

Miscible and Immiscible Blends of ABS with PMMA.

I. Morphology and Rheology

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SYNOPSIS

Melt blends of ABS and PMMA were prepared using three types of ABS having different acrylonitrile (AN) content, and PMMAs with different MW. From TEM micrographs, it was found that ABSs containing 24 and 27 wt % AN were miscible, and the one containing 35 wt % AN was immiscible with PMMA. Morphologically miscible blends showed well-defined semicircles in Cole–Cole plots, whereas immiscible ones showed immiscible drifts from the semicircle. In addition, as the compounding temperature increases, the dispersed PMMA phase became stratified, and more rubber particles, especially larger ones, migrated toward the PMMA phase. Miscible blends gave viscosities lower than additivity would predict, whereas immiscible ones gave positive (ABS-rich phase) and negative (PMMA-rich phase) deviations from the additivity. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Acrylonitrile–butadiene–styrene (ABS) resin itself is a multiphase polymer. The graft polymerization of styrene and acrylonitrile (AN) in the presence of polybutadiene (PB) latex, with subsequent blending with styrene-*co*-acrylonitrile (SAN), leads to rubber-toughened thermoplastics, and the resins have been used widely where toughness and good surface appearance is desired.^{1,2}

However, ABS has certain limitations such as lack of flame retardance, poor resistance to UV and ketones, in addition to relatively low use temperature. These limitations have been overcome to some extent by blending with other polymers. The major commercially available systems include ABS/poly(vinylchloride)³ and ABS/polycarbonate.^{4–7}

ABS is very blendable with a number of other polymers including blends with nylon,^{8,9} polypropylene,¹⁰ styrene-*co*-maleic anhydride (SMA) copolymer,¹¹ and with poly(*p*-phenylene tetraphthalamide),¹² leading to molecular composites.

When ABS is added to rather brittle thermoplastics, significant impact toughening is expected. With regard to ABS blends with poly(methylmethacrylate) (PMMA), no contribution concerning the phase behavior, migration of rubber particle (SAN grafted PB) into the PMMA phase, surface, and mechanical properties have so far been reported. Han and Yang¹³ reported the melt properties of the blends. These authors used ABS containing 26.5 wt % AN, and concluded that the blends are rheologically miscible.

It is believed that blends of ABS with PMMA would provide PMMA with impact toughening, and ABS with improved mechanical properties, surface characteristics, UV and flame retardance etc. Moreover, the property change should be strongly related to the phase behavior, morphological texture, and the migration of rubber particles into the PMMA phase.

In Part I, we consider the morphology and rheology of ABS/PMMA blends, and in Part II the mechanical and surface characteristics are investigated. Three types of ABS, with different AN content (24, 27, and 35 wt %) were employed, together with three types of PMMA with different molecular weight (M_w). Since the basic phase behavior of ABS/

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PMMA blends is expected to follow that of SAN/PMMA blends, which shows lower critical solution temperature (LCST) at $9 \leq \text{AN} \leq 29 \text{ wt } \%$,¹⁴ both miscible and immiscible blends are expected from the different ABS resins used.

EXPERIMENTAL

Materials

ABS and PMMA resins, listed in Table I, were provided by Hyosung BASF, Lucky, and Hannam Chemicals. The AN content of matrix SAN of ABS1 is 24, ABS2 is 27, and ABS3 is 35 wt %, respectively. Rubber content and weight average molecular weight (M_w) of the matrix SAN are given in the table. Molecular design of PMMA is relatively simple, i.e., molecular weight (M_w) and molecular weight distribution (M_{wd}) mainly govern the property. M_w and M_{wd} are in the decreasing order of PMMA1 > PMMA2 > PMMA3. Both ABS and PMMA resins received were dried in a forced circulation drying oven at 90°C, 4 h.

Compounding

Dried resins were hand mixed thoroughly at desired compositions, followed by melt mixing using a twin-screw extruder (HBI 90). Most blends were prepared at 222–228°C, and 30 rpm. Others, when the effect of compounding conditions on properties were to be examined, were prepared using different temperature profiles (212–218, or 232–238°C). Extrudates

were quenched in water, and pelletized, followed by injection molding (Battenfield Unilog 400). Injection was done with a temperature profile similar to that for extrusion.

Morphology

Morphology of the blends was measured using a transmission electron microscope (TEM). Tensile specimens were cut to 50 μm in thickness using a microtome, and the samples were stained with OsO_4 for over 1 week.

Rheology

Melt properties were determined from an RDS (Rheometrics Dynamic Spectrometer) using a parallel plate geometry with gap of 1.2 mm. Disks measuring 2.5 (diameter) \times 0.25 cm (thickness) were compression molded. Rate sweeps were done isothermally at 220°C. From the strain sweep, linear viscoelastic behavior was observed up to 15% strain, the level tested throughout the rate sweep.

RESULTS AND DISCUSSION

Morphology

Phase morphologies of the blends are shown in Figures 1–3. TEM micrographs of ABS1/PMMA1 (70/30 wt %) [Fig. 1(a)] show no SAN–PMMA phase separation, and rubber particles, on the order of 2500 Å in diameter, are evenly spread in the space. Several of the rubber particles are exceptionally large. However, the particle size distribution should be regarded as essentially unimodal. It should be mentioned that blends of ABS2 (containing 27 wt % AN) also gave homogeneous SAN–PMMA phase morphology (not shown).

On the contrary, the corresponding TEM micrographs of ABS3/PMMA3 (70/30) [Fig. 1(b)] blends show clean SAN (dark)–PMMA (bright) phase separation. In addition, rubber particles form a bimodal distribution, the larger about 2500 Å, and the smaller 500 Å in diameter. Careful examination indicates that the majority of rubber particles are contained in SAN domains.

The morphology of ABS blends with PMMA is not available in the open literature. ABS is a multiphase polymer system where *g*-ABSs are embedded in the SAN matrix. Grafting of SAN, rather than random copolymerization with butadiene, should lead to enhanced miscibility with SAN matrix.¹⁵

Table I The Characteristics of Base Resins

ABS Resins			
Resins	PB Content in Rubber (wt %)	AN Content of Matrix SAN (wt %)	M_w of Matrix SAN ($\times 10^{-3}$)
ABS1	25.5	24	124
ABS2	28	27	60
ABS3	38	35	80
PMMA Resins			
Resins	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	M_w/M_n
PMMA1	31	66	2.15
PMMA2	35	66	1.85
PMMA3	29.4	61	1.69

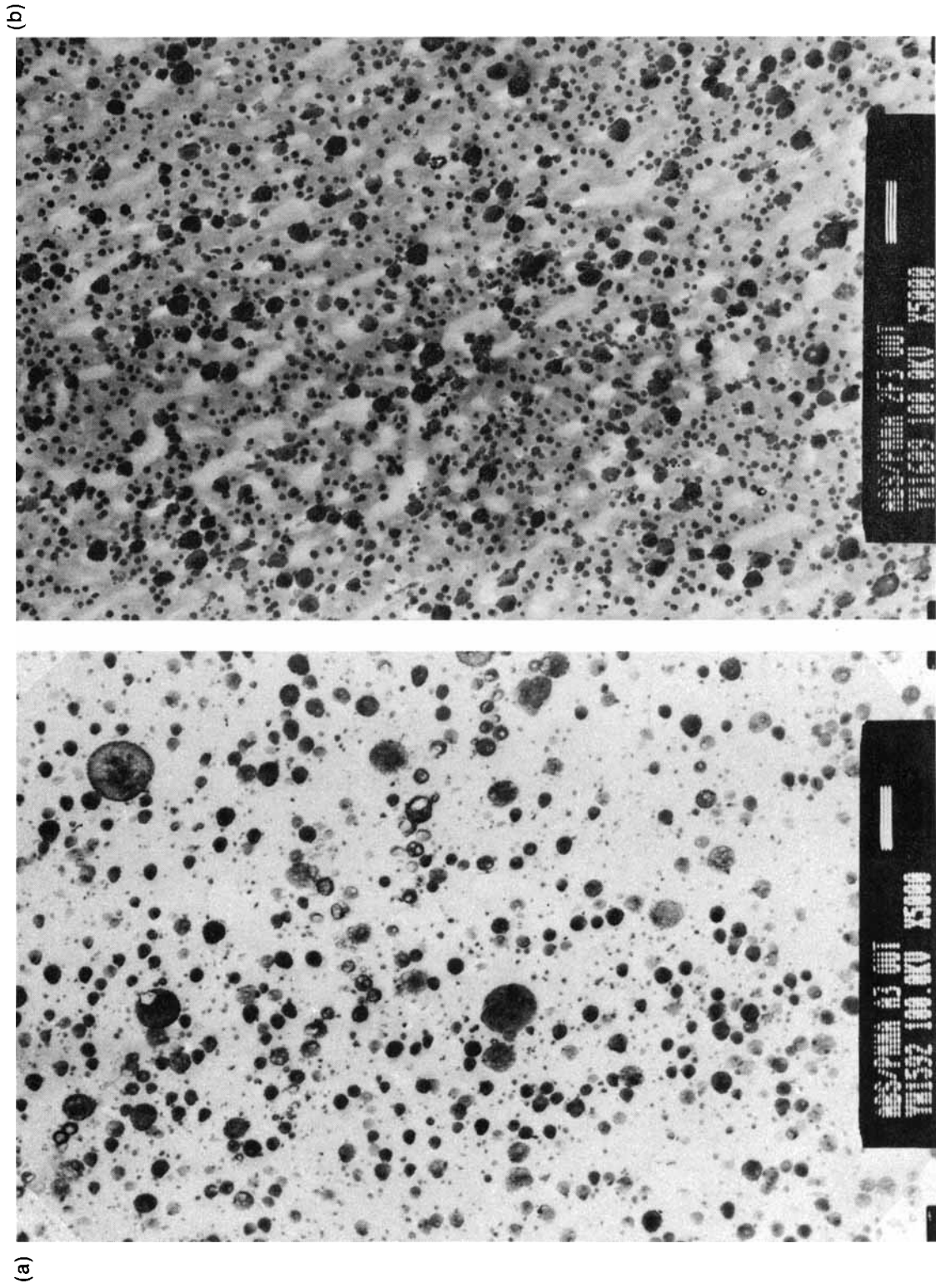


Figure 1 TEM microphotographs of ABS1/PMMA1, ABS3/PMMA3 blends. (a) ABS1/PMMA1 (70/30 wt %), (b) ABS3/PMMA3 (70/30).

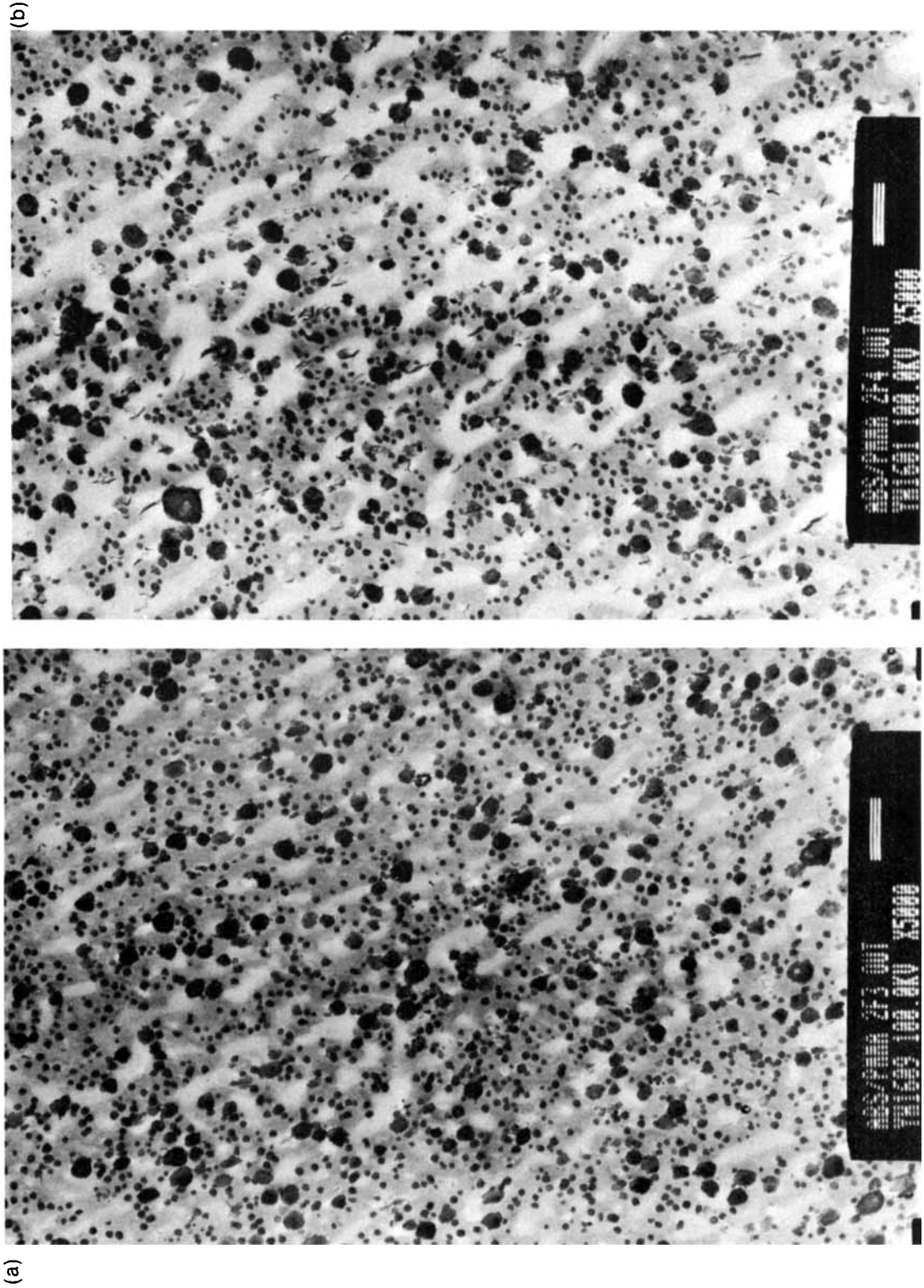


Figure 2 TEM microphotographs of ABS3/PMMA3 blends compounded at 222–228 °C. (a) ABS3/PMMA3 (70/30), (b) ABS3/PMMA3 (60/40), (c) ABS3/PMMA3 (50/50).

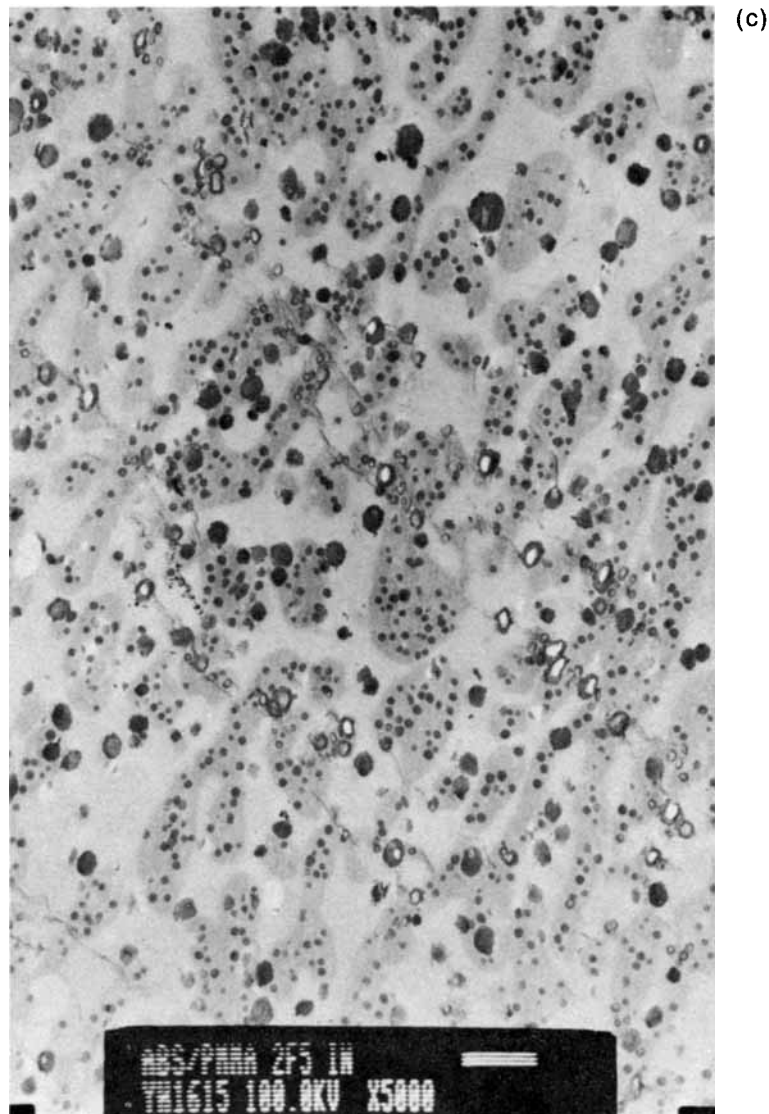


Figure 2 (continued from the previous page)

The miscibility of ABS with PMMA should depend primarily on the miscibility of SAN with PMMA. Though reports¹⁶⁻¹⁷ differ on the copolymer compositions leading to miscibility window and phase separation temperature, SAN/PMMA blends show LCST behavior. Following Paul et al.¹⁴ the miscibility window exists with AN content, 9–29 wt %, at 200–380°C.

The AN content of ABS3 falls outside the miscibility window, whereas that of ABS1 and ABS2 falls inside the window. The compounding temperature was lower than the LCST. It seems that the phase behavior of ABS/PMMA blends follows that of SAN/PMMA blends, and the rubber particles do not exert an effect on the phase behavior.

For the immiscible blends (ABS3/PMMA3), the change of morphology with composition (Fig. 2) and processing temperature (Fig. 3) was studied. At 70/30 (ABS/PMMA) blends, sea (SAN)-island (PMMA) morphology is dominant. It is also noted that most of the rubber particles (especially small ones) are retained in the SAN phase. Some large particles migrate into the PMMA phase. At 60/40, the dominant morphology is cocontinuous; however, there are also some PMMA islands. At 50/50 composition, again the dominant morphology is cocontinuous, but with some SAN islands. It seems that the morphology change with composition is smooth (i.e., an abrupt change from particle to fibril etc. does not occur), and phase inversion (or cocontin-

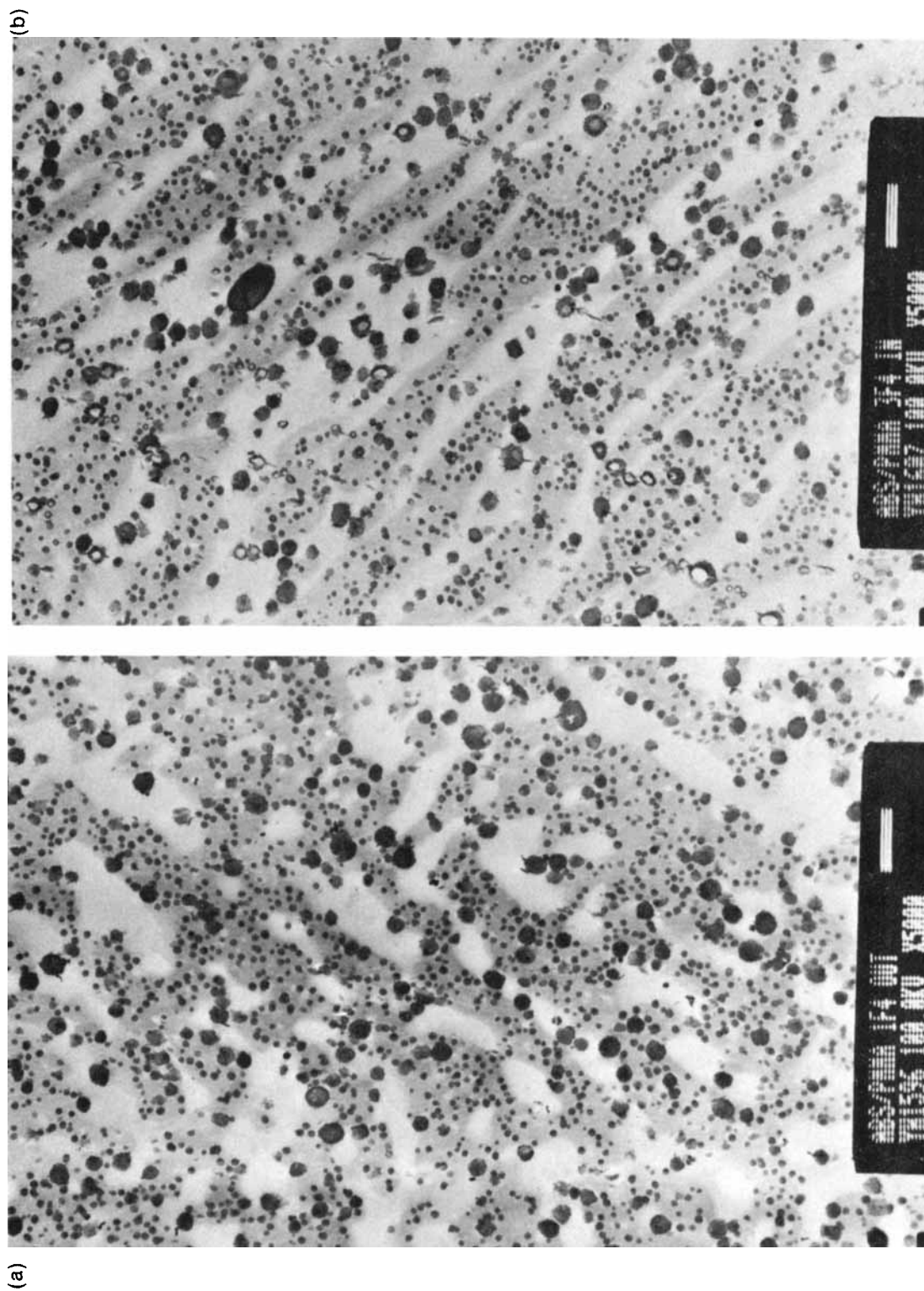


Figure 3 TEM microphotographs of ABS₃/PMMA₃ (60/40) blends, compounded at (a) 212–218°C, (b) 232–238°C.

uity) occurs at 40–50 wt % PMMA. This is in agreement with general criteria for phase inversion,^{18,19} i.e., the lower viscosity component forms a continuous phase at lower weight fraction.

With regard to morphology changes with compounding temperature, at lower compounding temperature [Fig. 3(a)], 212–218°C] the dispersed PMMA phase forms island morphology. As the temperature goes up, PMMA tends to stratify [Fig. 2(b), 222–228°C], and eventually becomes cocontinuous [Fig. 3(b), 232–238°C]. In addition, it is clear that more rubber particles migrate toward the PMMA phase with the increase of temperature. The two phenomena, i.e., stratification and particle migration, should come from the different temperature dependence of melt viscosity and elasticity for the two base resins.^{19,20} That is, the viscosity of PMMA is much more sensitive to temperature than ABS.²¹ Hence, as the temperature increases, the melt viscosity and elasticity of PMMA become lower than the ABS, or more precisely SAN. It is well known in multiphase polymer systems, that as the viscosity of the dispersed phase decreases, stratification of the dispersed phase is more feasible.¹⁹ The same argument may be applied with regard to particle migration.

The migration can also be favored from the reduced interactions between rubber particles and SAN matrix with the increase of temperature. Since the rubber particle is an SAN-graft-PB, strong in-

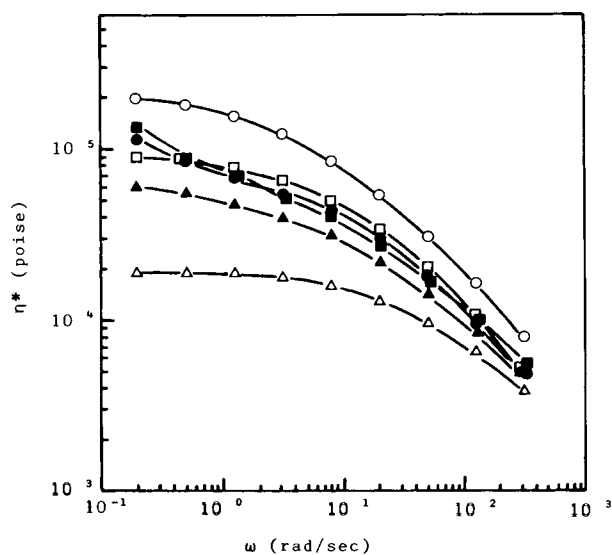


Figure 4 Complex viscosity functions for base resins at 220°C: (■) ABS1, (▲) ABS2, (●) ABS3, (○) PMMA1, (□) PMMA2, (△) PMMA3.

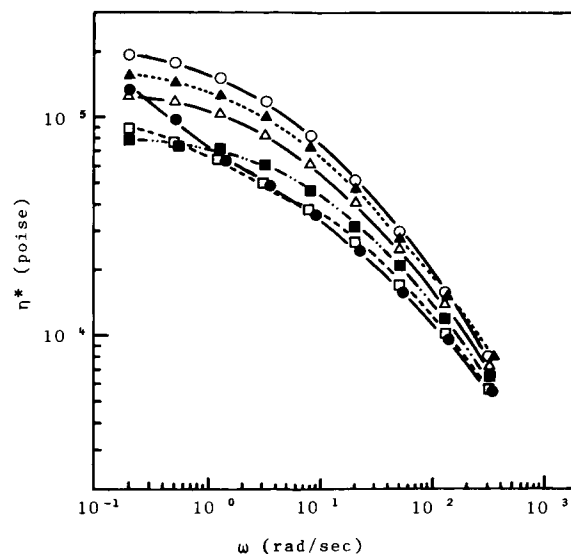


Figure 5 Complex viscosity vs. frequency for ABS1/PMMA1 blends at 220°C: (●) 100/0, (□) 90/10, (■) 70/30, (△) 50/50, (▲) 25/75, (○) 0/100.

terfacial interactions such as hydrogen bondings and dipole interactions are expected between rubber particles and SAN. These interactions should decrease at higher temperatures.

Melt Properties

Figure 4 shows the complex viscosity of the base resins. In immiscible polymer blends, rheology is often the response of morphology.^{20,22} The viscosity functions of ABS3 and ABS1 are similar to each other, with viscosity yield at low frequency. The viscosity of ABS2 is lower than that of the other two. With regard to the PMMA, viscosity decreases along PMMA1 → PMMA2 → PMMA3, over approximately one order of magnitude at low frequency. It is seen that the flow curves of PMMAs follow the molecular parameters described in Table I.

Typical viscosity functions of miscible and immiscible blends (based on the TEM micrograph) are shown in Figures 5–8, together with the viscosity-composition curve at low frequency ($\omega = 0.2$ rad/s) in Figure 9. At low frequencies, viscosity of miscible blends shows a sharp drop (with minima for ABS1/PMMA1 and ABS1/PMMA2 blends), whereas that of immiscible ones shows a sharp increase, especially in the ABS-rich compositions.

In miscible blends of ABS with PMMA, SAN is perfectly mixed with PMMA to form a homogeneous matrix for rubber particles. This should give a di-

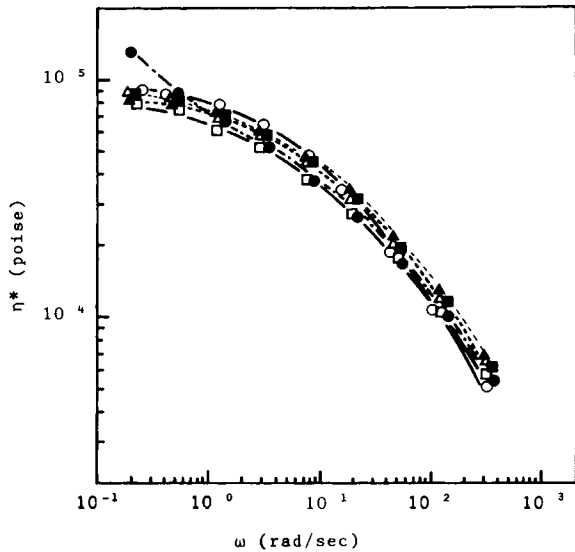


Figure 6 Complex viscosity vs. frequency for ABS1/PMMA2 blends at 220°C: (●) 100/0, (□) 90/10, (■) 70/30, (△) 50/50, (▲) 25/75, (○) 0/100.

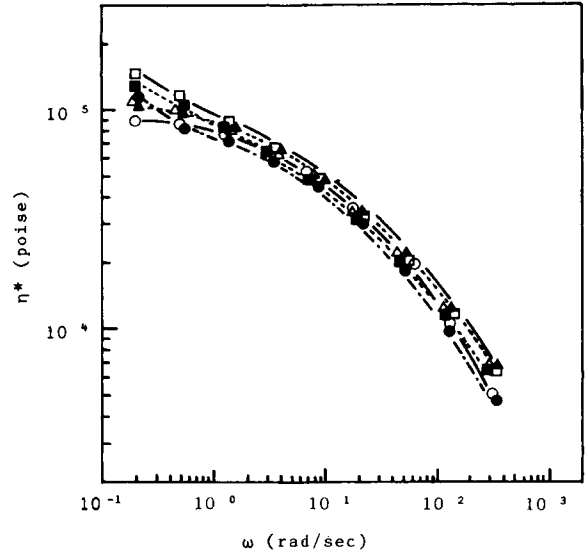


Figure 8 Complex viscosity vs. frequency for ABS3/PMMA2 blends at 220°C: (●) 100/0, (□) 90/10, (■) 70/30, (△) 50/50, (▲) 25/75, (○) 0/100.

lution effect for rubber particles, and the particle concentration would become lower than the critical value for viscosity yield.^{19,23-25}

In immiscible blends, SAN and PMMA form separated domains, and hence added PMMAs do not directly give a dilution effect for rubber particles. Dilution of rubber particles may be caused by the migration of rubber particles toward the PMMA phase. However, the amount of migration is insignificant,

and mainly restricted to the larger particles, which do not significantly affect flow behavior in ABS.²⁶ Therefore, the ABS-rich blends may show again viscosity yield. In addition, the existence of a viscosity maximum may indicate a specific interface adhesion, as first noted from coextruded sheet of ABS and PMMA.¹³ However, as the PMMA content increases, more of the rubber particles migrate into the PMMA phase. This produces a dilution effect

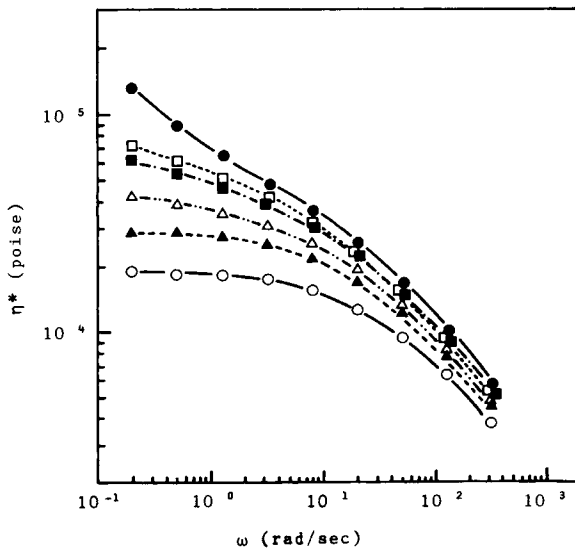


Figure 7 Complex viscosity vs. frequency for ABS1/PMMA3 blends at 220°C: (●) 100/0, (□) 90/10, (■) 70/30, (△) 50/50, (▲) 25/75, (○) 0/100.

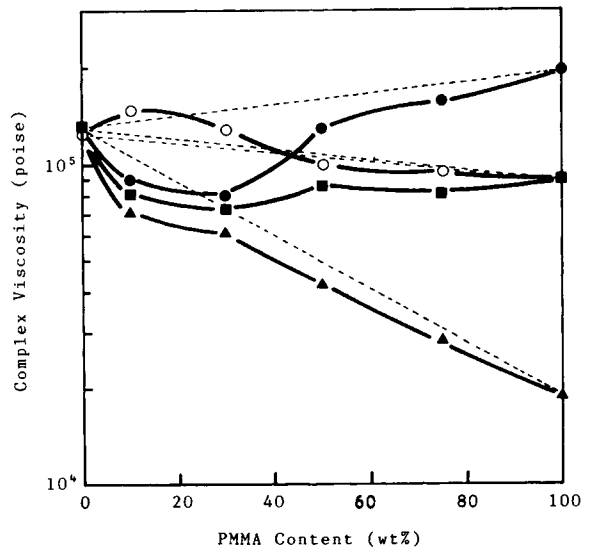


Figure 9 Complex viscosity vs. composition for ABS/PMMA blends at 220°C: (●) ABS1/PMMA1, (■) ABS1/PMMA2, (▲) ABS1/PMMA3, (○) ABS3/PMMA2.

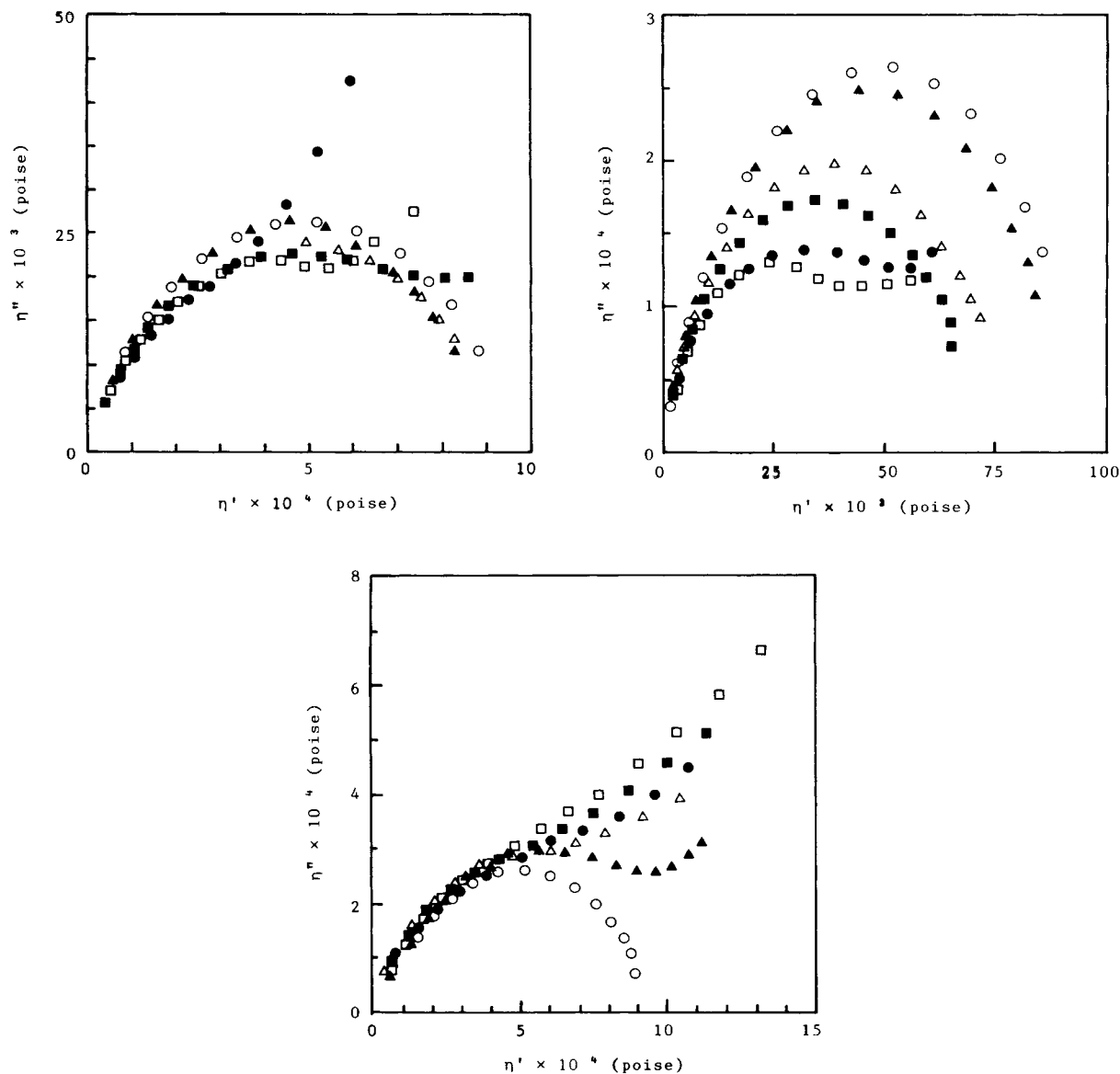


Figure 10 Cole-Cole plot for ABS/PMMA blends at 220°C: (a) ABS1/PMMA2, (b) ABS2/PMMA2, (c) ABS3/PMMA2; (●) 100/0, (□) 90/10, (■) 70/30, (△) 50/50, (▲) 25/75, (○) 0/100.

and the yield behavior disappears. The point of inflection noted at about 40 wt % PMMA (Fig. 9) may correspond to the phase inversion of the blend, as noted in the TEM micrographs.

Figure 10 shows the typical Cole-Cole plots of the blends. The plot is useful in determining the rheological miscibility of the blends.²⁷⁻²⁹ In this plot, a drift from a semicircle often represents immiscibility. The Cole-Cole plots for ABS itself, regardless of the type, shows a drift, indicative of the multiphase nature of ABS. The Cole-Cole plots for ABS3 blends show drift at all composition, again confirm-

ing immiscibility. The plots for ABS1 and ABS2 blends show drifts only in ABS-rich blends due to the particle effect, and they are well-defined semicircles in PMMA-rich blends.

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