Effects of Annealing in ABS Ternary Blends

B. K. KIM, L. K. YOON, X.-M. XIE

1 Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, South Korea
2 Department of Chemical Engineering, Tsinghua University, Beijing, China

Received 30 December 1996; accepted 1 March 1997

ABSTRACT: Acrylonitrile–butadiene–styrene terpolymer (ABS)/poly(methyl methacrylate) (PMMA) binary and ABS/PMMA/polycarbonate (PC) ternary blends were prepared using a corotating twin-screw extruder. Blend samples were annealed in a constant-temperature (215 and 225°C) hydraulic press up to 85 min. The changes in morphology and mechanical properties with annealing time were studied with transmission electron microscopy image analyzer, and tensile tester. With the increase in annealing time, the number of dispersed domains per cross-sectional area decreased and average domain size increased; this morphology coarsening became more responsible with time for the deterioration of blend properties. In ABS/PMMA/PC ternary blends, PMMA encapsulated PC in ABS matrix; this was predictable from the spreading coefficient calculation. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci 66: 1531–1542, 1997

Key words: acrylonitrile–butadiene–styrene terpolymer; ternary blends; annealing; morphology

INTRODUCTION

Acrylonitrile–butadiene–styrene terpolymer (ABS) resin is a blend which is generally manufactured from graft polymerization of acrylonitrile and styrene onto polybutadiene latex, followed by blending with poly(styrene-co-acrylonitrile) (SAN). Though ABS is a most successful rubber-toughened thermoplastic, it has certain limitations, such as the lack of flame retardance, poor resistance to ultraviolet (UV) and chemicals, and relatively low thermal stability. These limitations have been resolved to some extent by blending with other resins. These include ABS blends with poly(vinyl chloride) to improve flame resistance; with polycarbonate (PC) to improve heat distortion temperature, UV stability, and toughness; and with nylon to improve chemical resistance and dimensional stability.

Earlier studies on ABS blends with poly(methyl methacrylate) (PMMA) showed that the miscibility of these blends follows that of SAN/PMMA blends, which has a miscibility window depending on the acrylonitrile (AN) content of SAN. At about 7 ≤ AN ≤ 29%, the blend shows lower critical solution temperature behavior; below and above that content, the blend is immiscible. In immiscible blends, the migration of rubber particles into PMMA domains takes a significant role in determining the mechanical properties of the blends. In addition, the stratification of PMMA domains along the flow direction contributes to the improved surface gloss of the blends.

The properties of immiscible blends generally depend on the phase morphology, which is governed by a number of factors including the composition, interfacial tensions, viscosity, and elasticity ratio of the components, and compounding conditions. The mixtures in a twin-screw extruder
are not in their lowest energy states because of the large interfacial areas per volume; an interfacial energy-driven coarsening occurs until the mixture reaches thermodynamic equilibrium, where the total interfacial area is minimum.\textsuperscript{10} The coarsening process can significantly alter the morphology, and hence the properties, of multiphase polymer systems.

Most works regarding the blend morphology focus on the creation of a desired morphology, with few works devoted to the change in morphology with time. In this article we consider the influence of annealing on the phase morphology and mechanical properties of ABS/PMMA binary and ABS/PMMA/PC ternary blends. The AN content of free SAN of ABS was 35\%, which provides immiscibility between ABS and PMMA. Samples were annealed up to 85 min at 215 and 225°C. Coalescence was visualized by transmission electron microscopy (TEM) and quantitatively analyzed using an image analyzer. Changes in mechanical properties were measured as a function of annealing time. Attempts were made to relate the change of mechanical properties with phase coarsening.

**EXPERIMENTAL**

**Materials and Compounding**

ABS resin containing 23\% rubber (SAN-graft-polybutadiene, grafting ratio = 0.36, and the AN content of graft SAN = 30\%) and 77\% matrix SAN ($M_n = 50,000$, $M_w = 85,000$), of 35\% AN content, was kindly donated by Hyosung BASF. Commercial grades of PMMA (IH830; LG Chemicals, Korea) and PC (Trirex 3022IR; Samyang, Korea) as well as ABS were used after drying.\textsuperscript{9,11} Resins were first dry-blended to the desired compositions, followed by melt-mixing using a corotating twin-screw extruder (Berstorff, Germany) at 215–225°C and 180–200 rpm. From the extrudates, dumbbell-type specimens (1 mm thick) were compression-molded using a temperature-controlled hydraulic press at 215°C and 225°C for various periods of time (0, 5, 20, 40, and 85 min). Upon annealing, specimens were quenched in ice water and dried for 6 h at 60°C in an oven.

**Measurements**

Melt viscosities of base polymers were determined from type II Rheometrics Dynamic Spectrometer at 220°C (Fig. 1). PC shows a long Newtonian plateau (a characteristic of narrow molecular-weight distribution) which makes crossovers with ABS and PMMA viscosity functions at around the oscillating frequency $\omega = 4$ and $\omega = 20$ rad/s, respectively. Viscosity functions of ABS and PMMA are very close to each other, being the most favorable condition for dispersive mixing.\textsuperscript{8} Assuming that mixing in a twin-screw extruder corresponds to the shear rate ($\dot{\gamma}$) of about 100–200 L/s,\textsuperscript{12} the viscosity at the compounding condition (assume $\omega \approx \dot{\gamma}$) is in the increasing order of ABS $\approx$ PMMA $<$ PC.

Surface tensions of the base resins were determined from contact angle measurements, and the interfacial tensions were calculated by using the harmonic-mean equation given in eq. (2).\textsuperscript{13} We measured contact angle by dropping distilled water and methylene iodide on the compression-molded surfaces.

Morphology of the blends was observed using TEM (JSM-1200 transmission electron microscope EX II). For TEM measurement, annealed specimens were cut to 100 nm in thickness using a microtome, and the samples were stained with O$_3$O$_4$ for 72 h. Particle size distributions were determined from an image analyzer (Joyce Loebl Magiscan) using the TEM micrographs. A tensile tester (Tinius Olsen Series 1000) was operated at a crosshead speed of 5 mm/min. Tests were made at room temperature, and at least five runs were made to report the average.
RESULTS AND DISCUSSION

Figure 2 shows the TEM micrographs of ABS/PMMA (70/30 by weight) blends, which were annealed at 225°C for various periods of time. Typical island (PMMA)/sea (ABS) morphology was obtained, owing to the composition and squeezing flow in press. It is seen that most of the rubber
particles are retained in SAN due to the greater miscibility of rubbers with SAN than with PMMA. Some large particles migrated to the PMMA phase, or they were interposed at the SAN-PMMA interfaces, the migration driven by the large interfacial areas and elasticity of rubbers. The decrease in the number of the dispersed PMMA domains per unit cross-sectional area and an increase in the average domain size with time is evident. This change in morphology is driven by interfacial energy, which reduces the total interfacial areas of the system. This interfacial area reduction process is commonly called “coarsening,” which can significantly alter the morphology of multiphase polymer blends. When the samples were annealed at lower temperature (215°C) the coarsening process occurred slowly (not shown), since the migration of dispersed domains becomes much easier in less-viscous matrix.

Quantitative analysis of the TEM micrographs appears in Figure 3, where the changes in the number of domains and average domain sizes are ob-
Figure 4  Domain coarsening of ABS/PMMA/PC (7/3/1) blends with annealing time (225°C).
Figure 5  Domain coarsening of ABS/PMMA/PC (7/3/3) blends with annealing time (225°C).
Table I  Surface Tensions of Base Resins and Spreading Coefficient of ABS/PC/PMMA Blends

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\gamma$</th>
<th>$\gamma'$</th>
<th>$x^p$</th>
<th>$\gamma_{12}$</th>
<th>$\gamma_{32}$</th>
<th>$\gamma_{13}$</th>
<th>$\lambda_{31}$</th>
<th>$\lambda_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS (2)$^b$</td>
<td>48.5</td>
<td>26.83</td>
<td>0.447</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC (3)$^{b,c}$</td>
<td>40.8</td>
<td>29.91</td>
<td>0.267</td>
<td>3.736</td>
<td>3.015</td>
<td>0.048</td>
<td>0.673</td>
<td>$-0.769$</td>
</tr>
<tr>
<td>PMMA (1)$^b$</td>
<td>42.48</td>
<td>30.5</td>
<td>0.282</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a x^p = (\gamma - \gamma^p)/\gamma.$

$^b$ Matrix (2); one dispersed component (3); a second component (1). See discussion following eq. (2) in the Results and Discussion section.

$^c$ Value from Wu.13

**Figure 6**  Domain size distribution of ABS/PMMA/PC (7/3/1) blends with annealing time (225°C).
Figure 7  Domain size distribution of ABS/PMMA/PC (7/3/3) blends with annealing time (225°C).

The distribution of domain size became narrower with annealing time. The coarsening process occurs faster at higher temperature. 

Figures 4 and 5 show the time-dependent TEM micrographs of ABS/PMMA/PC ternary blends with different PC contents. It is seen that PMMA phases (the brightest phases) encapsulate PC and form islands in the sea of SAN. This result should come from the differences in interfacial tension among the components. Hobbs and colleagues\textsuperscript{14,15} introduced the concept of spreading coefficient and suggested that the morphologies of a number of multiphase blends be expected from the analy-
\[ \gamma_{ij} = \gamma_i + \gamma_j - \frac{4\gamma_d^i\gamma_d^j}{\gamma_d^i + \gamma_d^j} - \frac{4\gamma_p^i\gamma_p^j}{\gamma_p^i + \gamma_p^j} \]  

(2)

where \( \gamma_i \) and \( \gamma_j \) are the surface tensions; and superscripts \( d \) and \( p \) are its nonpolar and polar components, respectively. We calculated \( \gamma_d^i \) and \( \gamma_p^i \) according to the procedure described by Wu.\(^{13}\) We

Figure 8  Stress–strain behavior of ABS/PMMA (7/3) blends with annealing time: (a) 215°C; (b) 225°C.

Figure 9  Deterioration of tensile properties of the base resins with annealing time (ABS and PMMA annealed at 215°C and PC at 225°C): (a) modulus; (b) strength.
KIM, YOON, AND XIE

The spreading coefficient for PMMA on PC in the SAN matrix is 0.673 and the value for PC on PMMA in the same matrix is −0.769. Therefore, the PMMA phase has a tendency to envelop the PC phase, and these two components do not form dispersed phases separately in the SAN matrix. The result agrees well with our TEM micrographs.

Image analyses of the dispersed domains are shown in Figures 6 and 7. Prior to annealing, the dispersed domain size increases with increasing

defined \( \lambda_{31} \) as the ability of one dispersed component (3) to displace the matrix (2) from the surface of a second component (1). When \( \lambda_{31} \) is positive, component 3 will envelop component 1; but when both \( \lambda_{31} \) and \( \lambda_{13} \) are negative, the dispersed phase will remain separated. Table I shows the spreading coefficients and the surface tensions of base resins which were calculated from the contact angle measurements in the present experiments. The spread-

![Figure 10](image1.png)

**Figure 10** Deterioration of tensile properties of ABS/PMMA (7/3) blends with annealing time: (a) modulus; (b) strength.

![Figure 11](image2.png)

**Figure 11** Stress–strain behavior of ABS(7)/PMMA(3)/PC(x) blends with annealing time at 225°C: (a) \( x = 1 \); (b) \( x = 3 \).
The distribution of the dispersed phase should also make the coalescence easier. The distribution of domain size also becomes narrower with annealing time.

With the increase in dispersed domain size, PC domains also increase in size. The coalescence of encapsulated PC domains seems to occur in two steps, viz., the coalescence of PMMA domains, followed by the coalescence of PC domains within the PMMA domains. The decrease in the number of domains is faster for the dispersed PMMA domains than for the PC domains.

Figure 8 shows the stress–strain curves of ABS/PMMA blends, annealed for various times. The decreases in modulus, strength (yield and break), and elongation at break with annealing time are obvious. At higher temperature (225°C), these properties deteriorate faster. Such deteriorations of blend properties are due to the physical aging of the base resins and to the coalescence of the dispersed phases. To evaluate the relative contributions of the two mechanisms, the tensile properties of base resins were also measured as a function of annealing time. Figures 9 and 10 show the changes in modulus and tensile strength of the base resins and blends as a function of annealing time. It is seen that modulus and strength of the base polymers decrease with time, implying that the deterioration of blend properties is in part due to the aging of base polymers. The decrease is marginal for PC and PMMA, indicative of their high thermal stability, and it is relatively significant for ABS, especially at the early stage of annealing, due perhaps to the softening of rubbers. Modulus of the blend prior to annealing is greater than the simple additivity [dotted line in Fig. 10(a)] due to the migration of rubber particles from SAN to PMMA domains. The migration in ABS-rich blends lowers the rubber level in SAN, and it allows the SAN to exhibit its own mechanical properties. With increasing annealing time, however, the blend modulus decreases rapidly below the additivity, with a crossover in about 20 min of annealing. It seems that the difference between the additivity and blend data is caused mainly by the coarsening of the dispersed domains. Then, as annealing time increases, morphology coarsening becomes the prime cause for the deterioration of blend properties.

Figure 11 shows the stress–strain curves of ABS/PMMA/PC ternary blends. As in ABS/PMMA binary blends, modulus, strength, and elongation at break decrease with time, due in
part to the aging of the base resins but mostly to the morphology coarsening. With the addition and increase of PC content in the blends, modulus and strength (Fig. 12) of the blend increase, especially at long annealing time, which is a contribution of PC to the thermal stability.

One of the authors (B.K.K.) expresses his appreciation to Korea Research Foundation for the financial support of this work in the Program of International Joint Research.

REFERENCES