ABS/Phenoxy 용융블렌드

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Melt Blends of ABS with Phenoxy

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요 약 : ABS/phenoxy 용융블렌드를 전 조성에 걸쳐 제조하였으며, 주사전자현미경 관찰을 통해 이들 블렌드가 전형적인 비상용계 블렌드의 상분리 구조를 취하고 있음을 확인하였다. 블렌드에서 SAN의 T_g는 거의 일정하였으나 phenoxy의 T_g는 5~8°C 정도 증가하였다. ABS-rich 블렌드에서 인장물성(탄성율, 강도)은 혼합법칙 이상으로 향상되었으나 파단신율 및 내충격성은 현저히 감소하였으며 이러한 현상을 고무입자의 phenoxy상으로의 이동에 기인한 것으로 해석하였다. 용융점도는 ABS-rich 블렌드에서 약간의 항복거동을 보였으나 phenoxy 함량 증가와 더불어 조성에 따라 일률적인 감소를 보였다.

Abstract : ABS/phenoxy blends were prepared over the whole range of composition using a Brabender Plasticorder. Scanning electron micrographs(SEM) showed a typical two phase morphology. Glass transition temperature(T_g) of SAN was almost unchanged in the blends, while Tg of phenoxy increased by 5~8°C in the blends. Synergistic effect of tensile modulus and strength were noted in ABS-rich blends, where a drastic drop of ductility was seen, and the results were interpreted in terms of rubber particle migration into phenoxy phase. Melt viscosity showed yield in ABS-rich blends, and monotonically decreased with increasing phenoxy content.

INTRODUCTION

Acrylonitrile-butadiene-styrene(ABS) is one of the most succesful thermoplastic, which is generally manufactured by the graft polymerization of acrylonitrile(AN) and styrene onto polybutadiene (PB)(SAN-g-PB, or g-ABS), followed by blending with free styrene-co-acrylonitrile(SAN).[1,2] ABS has certain limitation such as lack of flame retardance, poor resistance to UV and ketones, and relatively low use temperature. However, these limitations have been resolved to some extent by blending with other resins. These are blends with PVC(improved flame resistance),[3] polycarbonate (improved heat distortion temperature, UV stabi-

lity, and toughness),[4~7] and with polyamide(improved chemical resistance and dimentional stability).[8]

Phenoxy(poly(hydroxy ether of bisphenol A)) is a tough and ductile thermoplastic with excellent oxygen barrier property, and it forms miscible blends with highly polar materials such as poly (butylene terephthalate),[9,10] polycaprolactone,[11] and poly(ethylene oxide).[12]

To the best knowledge of the present author, the phase behavior of ABS/phenoxy has not been appeared in open literature. These blends are important with regard to performance/cost improvement. This paper considers the morphological, thermal, mechanical, and rheological properties of

ABS/phenoxy blends.

EXPERIMENTAL

Materials and Compounding. Commercial grades of ABS(rubber content=29%, Hyosung BASF) and phenoxy(PKHH, Union Carbide), after drying for 3 days at 80℃ in vacuo were used for blending. Blending was performed using a Brabender plasticorder, L/D=30, rpm=50, and temperature profile of 230, 235, 240, 235℃(die). Specimens for mechanical tests were prepared by injection molding (BOY 22SVV Dipronic), with the same temperature profile as extrusion.

Morphology. Morphology of the blends was observed using a scanning electron microscopy (SEM, JSM820) and transmission electron microscopy(TEM, JSM-1200 EX Ⅱ). SEM micrographs were taken from the cryogenically (in liquid nitrogen) fractured surfaces of injection-molded tensile specimens. The fractured surfaces were sputtered with gold before viewing. For TEM measurments, injection molded tensile specimens were cut into slices with the thickness of 100 nm, and the samples were stained with OsO_4 for 72 hrs.

Thermal Properties. Thermal properties were measured using a DSC(differential scanning calorimeter, Du Pont 9900) following the enthalpy relaxation method.[13~15] Extrudates were sealed in DSC pan using a crimping and welding press(Du Pont). Before aging, samples were kept for 5 min at 180℃, followed by quenching in liquid nitrogen, and aging for 15 days at 75℃. The DSC thermograms were taken from room temperature to 150℃ at a heating rate of 10℃/min.

Mechanical Properties. Tensile properties were determined following the standard procedure described in ASTM D-638 with type Ⅳ specimens. A tensile tester(Tinius Olsen Series 1000) was operated at a crosshead speed of 5mm/min. Tests were made at room temperature, and at least five runs were made to report the average. Impact strength was determined from an Izod impact tester using notched specimen(ASTM D-256).

Rheological Properties. Rheological properties of the blends were measured using a parallel-plate rheometer(Rheometrics Dynamics Spectrometer, RDS Ⅱ).[16~18] Discs measuring 12.5 mm(radius) × 1.2 mm(height) were compression molded, and measurements were carried out isothermally at 220℃ with 15% strain level. The strain level was determined from a strain sweep which gives maximum torque value within the linear viscoelastic limit.

RESULTS ANS DISCUSSION

Morphology. Fig. 1 shows SEM micrographs of ABS/phenoxy blends, where a typical morphology of immiscible blends are shown. The dispersed domain is spherical particle in 90/10, 70/30, and 10/90 blends, and island/sea or dual continuity is obtained in 50/50 and 30/70 blend. It can be seen that most of rubber particles(black spots in the micrograph) are contained in SAN phase, however some of them have also migrated into the phenoxy phase.

Thermal Properties. Fig. 2 shows the glass transition temperature of ABS(SAN) and phenoxy in blend. It is seen that T_g of SAN is virtually unchanged in the blend, while T_g of phenoxy increased by approximately 5~8℃ in the blends. This indicates that ABS(SAN) is preferentially dissolved in phenoxy phase, resulting in the improvement of thermal resistance of phenoxy.

Mechanical Properties. Mechanical properties of the ABS/phenoxy blends are shown in Figs. 3 to 6. Tensile modulus(Fig. 3), determined from the initial slope of stress-strain curve, and tensile strength(Fig. 4) shows positive deviation from additivity, in most of the blend composition, especially in ABS-rich blends. Essentially identical trend was observed with ABS/PMMA blends.[19] Since the present ABS/phenoxy blends are immiscible, the synergistic effect should be related to the migration of rubber particles into phenoxy phase. The migration of rubber particles, in ABS-rich phase, might drive two conflicting effects. It will let the
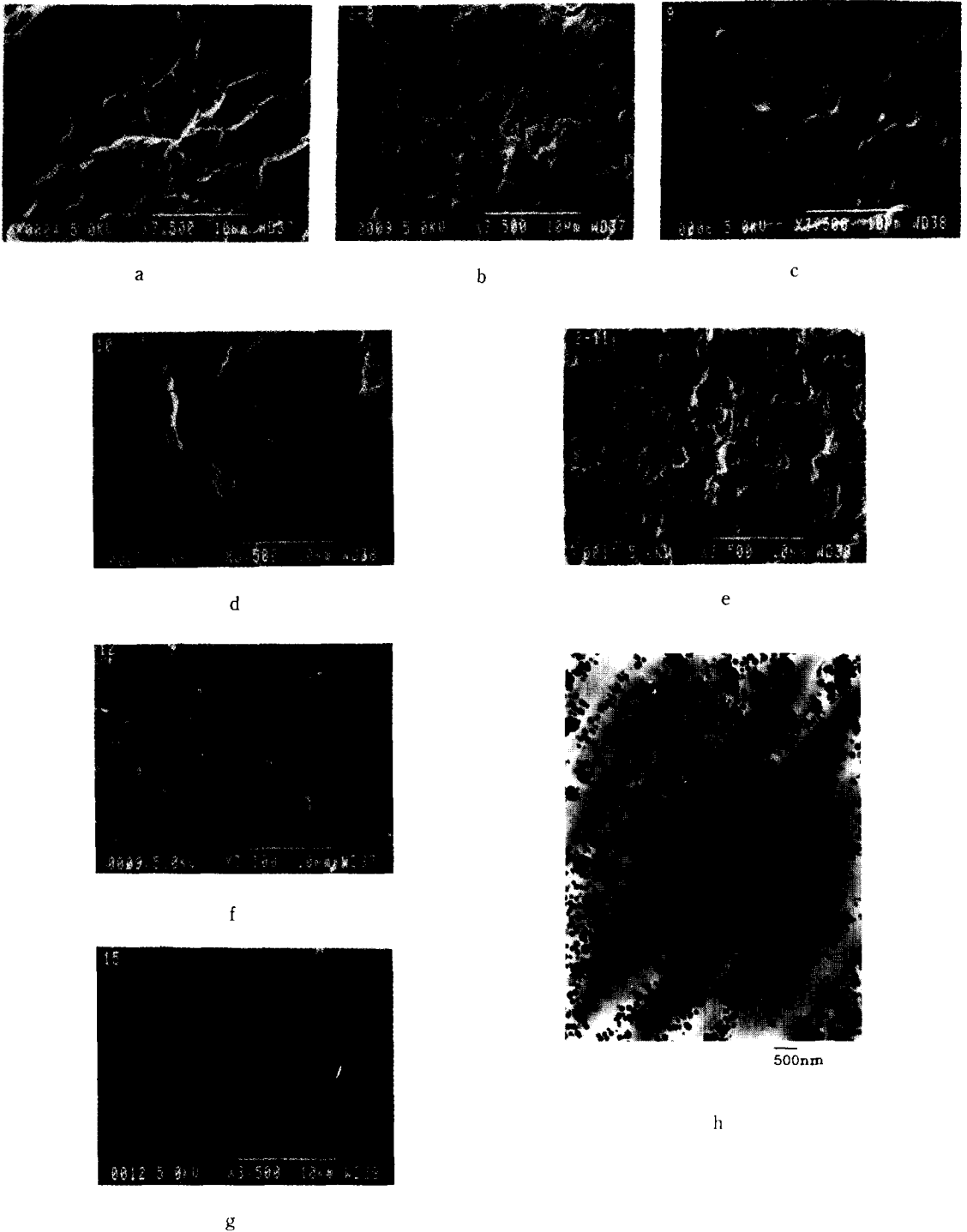
Chi Hoon Choi, Soo Min Lee, and Byung Kyu Kim

a

b

c

d

e

f

500nm

h

g

Fig. 1. SEM micrographs of ABS/phenoxy blends : a : 100/0, b : 90/10, c : 70/30, d : 50/50, e : 30/70, f : 10/90, g : 0/100, h : 70/30(TEM).
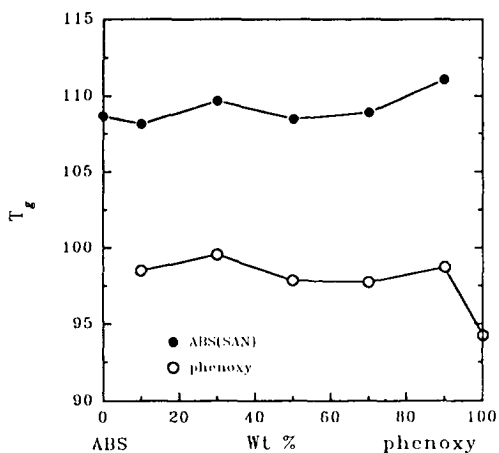
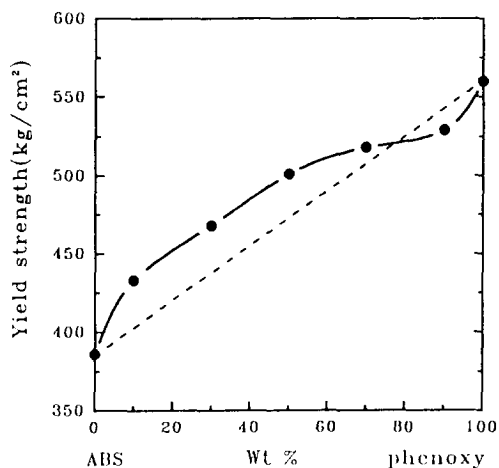**Fig. 2.** Glass transition temperature of ABS/phenoxy blends.

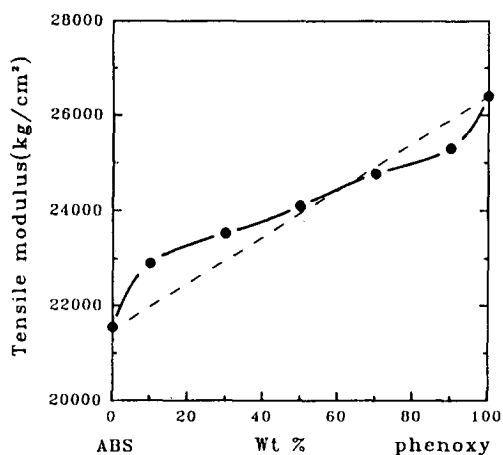**Fig. 4.** Yield strengh of ABS/phenoxy blends.

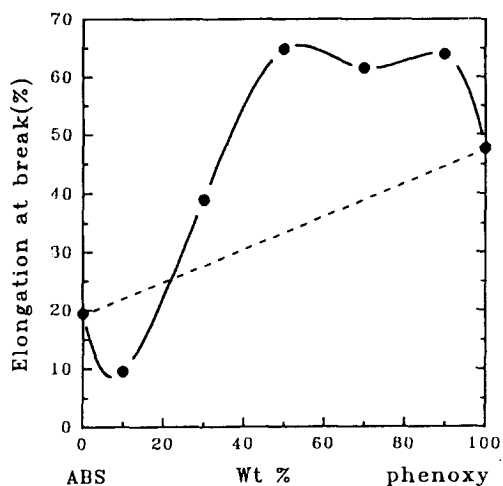**Fig. 3.** Tensile modulus of ABS/phenoxy blends.

Fig. 5. Elongation at break of ABS/phenoxy blends.

SAN exhibit its good mechanical strength due to the lowered rubber level in continuous phase. On the other hand, the ductility of ABS-rich blend will decrease significantly due to the insufficient particle concentration, probably below the brittle-ductile transition level, as seen in Figs. 5 and 6. As expected, the elongation at break(Fig. 5) shows a sharp minimum at 90/10, and a maximum is also obtained in phenoxy-rich blend. Improvements in blend ductility are obtained when dispersed domains are oriented along the direction of the test with high surface area.[20] In a separate experiment,

[21] we noted that the fibrils are much finer and well developed in phenoxy-rich composition of SAN/ phenoxy blends, when the specimens were fractured along the direction of mold flow, and this should contribute to the augmented ductility in phenoxy-rich blends. In addition, the plastic deformation of SAN in phenoxy matrix should also be accounted for the enhanced ductility for 10/90 blend. It has been observed that a small amount of brittle materials added to ductile matrix could augment the ductility above the level of matrix.[13,20] For example, for polycarbonate drastic increase of

ultimate elongation from 21(polycarbonate) to 63 % was reported by adding 10% polymethylmethacrylate to polycarbonate.[13] It is believed that the plastic deformation of brittle particles contributed to this improvement.

Impact strength(Fig. 6) of ABS is dramatically reduced upon adding a small amount(10 wt%) of phenoxy. When the matrix SAN of the present ABS was blended with the phenoxy, impact strength of SAN was slightly increased in the blend. Therefore, drastic drop of ABS impact strength in the blend is due to the migration of rubber particles from continuous SAN phase to dispersed phenoxy phase, resulting in the reduction in the particle concentration in continuous phase below that of brittle-ductile transition.

Rheological Properties. Fig. 7 shows the complex viscosities of the blends as a function of frequency. Viscosity of ABS is several times higher than phenoxy, especially at low frequency. This would yield fine breakup and well developed fibrils when phenoxy formed dispersed phase,[22] as mentioned earlier. Apparently viscosity yield is also seen for ABS-rich blends due mainly to the particle interactions.[19] In ABS, yield is solely due to the agglomeration of rubber particles, and in the ABS-rich blends, phenoxy domains should also contribute to the yield.

Viscosity-composition curve(Fig. 8) is very close to additivity rule(dotted line). This implies that a significant interfacial interactions exist between the ABS and phenoxy phase, otherwise interfacial slip should give viscosity decrease below the additivity.
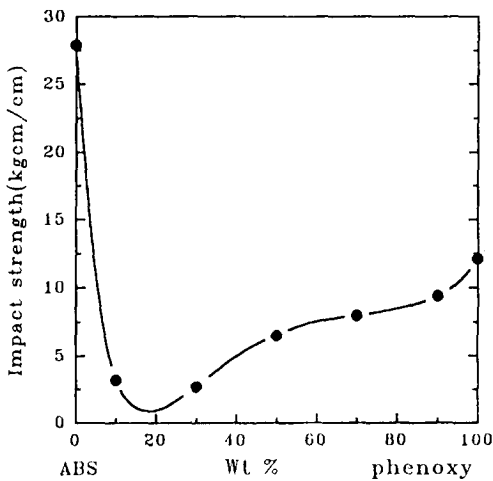

Fig. 7. Complex viscosity of ABS/phenoxy blends at 220℃.

Fig. 6. Notched Izod impact strength of ABS/phenoxy blends at room temperature.
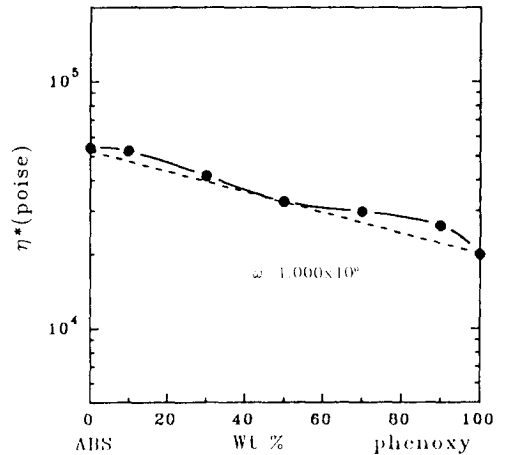

Fig. 8. Complex viscosity vs. composition of ABS/phenoxy blends at 220℃.

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