

Rheological Behavior of Blends of Poly(methyl Methacrylate) (PMMA) and Poly(acrylonitrile-*stat*-Styrene)-*graft*-Polybutadiene (ABS)

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Synopsis

The rheological behavior of blends of poly(methyl methacrylate) (PMMA) and poly(acrylonitrile-*stat*-styrene)-*graft*-polybutadiene (ABS) was investigated using a cone-and-plate rheometer. The rheological properties measured were shear stress (σ_{12}), viscosity (η), and first normal stress difference (N_1) as functions of shear rate ($\dot{\gamma}$) in steady shearing flow, and storage modulus (G') and loss modulus (G'') as functions of frequency (ω) in oscillatory shearing flow. It has been found that the rheological behavior of blends of ABS and PMMA was very similar to that of blends of poly(styrene-*stat*-acrylonitrile) (SAN) and PMMA, in that N_1 in logarithmic plots of N_1 versus σ_{12} , and G' in logarithmic plots of G' versus G'' , vary regularly with blend composition. This has led us to conclude that the rubber particles that are grafted on an SAN resinous matrix in ABS resin plays only a minor role in influencing the compatibility of ABS/PMMA blends, and that the SAN chains attached to the surface of rubber particles, and the SAN matrix phase, play a major role in compatibilizing ABS resin with PMMA.

INTRODUCTION

Poly(acrylonitrile-*stat*-styrene)-*graft*-polybutadiene (ABS) may be regarded as one of the most successful engineering thermoplastic resins that have been used extensively in many industrial applications. ABS resin is prepared either by a mechanical blending of poly(styrene-*stat*-acrylonitrile) (SAN) and poly(acrylonitrile-*stat*-butadiene) (ANB) or by polymerizing acrylonitrile and styrene in the presence of polybutadiene latex.¹ ABS resin prepared in this way consists of polybutadiene, polybutadiene grafted with acrylonitrile and styrene, and SAN. Because ABS resin has very good impact properties, serious attempts have been made in industry in recent years to blend it with other thermoplastic resins that are rather brittle. One such example is blends of ABS and polycarbonate (PC), which are commercially available. Very recently, some investigators^{2,3} have published the mechanical properties of blends of ABS and PC.

It should be pointed out that ABS resin may be considered as a multiphase polymer. As described in the monographs by Han,^{4,5} the rheological behavior of multiphase polymer systems in the molten state depends very much on the morphological state of the individual components, which in turn depends, among other factors, on the molecular weight (hence rheological properties) of the constituent components, the size, shape, distribution, and relative de-

formability of the dispersed phase, and the nature and extent of adhesion between the phases.

In the past, extensive research activities have been reported in the literature dealing with the rheological behavior of ABS resin.⁶⁻¹⁵ It has been found that the rheological properties of ABS resin depend on the rubber content, particle size and its distribution, the state of dispersion of rubber particles, the degree of grafting, and the molecular weight, as well as molecular weight distribution, of SAN matrix.^{12,13} Depending on the rubber content and the size of rubber particles, yield stress has been observed with a certain grade of ABS resin.^{8,13,14} However, little has been published in the literature about the rheological behavior of blends of ABS resin and other thermoplastic resins.

Very recently, we have coextruded ABS with poly(methyl methacrylate) (PMMA) using a multimanifold sheet-forming die, and found that the coextruded sheets of the ABS/PMMA system had unusually strong adhesion at the interface between the layers.¹⁶ This experimental observation has raised fundamental questions concerning the origin(s) of the strong interface adhesion, and has prompted us to investigate the rheological behavior of blends of ABS and PMMA. In this paper we report the results of our investigation.

EXPERIMENTAL

The polymers used are commercial grades of ABS (ABS 213, Dow Chemical) and PMMA (Plexiglas 920, Rohm and Haas). The acrylonitrile (AN) content in ABS was determined by element analysis and found to be 26.5 wt%. The following blend ratios by weight were chosen: (a) 80/20 ABS/PMMA, 60/40 ABS/PMMA, 40/60 ABS/PMMA, and 20/80 ABS/PMMA. These blends were prepared using a twin-screw compounding machine (ZSK-30, Werner & Pfleiderer).

A cone-and-plate rheometer (a Weissenberg Model R-16 Rheogoniometer) was used to measure (1) the steady shearing flow properties, viscosity (η), shear stress (σ_{12}), and first normal stress difference (N_1), as functions of shear rate ($\dot{\gamma}$); (2) the oscillatory shearing flow properties, storage modulus (G'), and loss modulus (G''), as functions of frequency (ω). These quantities were determined using the expressions described in the literature.^{17,18} Rheological measurements were taken at 200°C and 220°C.

RESULTS AND DISCUSSION

Figure 1 gives logarithmic plots of η versus σ_{12} for the ABS/PMMA blend system at 220°C. Similar results were obtained at 200°C, but due to limitations of space we shall not present them here. It is seen in Figure 1 that, over the range of shear stresses investigated, the ABS resin exhibits strong shear-thinning behavior while the PMMA exhibits virtually Newtonian behavior. Furthermore, as the amount of PMMA is increased in the blend, the shear-thinning behavior of the blend becomes less intense. Note that the ABS resin exhibits yield stress. Similar observations were reported earlier by other investigators.^{8,13,14} It should be remembered that ABS resin has a complex morphology and, therefore, its rheological properties are influenced by, among other factors, the particle size and its distribution, acrylonitrile (AN) content

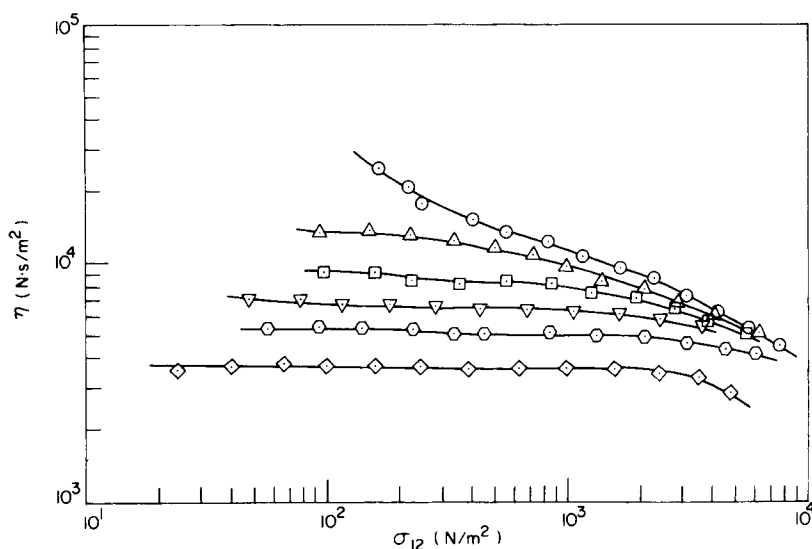


Fig. 1. Logarithmic plots of η versus σ_{12} for the ABS/PMMA blend system at 220°C. (○) ABS; (△) ABS/PMMA = 80/20; (□) ABS/PMMA = 60/40; (▽) ABS/PMMA = 40/60; (◇) ABS/PMMA = 20/80; (◇) PMMA.

in grafted SAN, and the state of dispersion of rubber particles. Zosel⁹ and Munstedt¹⁴ have studied the effect of particle size on the rheological behavior of ABS resins. Aoki^{13,15} has noted that yield stress was observed when ABS resin contained nonuniform-sized rubber particles, and a large number of them, giving rise to strong interactions between them.

It is seen in Figure 1 that the yield stress of ABS/PMMA blends decreases with increasing PMMA content. The numerical values of the yield stress, determined as a function of blend composition, are given in Table I. Note in Table I that the yield stress decreases with increasing temperature. The trend of decreasing yield stress with increasing PMMA content may be interpreted as being due to the addition of PMMA to ABS decreasing the distance between the neighboring rubber particles in the ABS resin, thus weakening the interactions between them. Note further that the viscosity of ABS resin is decreased gradually, approaching the viscosity of PMMA, as the amount of PMMA is increased in the blend. This would have been possible only when the PMMA added acted as a diluent to the ABS. If blends of ABS and PMMA

TABLE I
Numerical Values of Yield Stress for the ABS/PMMA Blend System

Material	Yield stress at 200°C (N/m^2)	Yield stress at 220°C (N/m^2)
ABS/PMMA = 100/0	125	60
ABS/PMMA = 80/20	55	20
ABS/PMMA = 60/40	34	7
ABS/PMMA = 40/60	18	4
ABS/PMMA = 20/80	4	2
ABS/PMMA = 0/100	0	0

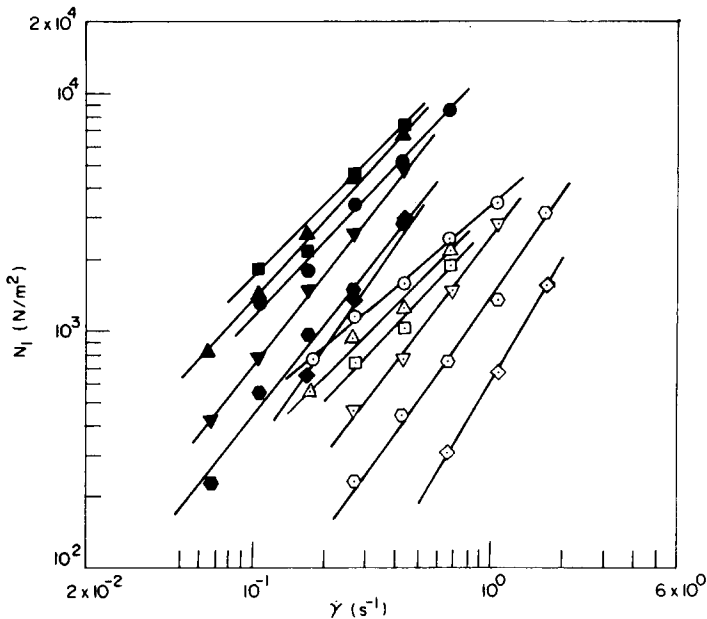


Fig. 2. Logarithmic plots of N_1 versus $\dot{\gamma}$ for the ABS/PMMA blend system at 220°C. (●, ○) ABS; (▲, △) ABS/PMMA = 80/20; (■, □) ABS/PMMA = 60/40; (▼, ▽) ABS/PMMA = 40/60; (●, ○) ABS/PMMA = 20/80; (◆, ◇) PMMA. Closed symbols are for 200°C and open symbols for 220°C.

formed two phases, such a *regular* behavior in the reduction of yield stress might not have been observed.

Figure 2 gives logarithmic plots of N_1 versus $\dot{\gamma}$ for the ABS/PMMA blends at 200°C and 220°C. It is seen that at 200°C values of N_1 of some blend compositions are greater than those of the constituent components, ABS and PMMA, but at 220°C values of N_1 decrease regularly with increasing PMMA content in the blend. One may be tempted to conclude from this observation that the melt elasticity of ABS/PMMA blends varies with temperature.

However, the use of logarithmic plots of N_1 versus σ_{12} should discourage drawing such a hasty conclusion, since as may be seen in Figure 3, the temperature dependence of N_1 is virtually eliminated in such plots, consistent with previous investigations.¹⁹⁻²⁶ Data at other temperatures for some blend compositions are not shown in Figure 3, in order to preserve clarity. It is of great interest to observe (Fig. 3) that values of N_1 decrease in a regular fashion as the amount of PMMA in the blend is increased. This *regular* behavior is observed always when a blend system is compatible, as demonstrated in our previous publications dealing with PMMA/PVDF blends,²⁷ SAN/PCL blends,²⁸ and SAN/PMMA blends.²⁹ It can, therefore, be concluded that ABS/PMMA blends may be considered to be compatible, at least from the rheological point of view.

Note that ABS resin may be considered as a blend consisting of SAN matrix phase and rubber particles on which SAN is grafted. Note further that grafted rubber particles are embedded in an SAN resinous matrix and that SAN chains are attached primarily to the surface of the rubber particles.

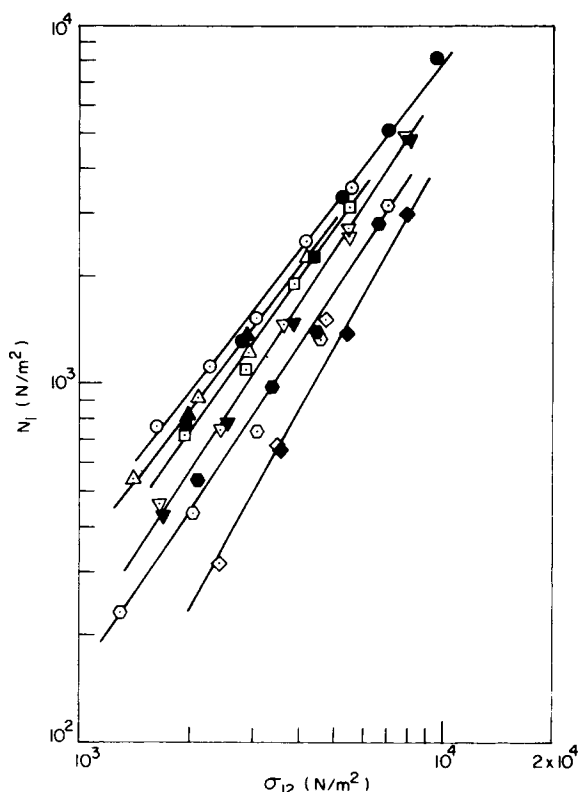


Fig. 3. Logarithmic plots of N_1 versus σ_{12} for the ABS/PMMA blend system. Symbols are the same as in Figure 2.

According to Bergen and Morris,⁶ about 100,000 SAN chains are attached to each rubber particle in the particular ABS resin they have investigated. It has been reported that SAN is compatible with PMMA.³⁰⁻³⁵ Since the grafted rubber particles in ABS resin have numerous SAN chains on their surfaces, the compatibility of ABS and PMMA can be treated in the same way as the compatibility of SAN and PMMA. In other words, the presence of rubber particles, grafted with SAN, in ABS resin appears to play only a minor role in influencing the compatibility of blends of ABS and PMMA.

Figure 4 gives logarithmic plots of G' versus ω , and Figure 5 logarithmic plots of G'' versus ω , at 200°C. Similar results were obtained at 220°C, but due to limitations of space we shall not present them here. Note that G' may be considered as representing the energy stored and G'' the energy dissipated in the fluid during oscillatory shearing flow. It is very difficult to make any statement from Figures 4 and 5 about the dependences of G' and G'' on blend composition.

However, as may be seen in Figure 6, when G' is plotted against G'' in logarithmic coordinates, the dependence of G' on blend composition becomes very clear. Note that logarithmic plots of G' versus G'' show little dependence on temperature, and that data at other temperatures are not shown for some blend compositions in order to preserve clarity in Figure 6. Comparison

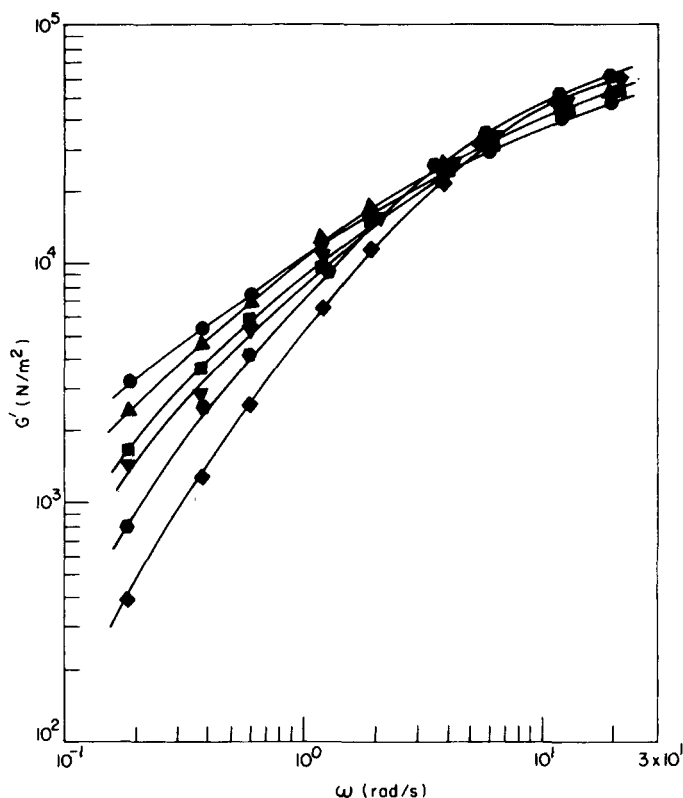


Fig. 4. Logarithmic plots of G' versus ω for the ABS/PMMA blend system at 200°C. (●) ABS; (▲) ABS/PMMA = 80/20; (■) ABS/PMMA = 60/40; (▼) ABS/PMMA = 40/60; (◆) ABS/PMMA = 20/80; (◆) PMMA.

of Figure 6 with Figure 3 shows that the dependence of G' on blend composition is exactly the same as the dependence of N_1 on blend composition. One can conclude from Figures 3 and 6 that the ABS is much more elastic than the PMMA and that the melt elasticity of the blend varies regularly with blend composition.

CONCLUDING REMARKS

It has been demonstrated above that the rheological behavior of blends of ABS and PMMA is very similar to that of blends of SAN and PMMA, in spite of the fact that ABS is a heterogeneous grafted copolymer while SAN is a homogeneous random copolymer. We attribute this to both the SAN chains, attached to the surface of the rubber particles, and the SAN resinous matrix in ABS playing the key role in compatibilizing ABS with PMMA, being very similar to blends of SAN and PMMA. In other words, the presence of rubber particles in ABS resin appears to play only a minor role in interfering with the compatibility of ABS with PMMA, as long as a sufficient number of SAN chains are attached to each of the rubber particles embedded in ABS resin. We thus conclude that, from the rheological point of view, blends of ABS and

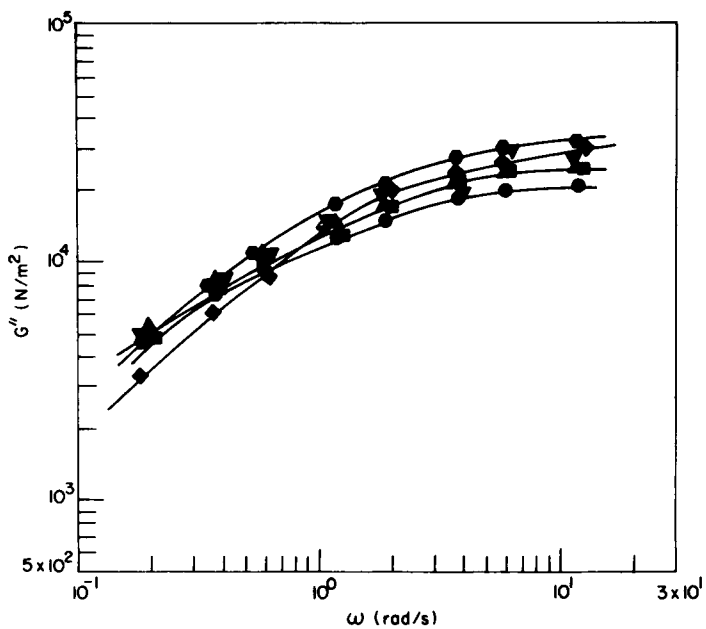


Fig. 5. Logarithmic plots of G'' versus ω for the ABS/PMMA blend system. Symbols are the same as in Figure 4.

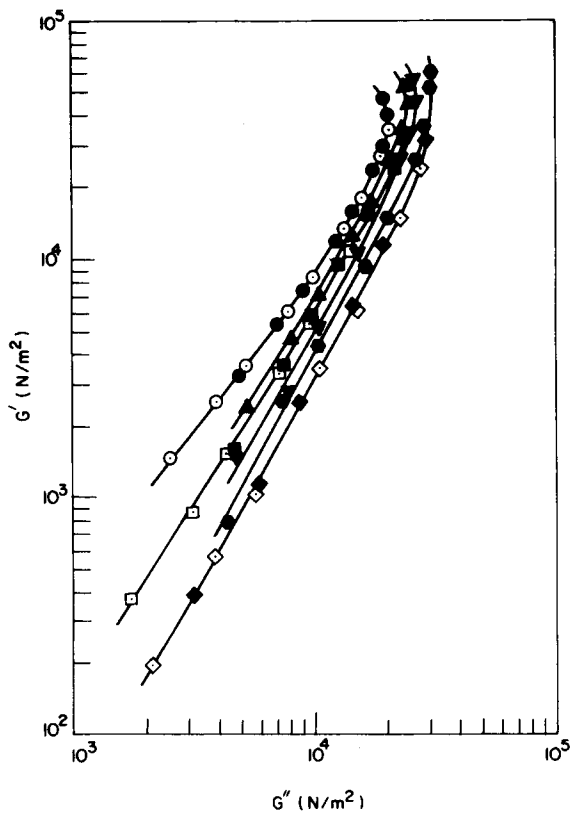


Fig. 6. Logarithmic plots of G' versus G'' for the ABS/PMMA blend system. Symbols are the same as in Figure 2.

PMMA are compatible due to the same mechanism that controls the compatibility of blends of SAN and PMMA.

We can now explain why the coextruded sheets of ABS and PMMA, produced in our laboratory,¹⁶ had excellent interfacial adhesion. We speculate that, while the two streams of molten ABS and PMMA were forced to flow side by side in a sheet-forming die, molecular interdiffusion took place across the initial interface, forming an interfacial layer, frequently referred to as *interphase*, where the two dissimilar molecules of SAN and PMMA stay together. We believe that the same mechanism is responsible for the compatibility exhibited by blends of ABS and PMMA. Without having an interphase formed between the constituent components, ABS and PMMA, the rheological behavior presented above would not have been possible.

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