

고무개질 열가소성 수지의 선형점탄성

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Linear Viscoelastic Properties of Rubber Modified Thermoplastic

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요 약 : SAN(styrene-co-acrylonitrile)과 SAN-graft-polybutadiene(PB)(g-ABS)을 Brabender Plasticorder에서 용융 블렌드 하여, 이들의 용융상태 및 고체 상태에서의 선형점탄성 거동을 RDS rheometer로 측정하였다. SAN에 g-ABS가 첨가됨에 따라 초기점도가 현저히 증가하였으며, 특히 g-ABS \geq 20 wt%에서 항복거동을 나타내었고, 높은 진동주파수 범위에서는 의소성이 뚜렷하게 증가하였다. 또한 SAN/g-ABS 블렌드에서 SAN의 함량이 증가함에 따라 g-ABS의 lower T_g 는 일률적으로 감소하는 경향을, higher T_g 는 다소 증가하는 경향을 보였으며, 이를 SAN 첨가에 따른 g-ABS의 graft SAN-PB 상분리로 해석하였다.

Abstract : Melt blends of SAN(styrene-co-acrylonitrile) with SAN-graft-polybutadiene(PB) rubber were prepared using a Brabender Plasticorder. Melt state as well as solid state linear viscoelastic properties were measured using an RDS rheometer. With rubber addition, melt viscosity increased drastically, with yield at \geq 20 wt% rubber content, together with the increased pseudoplasticity at high frequencies. The lower glass transition temperature(T_g) and the higher T_g of g-ABS were respectively decreased and increased with narrowed transition zone in the blends. This phenomenon was interpreted in terms of graft SAN-PB phase separation.

INTRODUCTION

Modification of thermoplastics by organic and inorganic filler has gained importance in recent years because of the possibility to improve the end-use properties of existing polymers.¹ With re-

gard to rubber modified polymers, the prime objective is toughening, and typical of such system include ethylene-propylene copolymer or ethylene-propylene-diene terpolymer modified polypropylene²⁻⁵ and nylon,⁶⁻⁹ and polybutadiene(PB) type rubber modified styrene-acrylonitrile copolymer

(SAN), which commonly is called ABS (acrylonitrile-butadiene-styrene). In these systems, rubber phase is dispersed in matrix polymer to form multiphase blends.

The rheological behavior of such rubber modified system is important since these polymers have to be processed similarly to the matrix polymer, and the added filler often exerts drastic effect on the melt flow.¹ Melt properties of ABS type polymers have sometimes been reported in the past, with an emphasis on the capillary measurement.¹¹⁻¹³ Following Münstedt,¹ temperature dependence of rubber modified SAN is independent of the kind of rubber and its concentration, and viscosity yield is observed at ≥ 10 wt% rubber.

In spite of the practical significance of ABS rheology in relation to its processing, few has been evolved in the literature. We consider the effect of rubber concentration on the viscoelastic properties of SAN grafted polybutadiene(PB) rubber modified SAN, both in melt and solid state using an RDS.

EXPERIMENTAL

SAN of weight average molecular weight, $M_w = 80,000$ (g/mole) containing 35 wt% AN(acrylonitrile), and g-ABS containing 38 wt% graft SAN based on total g-ABS wt were used for blending. Both of the resins were donated by Hyosung BASF.

Base resins were dried in vacuum at 80°C for 24 hrs, followed by dry blending in desired compositions up to 60 wt% g-ABS in the blends. Melt blends were prepared using a Brabender Plasticoder, with L/D=30, at 212~218°C, the extrudates were quenched, pelletized, and compression molded at 230°C, 200 kg/cm² to prepare disks measuring 1 mm(thickness) × 25 mm(dia) for RDS(Rheometric Dynamic Spectrometer) measurement in melt state. RDS measurements were done with a cone-and-plate fixture, isothermally at 220°C, and 10% strain level. The strain level, within the linear viscoelastic limit, was decided so that the data at low

as well as at high frequency range are stable throughout the rubber content. Temperature sweep from -150(with liquid N₂ purging) to 150°C was made using a stick bar sample, prepared by compression molding, at 2°C/min, 0.2% strain, and 6.28 rad/s.

RESULTS AND DISCUSSIONS

Fig. 1 shows the complex viscosity as a function of frequency (ω). It is seen that the viscosity function of SAN is typical of thermoplastics with narrow molecular weight distribution showing extended Newtonian plateau at low frequencies.^{14,15} On the other hand, the viscosity function of g-ABS is a typical of elastomer, i.e. nearly a straight line in log-log plot. It is demonstrated that the viscosity increases with g-ABS addition, with yield behavior at ≥ 20 wt% g-ABS. Viscosity rise is more pronounced at low frequencies than at high frequencies.¹ The yield behavior is again demonstrated in Fig. 2, where the complex viscosity is plotted against the complex shear stress, calculated from $\tau^* = \eta^* \times \omega$.

At high frequency, say $\omega \geq 10$ (rad/s), the viscosity functions (Fig. 1) have straight line segment regardless of composition, and the slope(n

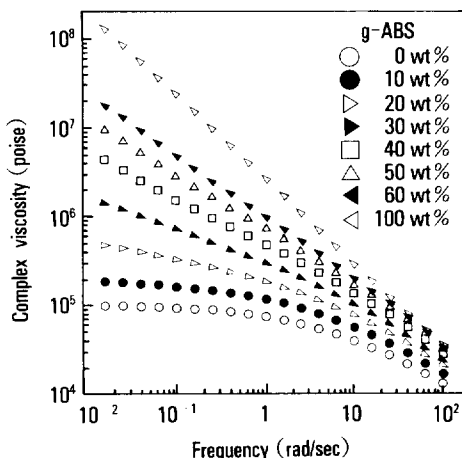


Fig. 1. Complex viscosity vs. frequency of SAN-g-PB/SAN blends at 220°C.

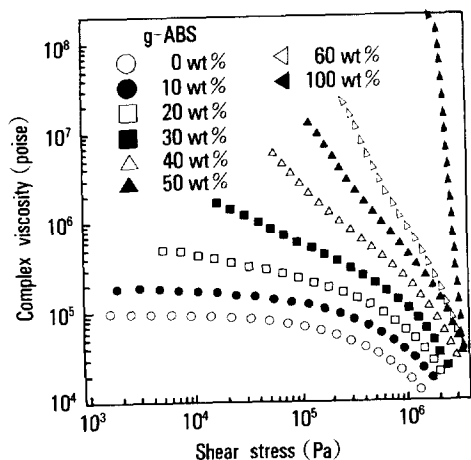


Fig. 2. Complex viscosity vs. complex shear stress of SAN-g-PB/SAN blends at 220°C.

-1) in power-law model) increases with g-ABS loading, indicating increased pseudoplasticity.¹⁴ Drastic increase of viscosity at low frequency, and increased pseudoplasticity at high frequency respectively pose problem in processing.¹⁶ The former gives difficulty in startup operation and the latter may induce, for example in tubular flow, blunter velocity profile and eventually plug flow at high shear rate or stress.

Fig. 3 summarizes viscosity-composition relationship at three different level of frequency. In immiscible polymer blends, viscosity-composition curve is often closely related to their morphology, especially at low rate of shear.^{15,17} At low shear rate, the deformation is mainly viscous one and represents interparticle interactions. With strong particle-particle interactions positive deviation of viscosity over the additivity rule is often observed. The present results show positive deviation throughout the frequencies. At low frequency ($\omega = 10^{-2}$ rad/s), the data points lie on the additive line up to 10 wt% g-ABS, beyond which they lie above the line. This should indicate increased particle interactions with more addition of g-ABS.

With regard to viscosity buildup, couple of model, other than the Einstein type equation or hydrodynamic volume model, have been suggested by M \ddot{u} nstedt.¹ His model is based on structure build-

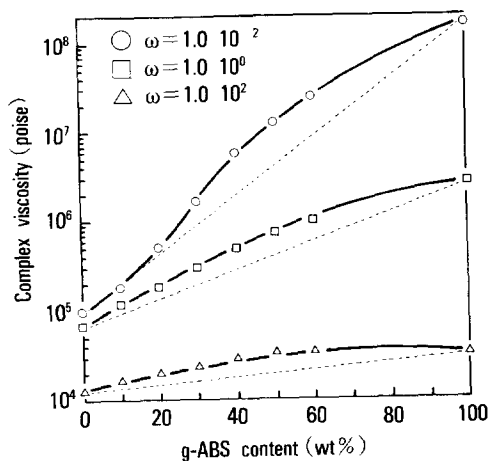


Fig. 3. Complex viscosity vs. composition of SAN-g-PB/SAN blends at 220°C.

dup, where either larger particles form the wall of cell in which matrix polymer are contained, or bridging of rubber molecules. The latter model assumed the core-shell morphology of rubber in SAN, with the rubber obtained from grafting of SAN onto PB. However, question remains whether the binding force between rubber particles in one case, and the grafted molecular layers in the other are strong enough to account for the yield stress occurring.

Figs. 4 and 5 show η' (dynamic viscosity) and η'' (loss part of η^*) as a function of ω . Note that the magnitude of η^* is defined as $|\eta^*| = (\eta'^2 + \eta''^2)^{1/2}$, where η' and η'' respectively correspond to viscosity and fluid elasticity within the linear viscoelastic limit. Therefore η' and η'' are related to G' (storage modulus) and loss modulus (G'') by $G' = \omega \eta''$ and $G'' = \omega \eta'$. G' and G'' as a function of ω are plotted in Figs. 6 and 7.

An interesting feature is seen in $\eta' - \omega$ (or $G'' - \omega$) plot, where η' (or G'') of g-ABS crosses over the others including SAN. At low frequencies, η' (G'') of g-ABS is larger than SAN, and at higher frequencies, the magnitude is reversed. On the other hand, the elasticity (η'' or G') of g-ABS is greater than the SAN throughout the frequencies tested. This implies, though not verified in this experiment, that the rubber would migrate toward the

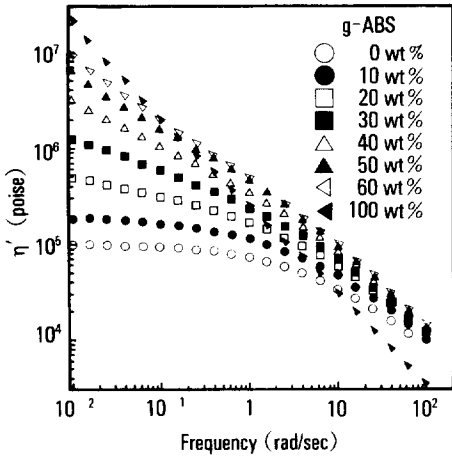


Fig. 4. Dynamic viscosity vs. frequency of SAN-g-PB/SAN blends at 220°C.

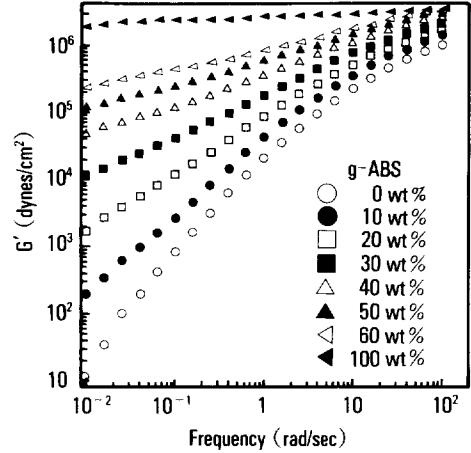


Fig. 6. Storage modulus vs. frequency of SAN-g-PB/SAN blends at 220°C.

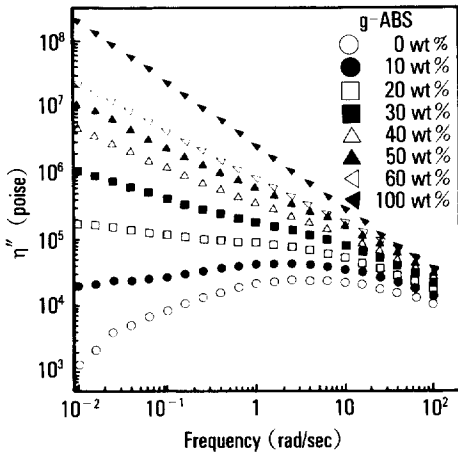


Fig. 5. Loss part of complex viscosity vs. frequency of SAN-g-PB/SAN blends at 220°C.

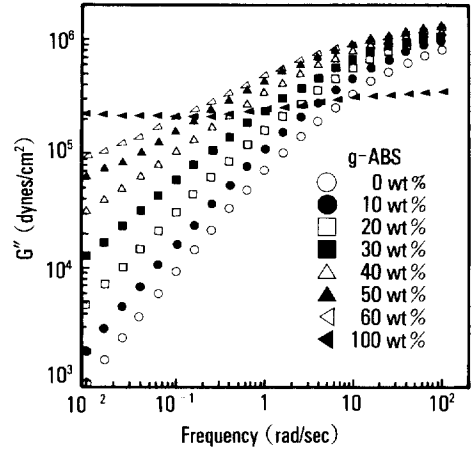


Fig. 7. Loss modulus vs. frequency of SAN-g-PB/SAN blends at 220°C.

wall or center depending on the geometry.^{12,17} In general, lower viscosity, and higher elasticity component migrates toward the wall in tubular flows.^{17,18} In addition, when the elasticity of dispersed phase exceeds that of matrix, fluid elasticity acts to increase the interfacial tension, and inclusion of matrix phase in the dispersed domain is not feasible.^{19,20}

With the g-ABS viscosity lower than the SAN at high frequency (resembling compounding condition), viscosity rise over the additivity should mai-

nly come from the particle interactions.¹⁷

The increase of elasticity (G') with g-ABS addition is seen in Fig. 8, where G' is plotted against G'' . In such plot, temperature effect is virtually neglected and a temperature independent master curve is obtained. It is seen that the deformation of SAN is viscous than elastic except at high frequencies, whereas that of g-ABS is significantly elastic one. Elasticity increase with g-ABS in blends should again come from the particle effect, but not from morphology change.

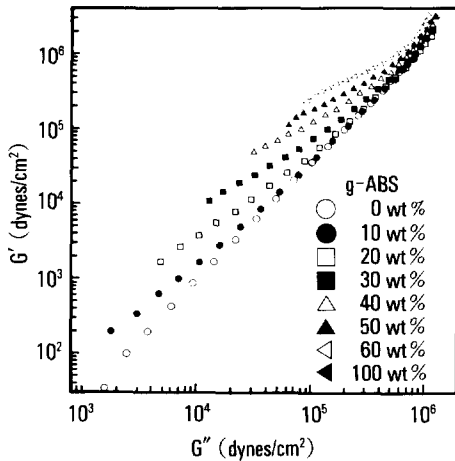


Fig. 8. Storage modulus vs. loss modulus of SAN-g-PB/SAN blends at 220°C.

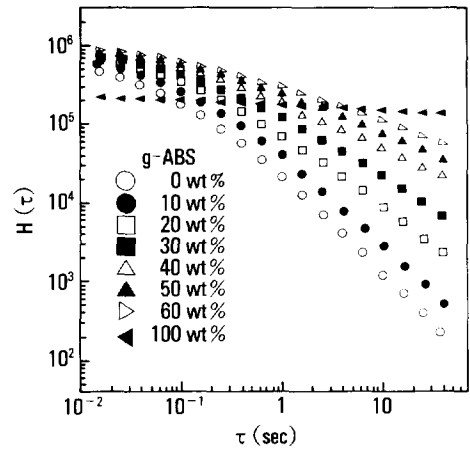


Fig. 9. Relaxation spectrum of the blends of SAN-g-PB/SAN blends at 220°C.

Fig. 9 shows the relaxation spectrum of the blends, prepared following the Ninomiya-Ferry's first order approximation.^{21,22} With the addition of g-ABS, the relaxation of the blends extends longer time, as expected, and longer cycle time in injection molding is dictated.

The transitions behavior of the blends was studied from temperature sweep in RDS. It is expected that g-ABS shows two major dispersions, one for PB chain relaxation at low, and the other for graft SAN relaxation at high temperature. These are found at -79.4 and 117°C, respectively (Figs. 10 and 11). On the contrary, SAN(matrix) shows one major relaxation at 119°C. It is seen that, with the addition of free SAN to g-ABS, the lower T_g of g-ABS moves toward the lower temperature -79.4 (g-ABS) → -85.1°C (g-ABS 10/SAN 90). Though not in monotonic order, the higher T_g of g-ABS also increases in the blends. This should indicate graft SAN-PB phase separation of g-ABS, with the addition of free SAN. It is natural to expect that the grafted SAN of g-ABS is miscible with the free SAN, and hence in blend the graft SAN will form the outer layer of rubber particle to form one single phase with free SAN, with the exclusion of PB phase into a separate one. The sign of phase separation is also seen from the narrowed tempe-

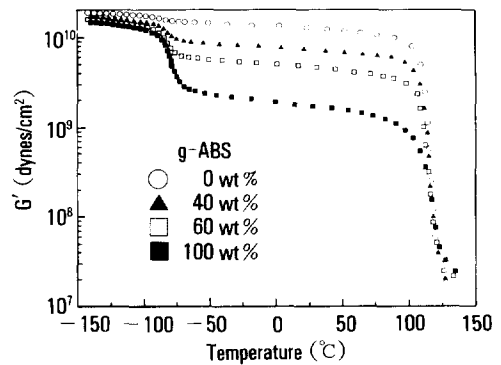


Fig. 10. Storage modulus vs. temperature of SAN-g-PB/SAN blends.

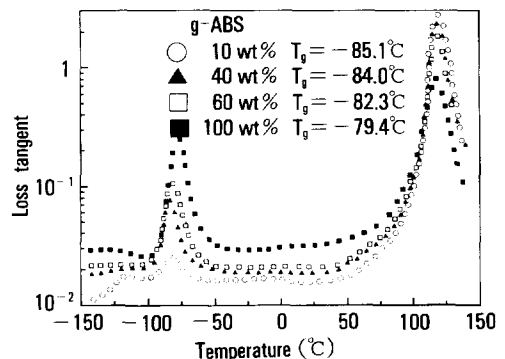


Fig. 11. Loss tangent vs. temperature of SAN-g-PB/SAN blends at 220°C.

perature range for transition,²³ especially for lower T_g region. With the microphase separation of graft, block, or segmented polymers, more distinct T_g of each phase will appear.^{2,23} More generally in blends, when there are interactions between the component polymers, T_g 's of the two component approach to the other, and when they are phase separated, each T_g will show up independently. With the microphase separation, T_g of PB(lower T_g) will decrease, and that of grafted SAN will increase as far as the third component forming miscible blend with graft SAN has T_g higher than that of PB.

Essentially identical phenomenon was observed from segmented polyurethane(PU) blends with sulfonated polystyrene(PS).²⁴ PU as it alone was not phase separated, however, with the addition of sulfonated PS, blends of sulfonated PS with the hard segment of PU in one phase, with the exclusion of soft segment into a separate phase was observed. The results were to lower the soft segment T_g and to increase the hard segment T_g .

In g-ABS/SAN blends, the reason that the T_g of grafted SAN(higher T_g) does not increase monotonically with the addition of free SAN(though increased in blends) may be because the third component added was SAN(not significantly different in T_g with grafted SAN), or the fraction of graft SAN in g-ABS(38 wt%) is insufficient, or more likely due to the both.

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