend with PC appeared to be right on the edge of miscibility (Kim et al., 1999; Kim and Paul, 1992). If commercially available polymers could be used as a compatibilizer, it could be an effective strategy for commercial success of blend.

2. Materials and procedure

Polymers used in the experiments and their pertinent information were listed in Tables 1. PC, ASA (ASA-1, ASA-2, ASA-3, and ASA-4), SAN, and PMMA were provided by LG Chemicals. TMPC-b-SAN copolymers were synthesized in this laboratory. The detail procedure for the synthesis of TMPC-b-SAN was described elsewhere (Kang et al., 2000; Matsumoto and Kanayama, 1988). PC/SAN blends (or PC/ASA blends) were prepared by melt mixing. PC and SAN (or PC and ASA) were mixed in a torque rheometer (Hanke Rheomix) for 15 min. at 60 rev/min and 240°C. Blends of PC and ASA were also prepared by melt mixing in a twin extruder at 240°C.

Interfacial tension between PC and SAN, or that between PC and SAN containing various amount of compatibilizer, was measured with an imbedded-fiber retraction (IFR) technique (Carriere et al., 1989; Carriere and Cohen, 1991; Cohen and Carriere, 1989; Ellington et al., 1994). Fibers of PC containing various amounts of compatibilizer were produced with an Instron fiber spinning apparatus. SAN copolymer sheets of 0.15 mm thickness containing compatibilizer were also prepared by compression molding at 220°C. PC fibers and SAN plates were dried under vacuum at 170°C and 110°C, respectively, for 24 hours to ensure that no elastic effects related to the fiber orientation occurred. PC fibers were then placed between two sheets of SAN copolymer. The samples were subsequently transferred to a microscope equipped with a hot stage and a temperature controller. The samples were annealed at 180°C for 2 hours prior to observing the fiber retraction process with an image analyzer at 240°C. Note that PC fiber and SAN plate contained the same amount of compatibilizer. The zero shear viscosities (ho) of PC and SAN copolymer were measured by using a Rheometrics dynamic spectrometer (RDS-II, Rheometrics Inc.) over the shear rate range from 10⁻¹ to 10⁻¹ rads⁻¹ under a nitrogen atmosphere at 240°C. Values for ho obtained from the low-frequency plateau viscosities are listed in Table 1.

The mechanical and thermal properties of PC/ASA blends were measured according to the ASTM (American standard testing method). To examine weld-line strength of blends, specimens having the same shape with the tensile test bar and containing weld-line at the center of sample bar were prepared by injecting molding (See Fig. 1). Ten-

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Table 1. Polymers used in this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Copolymer composition</th>
<th>Mw / Mn</th>
<th>Rubber content</th>
<th>Zero shear viscosity (pa·s)</th>
<th>Sources</th>
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<tbody>
<tr>
<td>PC</td>
<td>-</td>
<td>32,400</td>
<td>-</td>
<td>4,990</td>
<td>LG Chemicals (200-15)</td>
</tr>
<tr>
<td>ASA-1</td>
<td>24% AN</td>
<td>-</td>
<td>30 wt%</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>30 wt%</td>
<td>-</td>
<td>LG Chemicals (ASA 927)</td>
</tr>
<tr>
<td>ASA-3</td>
<td>24% AN</td>
<td>-</td>
<td>30 wt%</td>
<td>-</td>
<td>LG Chemicals (ASA 925)</td>
</tr>
<tr>
<td>ASA-4</td>
<td>24% AN</td>
<td>-</td>
<td>30 wt%</td>
<td>-</td>
<td>LG Chemicals (ASA 929)</td>
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<tr>
<td>SAN 24</td>
<td>24% AN</td>
<td>174,500</td>
<td>-</td>
<td>950</td>
<td>LG Chemicals (SAN 80HF)</td>
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<tr>
<td>PMMA</td>
<td>-</td>
<td>103,000</td>
<td>-</td>
<td>-</td>
<td>LG Chemicals (HI 830)</td>
</tr>
<tr>
<td>TMPC-b-SAN</td>
<td>-</td>
<td>108,000</td>
<td>-</td>
<td>-</td>
<td>synthesized</td>
</tr>
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</table>

†Information was provided by supplier.
‡Mw of TMPC = 42,000

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Fig. 1. Specimen for the test of weld-line strength.
sile strength of these sample bars was defined as weld-line strength. Dynamic mechanical properties such as storage modulus and loss modulus (or tan δ) were measured with Dynamic Mechanical Testing Apparatus (DMTA, Polymer Lab.). Blend morphology was observed with scanning electron microscope (SEM, model: JEOL, JSM-840A) and transmission electron microscope (TEM, model: JEOL, JEM-2000EX II). To obtain image contrast for SEM observation PC rich-phase in the blend samples were etched out by immersing in an aqueous solution containing 30 wt% NaOH. Samples were stained with RuO₄ and then microtomed for TEM observation.

3. Results and discussion

3.1. Compatibilization of blend and its weld-line strength

Since acrylic rubber particles in ASA enclosed with grafted SAN on rubber particle or free SAN, PC formed interface with SAN matrix of ASA. It is well recognized that the interactions between PC and SAN copolymers containing various amounts of AN are not favorable enough to produce complete miscibility, although the evidence for varying extents of miscibility has been reported (Callaghan et al., 1993; Cheng et al., 1992; Guest and Daly, 1989; Keitz et al., 1984; Quentens et al., 1991). Among the various PC/SAN blends, it was also known that PC blend with SAN containing about 24 wt% AN (SAN 24) showed optimum interfacial adhesion regardless of blend compositions. Because of this, the experiments reported hereafter were performed SAN 24.

The interfacial tension between PC and SAN 24 as a function of the TMPC-b-SAN content (or PMMA content) was also measured by the imbedded fiber retraction (IFR) technique that was developed as a dynamic method for measuring the interfacial tension between molten, high molecular weight polymers (Carriere et al., 1989; Carriere and Cohen, 1991; Cohen and Carriere, 1989; Ellingson et al., 1994). The changes in the interfacial tension of PC/SAN 24 blend as a function of the compatibilizer content were given in Fig. 2. The interfacial tension decreased very rapidly for compatibilizer content ranging from 0 to 5 phr (parts per hundred resin) and then leveled off. As exhibited in Fig. 2, both compatibilizers, i.e., TMPC-b-SAN and PMMA, were effective in reducing interfacial tension between PC and SAN even though TMPC-b-SAN was more effective than PMMA.

When two cold-fronts meet during injection molding process, weld-line is formed. Since the product formed by the injection molding exhibited poor mechanical strength at around weld-line, enhancement of mechanical strength at weld-line is an important issue for the application of immiscible blend. Specimens shown in Fig. 1 were prepared by injection molding to examine the effects of compatibilizer on the weld-line strength of PC/ASA blend. Weld-line was formed at the center of tensile test bar by injecting polymer melt at both ends. Tensile strength examined with specimen shown in Fig. 1 was defined as weld-line strength. Fig. 3 exhibited weld-line strength of PC/ASA-2 = 6/4 blends containing various amounts of compatibilizer. The weld-line strength of blend continuously increased with increase of compatibilizer content up to 5 phr and then leveled off at a fixed value. Because of this, the experimental results reported hereafter were those...
for blends containing 5 phr compatibilizer. As listed in Table 2, blends (PC/ASA-2 = 6/4) exhibited similar mechanical and thermal properties whether blends contained compatibilizer or not. However, blends exhibited huge difference in weld-line strength. Weld-line strength of blend corresponded to about 35% of its tensile strength when blend did not contain compatibilizer. However, weld-line strength of blend recovered up to 85% of its tensile strength when blend contains 5 phr TMPC-b-SAN as compatibilizer. The result related to weld-line strength indicated that both of TMPC-b-SAN and PMMA could be used as excellent compatibilizer for PC/ASA blends, even though the former was better than the latter as exhibited in Fig. 3. Cross sectional morphology of weld-line was observed with SEM. In here, PC rich-phase was etched out with 30 wt% NaOH aqueous solution. As shown in Fig. 4, changes in morphology also confirmed that compatibility of PC/ASA blend could be enhanced by adding proper compatibilizer.

**3.2. Mechanical properties of PC/ASA blends**

Four different types of ASA terpolymers were blended with PC. Average diameter of the rubber particles in ASA-1 and ASA-2 was the same (0.4 µm), while rubber particles in ASA-1 contained SAN within the rubber phase. Rubber particles in ASA-3 (average diameter of rubber particles: 0.1 µm) and those in ASA-4 (average diameter of rubber particles: 0.6 µm) did not contain SAN within the rubber phase. Blends containing 60 wt% of PC, 40 wt% of ASA, and 5 phr of TMPC-b-SAN (or PMMA) as compatibilizer were prepared and then their mechanical and thermal properties were examined. As listed in Table 3, blends exhibited similar mechanical properties except the impact strength. At around room temperature, impact strength of blends containing ASA-3 (or ASA-4) lower than that of other blends containing ASA-1 (or ASA-2). Blends containing ASA-1 (or ASA-2) exhibited similar impact strength at around room temperature. It means that impact strength of blends at around room temperature was affected by rubber particle size, while it did not depend on whether SAN was included within rubber particles or not. Impact strength of blend at low temperature an important issue for the automobile application. Blend containing ASA-2 exhibited higher impact strength at low temperature (−10°C) than that containing ASA-1, even though these blends exhibited similar impact strength at around room temperature.

### Table 2. Mechanical and thermal properties of PC/ASA =6/4 blends with or without compatibilizer

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>ASTM D638</td>
<td>57</td>
<td>58</td>
<td>58</td>
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<tr>
<td>Tensile elongation (%)</td>
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<td>Flexural modulus (MPa)</td>
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<td>2350</td>
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<tr>
<td>Izod impact strength (25°C, J/m)</td>
<td>ASTM D256</td>
<td>657</td>
<td>686</td>
<td>686</td>
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<tr>
<td>Izod impact strength (−10°C, J/m)</td>
<td>ASTM D256</td>
<td>284</td>
<td>294</td>
<td>284</td>
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<tr>
<td>HDT (1/4&quot;, 265 kg/cm², °C)</td>
<td>ASTM D648</td>
<td>105</td>
<td>106</td>
<td>105</td>
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<tr>
<td>Weld-line strength (MPa)</td>
<td>ASTM D638</td>
<td>20</td>
<td>49</td>
<td>46</td>
</tr>
</tbody>
</table>

1) compatibilizer content of blends: 5 phr.

Fig. 4. Cross sectional morphologies at weld-line; (a) blend does not contain compatibilizer; (b) blend contains 5 phr TMPC-b-SAN copolymer as compatibilizer.
PC/ASA blends having enhanced interfacial and mechanical properties

Table 3. Mechanical and thermal properties of PC/ASA blends

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<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>ASTM D638</td>
<td>59</td>
<td>58</td>
<td>58</td>
<td>57</td>
<td>60</td>
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<tr>
<td>Tensile elongation (%)</td>
<td>ASTM D638</td>
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<td>150</td>
<td>70</td>
<td>155</td>
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<tr>
<td>Flexural strength (MPa)</td>
<td>ASTM D790</td>
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<td>88</td>
<td>87</td>
<td>88</td>
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<tr>
<td>Flexural modulus (MPa)</td>
<td>ASTM D790</td>
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<td>2332</td>
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<td>Izod impact strength (25°C, J/m)</td>
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<td>686</td>
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<td>568</td>
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<td>Izod impact strength (−10°C, J/m)</td>
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<td>294</td>
<td>284</td>
<td>167</td>
<td>196</td>
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<td>HDT (1/4”, 265 kg/cm², °C)</td>
<td>ASTM D648</td>
<td>106</td>
<td>106</td>
<td>105</td>
<td>105</td>
<td>107</td>
</tr>
</tbody>
</table>

1) Blends contain 60 wt% PC, 40 wt% ASA, and 5 phr compatibilizer.

Fig. 5. Dynamic mechanical behavior (tan δ) of PC/ASA-1 and PC/ASA-2 blends.

Fig. 6. Cross sectional morphologies of blends; (a) blend does not contain compatibilizer; (b) blend contains 5 phr PMMA copolymer as compatibilizer.

temperature. To understand the difference in the impact strength at low temperature, glass transition temperatures (T_g) of blend were examined with DMTA. Fig. 5 exhibited tan δ of blends containing ASA-1 and ASA-2. T_g of acrylic elastomer in ASA-1 was −17°C while that of acrylic elastomer in ASA-2 was −34°C. Note that T_g of polybutylacrylate is about −40°C. T_g shift of rubber phase in ASA-2 might come from grafted SAN on the rubber particle, while that of ASA-1 might come from grafted SAN as well as SAN included within rubber particles. The T_g shift of the rubber phase to the high temperature resulted in poor impact strength at low temperature. These results indicated that PC/ASA blend having optimum impact strength might be produced when average diameter of rubber particles that do not contained SAN within rubber phase is about 0.4 μm.

3.3. Changes in blend morphology with compatibilizer

The effects of compatibilizer on the morphology of the blend (PC/ASA = 6/4) were explored with SEM and TEM. Samples were prepared by melt mixing and then compress molded at 240°C. Fig. 6 exhibited microphotographs of blends with (Fig. 6-b) or without (Fig. 6-a) compatibilizer. As shown in Fig. 6, compatibility of blend was enhanced...
by adding TMPC-b-SAN as compatibilizer. Fig. 7 exhibited blend morphology observed with TEM by staining rubber phase and PC-rich phase with RuO$_4$. Since staining speed of SAN-rich phase (bright), PC-rich phase (slightly dark), and rubber phase (dark) is different, contrast among these three phases was obtained with RuO$_4$ staining (Cheng et al., 1992). As shown in Fig. 7, when blends contained TMPC-b-SAN as compatibilizer, SAN rich-phase was well dispersed in PC rich-phase and aggregated rubber particles included within SAN rich-phase.

Morphology of blend prepared by compression molding was similar regardless of the sampling position. However, morphology of blend prepared by injection molding depends on the position. Figs. 8 and 9 exhibited cross sectional morphologies of tensile bar (center of cross section) at two different positions, 1 and 2 in Figs. 8 and 9. Compatibility of blend containing PMMA (or TMPC-b-SAN) as compatibilizer decreased with the distance from the gate. Even though changes in the morphology of blend containing TMPC-b-SAN copolymer was also observed (Fig. 8), dimensional stability of blend containing TMPC-b-SAN was better than that of blend containing PMMA (Fig. 9). Compatibilizer added to blend not only reduced the interfacial tension but also introduced a steric stabilization of the dispersed phase (Paul et al., 1988). The more effective compatibilizer was used, the more stable dispersed phase is formed. Blend containing TMPC-b-SAN as compatibilizer exhibits better dimensional stability than that containing PMMA as compatibilizer. Even though PC/ASA blend containing TMPC-b-SAN as compatibilizer exhibited better interfacial properties than that...
PC/ASA blends having enhanced interfacial and mechanical properties

containing PMMA as compatibilizer, experimental results confirmed that commercially available PMMA could be also used as a promising compatibilizer of PC/ASA blend. As conclusion, PC/ASA blend that satisfied required properties for the application of automotive parts such as automotive grilles and exteriors could be developed by adding proper compatibilizer as well as by controlling morphology of acrylic elastomer and its size.

4. Summary

Blend of PC and ASA having improved mechanical properties and weld-line strength was developed for the automobile application. To enhance the interfacial adhesion between PC and SAN matrix of ASA, two different types of compatibilizers, i.e., TMPC-b-SAN and PMMA were added to PC/ASA blend. Both were effective in improving interfacial properties (or weld-line strength) of PC/ASA blend even though TMPC-b-SAN was more effective than PMMA. Weld-line strength of blend containing TMPC-b-SAN copolymer reached up to 85% of its tensile strength, while weld-line strength of blend that did not contain compatibilizer was 35% of its tensile strength. Except impact strength, mechanical properties of PC/ASA blends examined here were similar regardless of rubber particle size and shape. PC/ASA blend exhibited optimum impact strength when average diameter of rubber particles that do not contain SAN within rubber phase is about 0.4 µm.

Acknowledgement

This study was supported by research grants from the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), an official KOSEF-created engineering research center (ERC) at Korea University, Seoul, Korea.

References


