

Criteria for Rheological Compatibility of Polymer Blends

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Synopsis

Criteria for rheological compatibility of polymer blends are suggested. The criteria suggested make use of plots of first normal stress difference (N_1) against shear stress (σ_{12}), and of storage modulus (G') against loss modulus (G''). Compatible blend systems considered are (1) blends of two different grades of low-density polyethylene, (2) blends of poly(vinylidene fluoride) and poly(methyl methacrylate), (3) blends of poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene, and (4) blends of poly(styrene-co-acrylonitrile) and poly(styrene-co-maleic anhydride). And incompatible blend systems considered are (1) blends of nylon 6 and poly(ethylene-co-vinyl acetate) and (2) blends of nylon 6 and an ethylene-based multifunctional polymer. It has been found that plots of N_1 vs. σ_{12} and G' vs. G'' give (a) temperature-independent correlations for both compatible and incompatible blend systems; (b) composition-independent correlations for compatible blends; (c) composition-dependent correlations for incompatible blends.

INTRODUCTION

During the last two decades, much has been discussed in the literature about the compatibility of polymer blends, using various experimental techniques, such as dynamic mechanical analysis, thermal analysis, light scattering, small-angle X-ray diffraction, gel permeation chromatography, electron microscopy, carbon-13 NMR, and excimer fluorescence. Also, from a theoretical point of view, solution thermodynamic theories have been extended to discuss polymer-polymer miscibility. Recent monographs¹⁻³ summarize the efforts spent on the subject by a number of investigators.

From a practical point of view, interest in polymer blends stems from the desire for developing new polymeric materials with low cost. However, without having good miscibility between the two polymers chosen for blending, the mechanical and/or physical properties aimed at are not achievable. Therefore, the development of theories and experimental techniques that may be useful for determining polymer-polymer miscibility has been the primary focus in polymer blend research.

In spite of the great effort spent on finding pairs of compatible polymers, not many such pairs have enjoyed commercial success. Some compatible pairs are: poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/polystyrene (PS); poly(methyl methacrylate) (PMMA)/poly(vinylidene fluoride) (PVDF); poly(vinyl chloride) (PVC)/poly(ethylene-co-vinyl acetate) (EVA); poly(vinyl chloride) (PVC)/poly(butadiene-co-acrylonitrile).

From the point of view of polymer processing, measurements and/or theoretical predictions of the rheological properties of polymers are very

essential. For this reason, much effort has been spent on relating the rheological behavior of polymers to their processing characteristics.⁴ Compared to the amount of effort spent on homopolymers, however, relatively little effort has been put on investigating the rheological properties of polymer blends. A monograph by Han⁵ summarizes recent research efforts on the subject.

It should be pointed out that the majority of the published rheological investigations of polymer blends has dealt with heterogeneous (i.e., immiscible or incompatible) systems. This is understandable, in that it is much easier to find incompatible blend systems than compatible blend systems. As pointed out by Han,^{4,5} the rheological behavior of incompatible blend systems depends, among other things, on the morphological state of the blend in the molten state, which in turn depends on the variables associated with the preparation of blends, such as the intensity of mixing, the mixing temperature, and the duration of mixing.

Indeed, only a few publications⁶⁻⁸ deal with the rheological behavior of compatible blend systems. About a decade ago, Prest and Porter⁶ reported on the steady and oscillatory shearing flow properties of PPO/PS blends. They correlated the first normal stress difference (N_1) to the storage modulus (G'), measured at various temperatures and shear rates (or frequencies), by using the time-temperature superposition principle. They showed that the values of N_1 and G' increase with an increasing amount of PPO in the blend. Very recently, Chuang and Han⁷ reported on the steady and oscillatory shearing flow properties of PMMA/PVDF blends, and Aoki⁸ reported on the oscillatory shearing flow properties of poly(styrene-co-acrylonitrile)/poly(styrene-co-maleic anhydride) blends.

Having conducted measurements of the rheological properties of both compatible and incompatible polymer blend systems, we have come up with an idea suggesting a means for determining the rheological compatibility of polymer blends. In this paper, we will expound on the idea, with specific examples.

EXPERIMENTAL

Materials

We will consider the following blend systems, which were investigated recently in our laboratory. They are: (1) a compatible blend system consisting of two polymers having the same molecular structure but different molecular weights, namely, two different grades (MN722 and MN714, U.S. Industrial Chemical Company) of low-density polyethylene (LDPE); (2) a compatible blend system having different molecular structures, namely, blends of poly(methyl methacrylate) (PMMA) (Rohm and Haas, Plexiglas 920) and poly(vinylidene fluoride) (PVDF) (Pennwalt Corp., Kynar 960); (3) an incompatible blend system having no intermolecular or chemical interaction between the constituent components, namely, blends of nylon 6 (American Enka Co.) and poly(ethylene-co-vinyl acetate) (EVA) (DuPont Co.); (4) an incompatible blend system having functional groups in the respective constituent components, so that chemical reactions can take

place during melt blending, namely blends of nylon 6 (American Enka Co.) and CXA 3101. Note that CXA 3101 is an ethylene-based multifunctional polymer, commercially available from E.I. Du Pont de Nemours and Co., which contains carboxyl or anhydride groups that can react, during melt blending, with the amino end groups of nylon 6. Infrared (IR) spectroscopic analysis shows that CXA 3101 has 18.1 wt % of vinyl acetate and 2.1 wt % of —COOH groups.

These blends were prepared, using a twin-screw compounding machine (Werner and Pfleiderer, ZSK-30). It should be pointed out that the method of blend preparation can greatly influence the rheological properties, especially for incompatible blend systems, because the morphological state of dispersion in the molten state, which in turn is controlled by the method of blend preparation, greatly influences the rheological properties of heterogeneous blends.^{4,5} Note further that twin-screw compounding machines are much more powerful for mixing very viscous materials than single-screw extruders.

In addition to our own experimental work, we have considered the literature data on the rheological properties of compatible blend systems, namely blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) by Prest and Porter⁶ and blends of poly(styrene-co-acrylonitrile) (SAN) and poly(styrene-co-maleic anhydride) (SMA) by Aoki.⁸

Rheological Measurement

In our work, both steady-state shearing flow properties (i.e., the first normal stress difference N_1 and shear stress σ_{12} as a function of shear rate $\dot{\gamma}$) and oscillatory (or dynamic) shearing flow properties (i.e., storage shear modulus G' and loss shear modulus G'' as a function of frequency ω) were measured with a cone-and-plate rheometer (a Weissenberg Model R-16 Rheogoniometer). In the work of Prest and Porter,⁶ both steady and oscillatory shearing flow properties were measured with a cone-and-plate rheometer (Rheometrics Mechanical Spectrometer). Aoki,⁸ however, measured only oscillatory shearing flow properties, using a concentric cylinder-type rheometer (Thixotrometer, Iwamoto Seisakusho Co.). The basic principles and the mathematical formulae used in the analyses of the experimental data by these investigators are well documented in the literature.^{9,10}

EXPERIMENTAL CORRELATIONS

LDPE Blends

Figure 1 gives plots of N_1 and σ_{12} vs. $\dot{\gamma}$, and Figure 2 plots of G' and G'' vs. ω , for the MN722/MN714 blend system at two temperatures, 160 and 180°C. It is seen that N_1 and σ_{12} , and also G' and G'' , decrease with increasing temperature, and these values increase monotonically as the amount of the more viscous component, MN722, in each blend is increased.

Figure 3 gives plots of N_1 vs. σ_{12} , and of G' vs. G'' , for MN722 at two temperatures, 160 and 180°C. Similar plots are given in Figure 4 for MN714, in Figure 5 for 40/60 MN722/MN714 blend, and in Figure 6 for 60/40 MN722/MN714 blend. Note that these plots were prepared using Figures

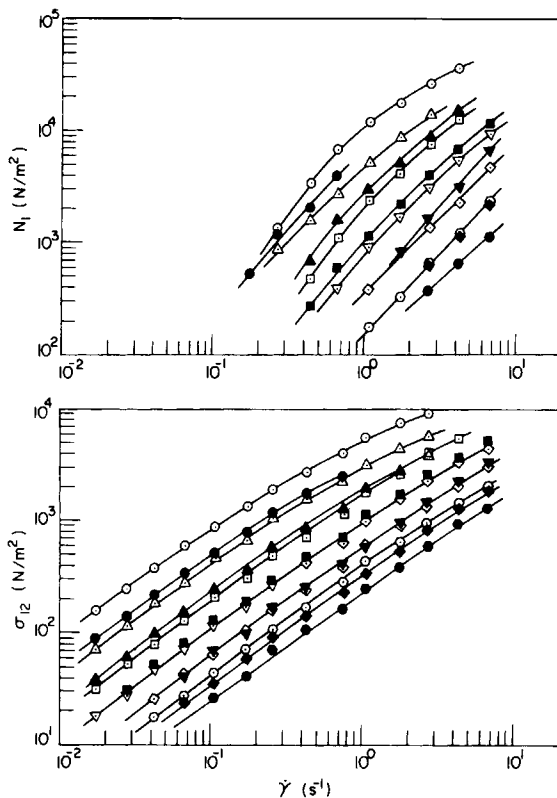


Fig. 1. N_1 and σ_{12} vs. $\dot{\gamma}$ for MN722/MN714 blends: (\odot, \bullet) MN722; (\odot, \blacktriangle) MN722/MN714 = 80/20; (\square, \blacksquare) MN722/MN714 = 60/40; ($\nabla, \blacktriangledown$) MN722/MN714 = 40/60; (\diamond, \blacklozenge) MN722/MN714 = 20/80. (\odot, \bullet) MN714. Open symbols at 160°C and closed symbols at 180°C.

1 and 2, and each data point has different values of $\dot{\gamma}$ or ω . It is seen that, regardless of whether they are homopolymers or blends, such plots yield correlations which become independent of temperature. In other words, one does not need a shift factor for obtaining temperature-independent reduced plots. Note in Figures 3-6 that N_1 values are about twice as large as G' values, behavior to be expected at low rates of deformation, from a theoretical point of view.¹¹

Figure 7 gives plots of N_1 vs. σ_{12} , and of G' vs. G'' for MN722/MN714 blends at 160°C, and Figure 8 similar plots at 180°C. It is seen that these plots yield correlations which become independent of blend composition. Comparison of Figures 7 and 8 reveals that plots of N_1 vs. σ_{12} , and of G' vs. G'' also become independent of temperature, which was also pointed out above in reference to Figures 3-6.

PMMA/PVDF Blends

Figure 9 gives plots of N_1 and σ_{12} vs. $\dot{\gamma}$, and Figure 10 plots of G' and G'' vs. ω , for the PMMA/PVDF blend system, at two temperatures, 210 and 230°C. It was demonstrated earlier⁷ that both N_1 - σ_{12} and G' - G'' plots for the homopolymers, PMMA and PVDF, and their blends, give rise to correlations that are independent of temperature.

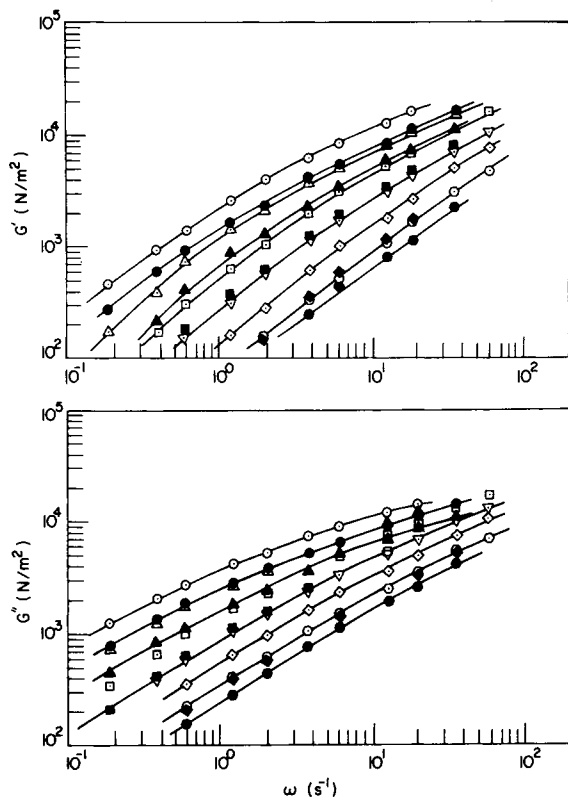


Fig. 2. G' and G'' vs. ω for MN722/MN714 blends. Symbols are the same as in Figure 1.

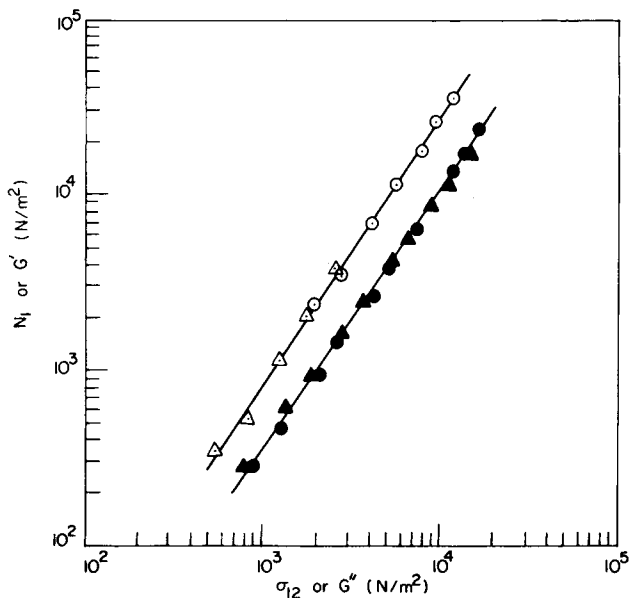


Fig. 3. N_1 vs. σ_{12} (open symbols) and G' vs. G'' (closed symbols), for MN722 at two temperatures ($^{\circ}\text{C}$): (\circ, \bullet) 160; ($\triangle, \blacktriangle$) 180.

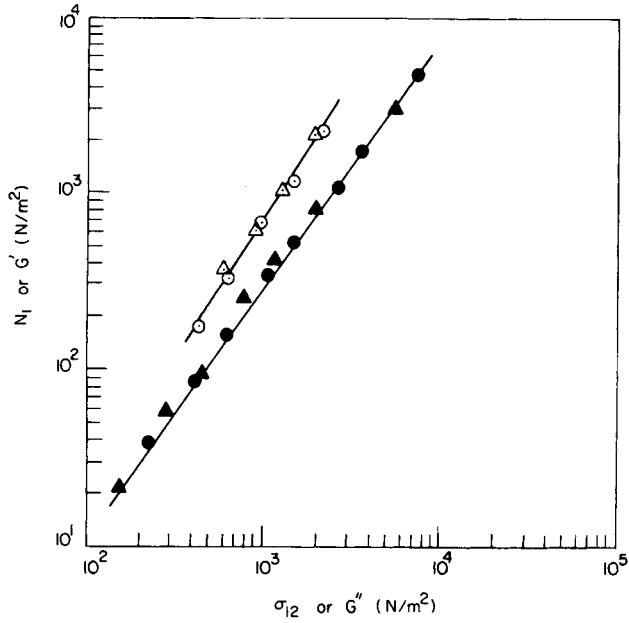


Fig. 4. N_1 vs. σ_{12} (open symbols) and G' vs. G'' (closed symbols), for MN714 at two temperatures ($^{\circ}\text{C}$): (\circ, \bullet) 160; ($\triangle, \blacktriangle$) 180.

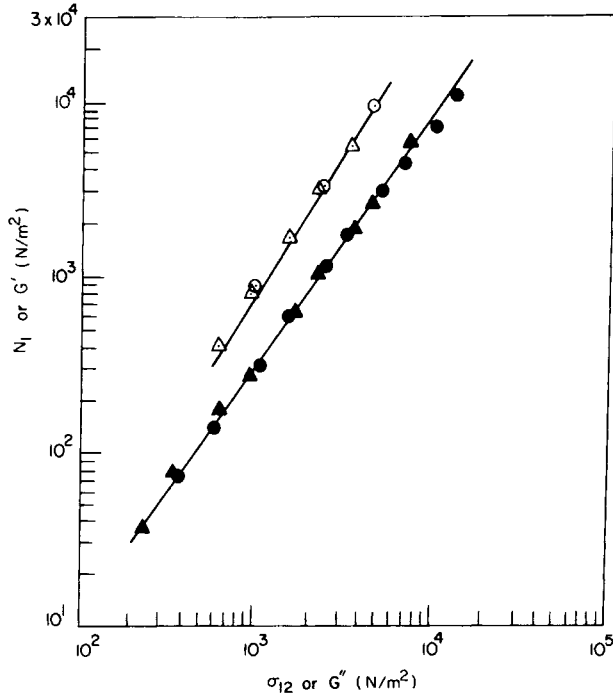


Fig. 5. N_1 vs. σ_{12} (open symbols) and G' vs. G'' (closed symbols), for MN722/MN714 = 40/60 at two temperatures ($^{\circ}\text{C}$): (\circ, \bullet) 160; ($\triangle, \blacktriangle$) 180.

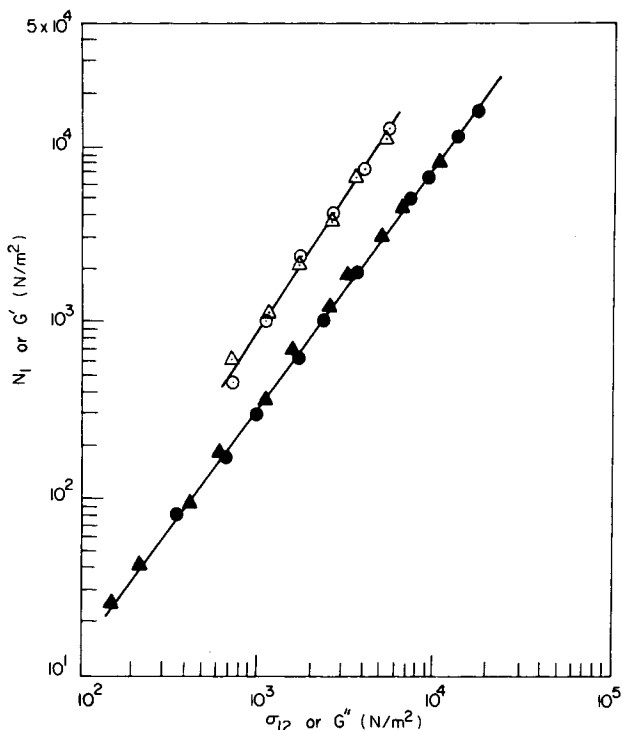


Fig. 6. N_1 vs. σ_{12} (open symbols) and G' vs. G'' (closed symbols), for MN722/MN714 = 60/40 at two temperatures ($^{\circ}\text{C}$): (\circ, \bullet) 160; ($\triangle, \blacktriangle$) 180.

Figure 11 gives plots of N_1 vs. σ_{12} , and Figure 12 plots of G' vs. G'' , for the PMMA/PVDF blend system at two temperatures, 210 and 230 $^{\circ}\text{C}$. It should not be surprising to observe that PMMA and PVDF, which have different molecular structures, exhibit different N_1 values at the same σ_{12} value. What is of great interest in Figures 11 and 12, however, is that the N_1 and G' values become virtually independent of blend composition.

PPO/PS Blends

Figure 13 gives plots of G' and G'' vs. ωa_T , for the PPO/PS blend system, as reported by Prest and Porter,⁶ in which a_T is a shift factor used for obtaining a temperature-independent correlation. It is seen in Figure 13 that G' values increase with an increasing amount of PPO in the blends. However, when G' is plotted against G'' , correlations are obtained which become independent of blend composition, as shown in Figure 14. Using the data reported by Prest and Porter,⁶ we have prepared plots of N_1 vs. σ_{12} for the PPO/PS blends, as given in Figure 15. It is seen in Figure 15 that N_1 - σ_{12} plots also give composition-independent correlations.

SAN/SMA Blends

Figure 16 gives plots of G' and G'' vs. ωa_T , for the SAN/SMA blend system, as reported by Aoki,⁸ in which a_T is a shift factor. It is seen in

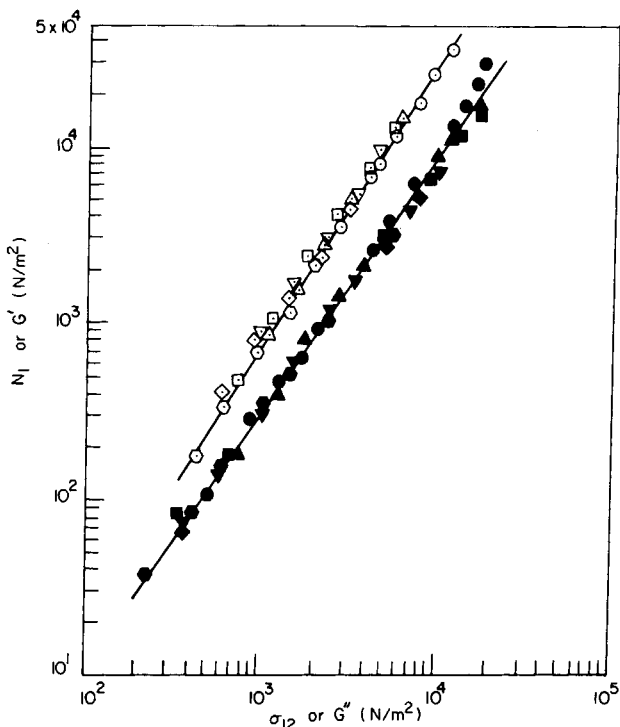


Fig. 7. N_1 vs. σ_{12} (open symbols) and G' vs. G'' (closed symbols), for MN722/MN714 blends at 160°C: (○,●) MN722; (○,●) MN714; (△,▲) MN722/MN714 = 80/20; (□,■) MN722/MN714 = 60/40; (▽,▼) MN722/MN714 = 40/60; (◇,◆) MN722/MN714 = 20/80.

Figure 16 that G' and G'' values increase monotonically with an increasing amount of SMA in the blend, and G' and G'' values lie between those of the constituent components, SAN and SMA. However, when G' is plotted against G'' , correlations are obtained which become independent of blend composition, as shown in Figure 17.

Nylon 6/EVA Blends

Figure 18 gives plots of N_1 and σ_{12} vs. $\dot{\gamma}$, and Figure 19 plots of G' and G'' vs. ω , for the nylon 6/EVA blend system at two temperatures, 230 and 240°C. It is of interest to note that the N_1 values (and also G' values) of certain blends are greater than those of EVA and that N_1 and G' values decrease with increasing temperature.

Figure 20 gives plots of N_1 vs. σ_{12} , and Figure 21 plots of G' vs. G'' , for the nylon 6/EVA blend system at two temperatures, 230 and 240°C. Similarly to the compatible blend systems presented above, N_1 - σ_{12} and G' - G'' plots show temperature independency. However, such plots exhibit a strong dependency on blend composition, behavior quite different from that of compatible blend systems. (Compare Fig. 20 with Figs. 7, 11, and 15, and compare Fig. 21 with Figs. 8, 12, and 14). Note in Figures 20 and 21 that 20/80 and 40/60 nylon 6/EVA blends have N_1 and G' values greater than the constituent components do, i.e., N_1 and G' values go through a maximum at a certain blend composition.

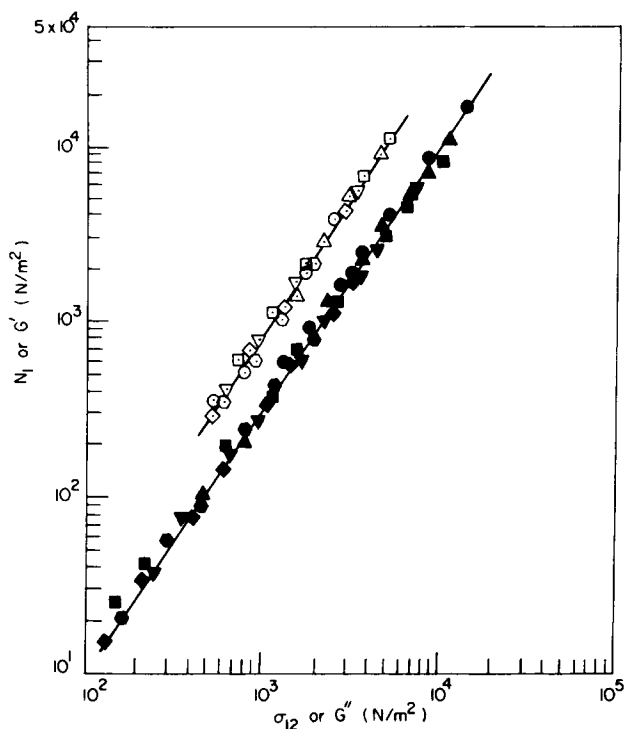


Fig. 8. N_1 vs. σ_{12} (open symbols) and G' vs. G'' (closed symbols), for MN722/MN714 blends at 180°C. Symbols are the same as in Figure 7.

Nylon 6/CXA 3101 Blends

Figure 22 gives plots of N_1 and σ_{12} vs. $\dot{\gamma}$, and Figure 23 plots of G' and G'' vs. ω , for the nylon 6/CXA 3101 blend system at two temperatures, 230 and 240°C. It is seen in these figures that some nylon 6/CXA 3101 blends have N_1 and G' values greater than the constituent components. However, when N_1 is plotted against σ_{12} as given in Figure 24, and with the exception of the 80/20 nylon 6/CXA 3101 blend, N_1 values of three other blends become very close to those of CXA 3101.

On the other hand, it is seen in Figure 25 that 40/60 nylon 6/CXA 3101 blend has G' values greater than those of the other blends and of the constituent components, i.e., the G' value goes through a maximum at a certain blend composition. It is seen therefore that the dependency of N_1 on blend composition is different from the dependency of G' on blend composition.

DISCUSSION

Compatible Blends Consisting of Homopolymers Having the Same Molecular Structure

From the molecular point of view, the rheological properties of polymer melts are influenced by their molecular friction coefficient, the molecular weight, and the distribution of molecular weight. Therefore, when two polymers of the same molecular structure, but of different molecular weights

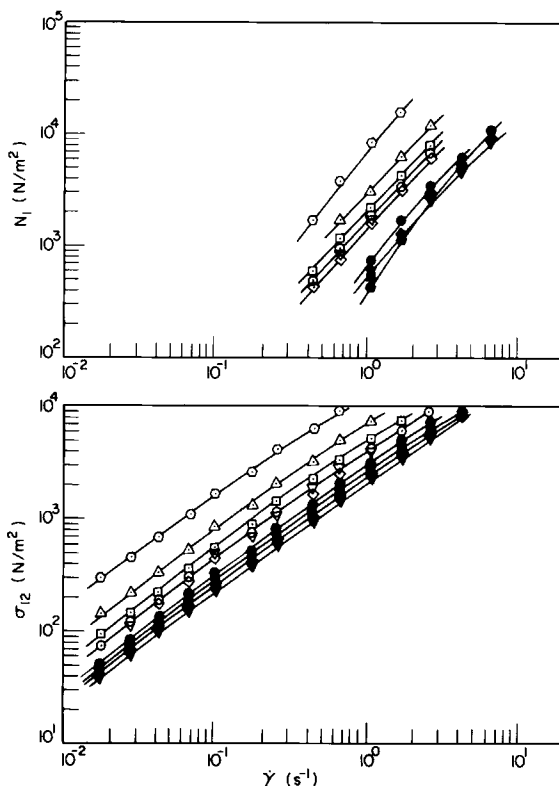


Fig. 9. N_1 and σ_{12} vs. $\dot{\gamma}$ for PVDF/PMMA blends: (\odot, \bullet) PVDF; ($\triangle, \blacktriangle$) PVDF/PMMA = 20/80; (\square, \blacksquare) PVDF/PMMA = 40/60; ($\nabla, \blacktriangledown$) PVDF/PMMA = 60/40; (\diamond, \blacklozenge) PVDF/PMMA = 80/20; (\circ, \bullet) PMMA. Closed symbols at 210°C and open symbols at 230°C.

or of different molecular weight distributions, are melt-blended thoroughly, the resultant polymer would have the same molecular structure but a different molecular weight and a different molecular weight distribution, lying between those of the constituent components. The blends thus obtained would form an isotropic medium that has no separate domain occupied by the respective constituent components. The LDPE blends (i.e., blends of MN722 and MN714) considered above certainly belong to this category. Therefore, it is not surprising to observe that these blends follow the same correlation, independent of blend composition, as MN722 and MN714 do individually (see Figs. 7 and 8).

Compatible Blends Consisting of Homopolymers or Copolymers Having Different Molecular Structures

Polymers having different molecular structures are expected, in general, to exhibit different rheological responses, because the friction coefficient, the molecular weight, and the distribution of molecular weight of two or more dissimilar polymers would be different. Therefore, for instance, the homopolymers PMMA and PVDF and the homopolymers PPO and PS discussed above are expected to have different values of N_1 when plotted

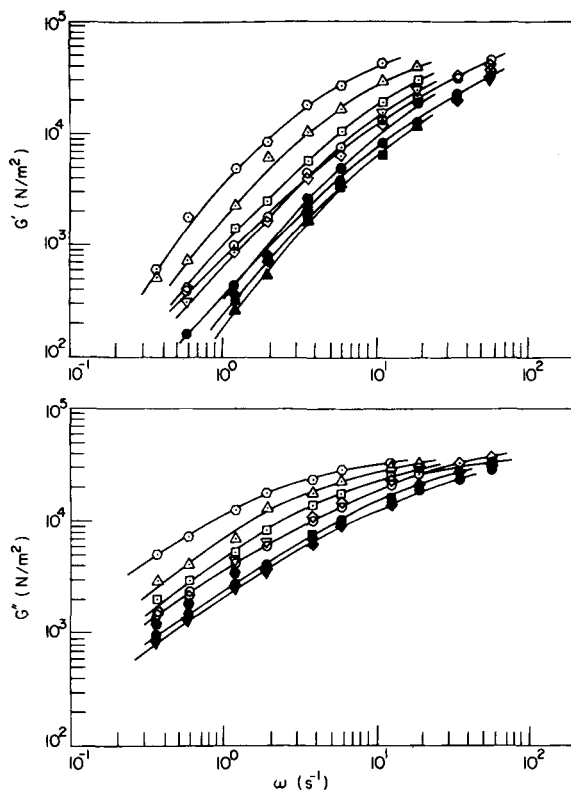


Fig. 10. G' and G'' vs. ω for PVDF/PMMA blends. Symbols are the same as in Figure 9.

against σ_{12} , and also different values of G' when plotted against G'' . Thus the experimental observations given in Figures 11 and 12 should be of no surprise.

Since all three blend systems considered above, namely, PMMA/PVDF blends, PPO/PS blends, and SAN/SMA blends, are believed to be compatible, they must form an isotropic medium that has no separate domains occupied by the respective constituent components. In the light of the observations made on the MN722/MN714 blend system, the N_1 values of PMMA/PVDF, PPO/PS, and SAN/SMA blends, when plotted against σ_{12} , are expected to be independent of blend composition. Likewise, the G' values of the blend systems, when plotted against G'' , would be independent of blend composition. The rationale behind this expectation lies in that, in compatible blends, the ratio of the amount of energy stored (i.e., N_1 and G') to the amount of energy dissipated (i.e., σ_{12} and G'') would be independent of blend composition. In other words, a variation in blend composition will bring about a variation in both N_1 and σ_{12} , and also in both G' and G'' , such that the ratios N_1/σ_{12} and G'/G'' remain independent of blend composition. This has been borne out to be the case, as demonstrated in Figures 11 and 12 for PMMA/PVDF blends and in Figures 14 and 15 for PPO/PS blends.

It is of great interest to observe in Figure 17 that, although they are of

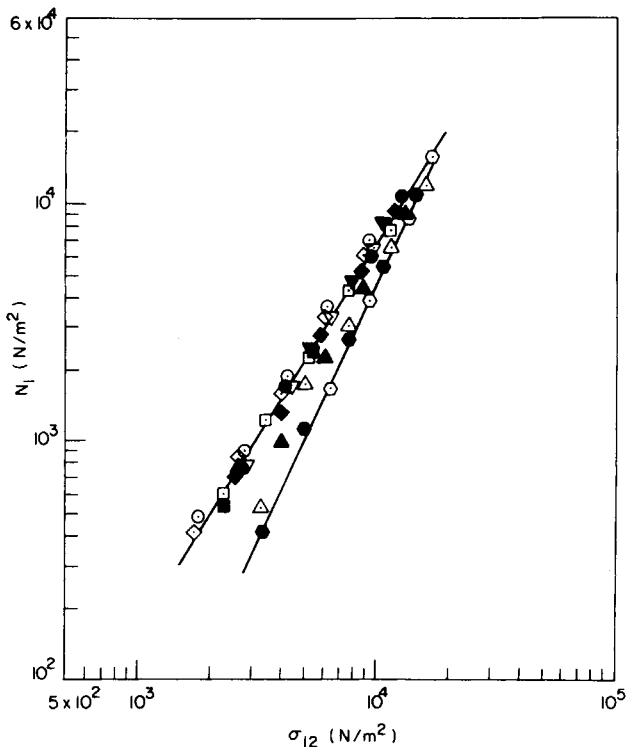


Fig. 11. N_1 vs. σ_{12} for PVDF/PMMA blends: (○, ●) PVDF; (◐, ◑) PMMA; (△, ▲) PVDF/PMMA = 20/80; (◻, ◼) PVDF/PMMA = 40/60; (◊, ◈) PVDF/PMMA = 60/40; (◇, ◆) PVDF/PMMA = 80/20. Open symbols at 210°C and closed symbols at 230°C.

different molecular structures, when plotted against G'' , SAN and SMA have the same G' values. Since the SAN/SMA blends are compatible, it is not surprising to observe that they follow the same correlation as that of the constituent components, behavior very similar to that of MN722/MN714 blends, as shown in Figures 7 and 8.

Incompatible Blends without Intermolecular Interaction

It has been amply demonstrated in the literature^{4,5,7,12-16} that when two polymers are incompatible and have no intermolecular interaction, they form two phases. The specific type of two-phase behavior obtained (e.g., cocontinuous phase; discrete-continuous phase; interlocked or interpenetrating network) depends, among many things, on the blend ratio, the processing conditions at which blends are prepared, and the rheological properties of the constituent components, which, in turn, depend on the molecular weight and the distribution of molecular weight.

The nylon 6/EVA blends considered above form two phases, giving rise to discrete-continuous phase morphology, as may be seen in Figure 26. Note in Figure 26 that EVA forms the discrete phase (i.e., droplets) dispersed in the continuous nylon phase for the 60/40 nylon 6/EVA blend, and nylon

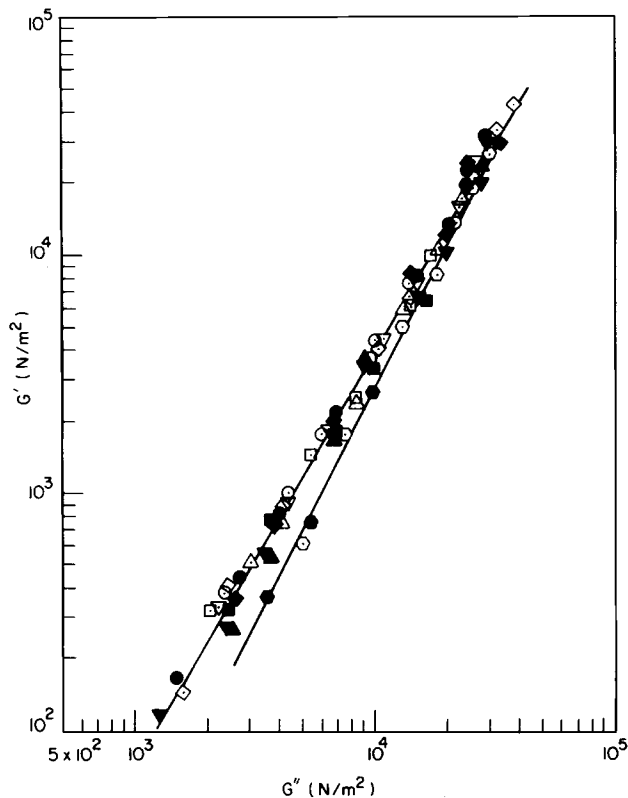


Fig. 12. G' vs. G'' for PVDF/PMMA blends. Symbols are the same as in Figure 11.

6 forms the discrete phase dispersed in the continuous EVA phase for the 20/80 nylon 6/EVA blend. As pointed out by Han and co-workers,^{7,13-16} the rheological behavior of two-phase polymer blends depends, among many things, on the domain size and deformability of the discrete phase. Since the domain size of the discrete phase depends on blend composition and the deformability of the discrete phase depends on the extent of shear stress exerted, the observed dependency of N_1 on σ_{12} , and also the dependency of G' on G'' , given in Figures 20 and 21, should be of no surprise.

Note that there exists no intermolecular or chemical interaction between nylon 6 and EVA. Therefore, each blend with a different blend ratio would have different domain sizes, and thus its rheological responses would be different. It should be pointed out that the N_1 values of two-phase blends possessing discrete-continuous phase morphology are greatly influenced by the deformability of the discrete phase (i.e., the droplets). Note further that the deformability of the droplets is greatly influenced by their sizes. Therefore, one would expect to see a strong dependence of N_1 - σ_{12} and G' - G'' plots on the domain size of the discrete phase and thus on blend composition. Note that, depending on the domain size, certain blends can have N_1 values greater than those of other blends or of the constituent components. This has been borne out to be the case, as may be seen in Figures 20 and 21.

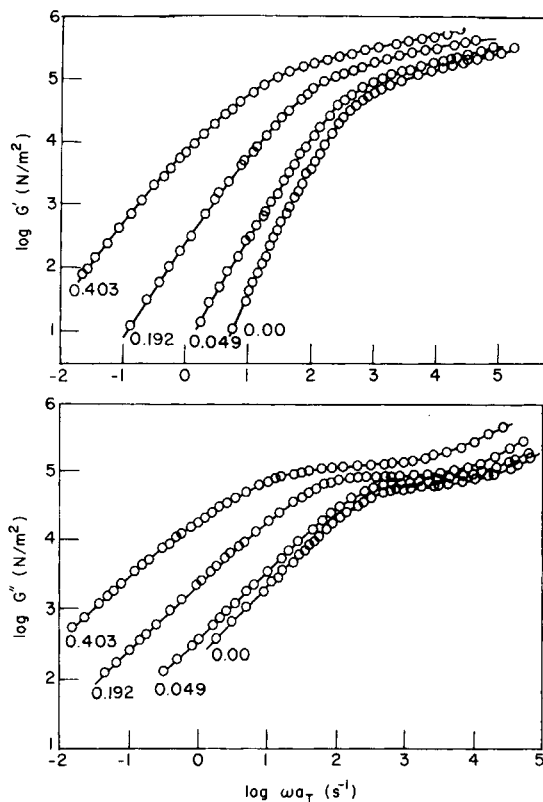


Fig. 13. $\log G'$ and $\log G''$ vs. $\log \omega a_T$ for PPO/PS blends.⁶ The numerical values shown in the figure represent the weight fraction of PPO.

Incompatible Blends with Chemical Interactions

It can be easily surmised that when two incompatible polymers have chemical interactions during melt blending, the rheological responses of such blends would be different from those having no chemical interaction. In order to investigate the effect of the extent of chemical interactions between the constituent components on the rheological responses of their blends, we have chosen nylon 6/CXA 3101 blends. Specifically, we were interested in comparing the rheological responses of nylon 6/EVA blends with those of nylon 6/CXA 3101 blends. It should be noted that CXA 3101 has EVA as a major ingredient, and carboxyl or anhydride groups that can react chemically with the amino end groups of nylon 6.¹⁷ We were interested in investigating the effect, if any, of the extent of chemical reactions between the carboxyl or anhydride groups present in the CXA 3101 and the amino end groups of nylon 6 on the rheological responses of the nylon 6/CXA 3101 blends.

Figure 27 gives micrographs of the tensile fracture surfaces of 20/80 and 60/40 nylon 6/CXA 3101 blends. Note in Figure 27 that, in the 20/80 nylon 6/CXA 3101 blend, nylon 6 forms the discrete phase dispersed in the continuous CXA 3101 phase and, in the 60/40 nylon 6/CXA 3101 blend, CXA

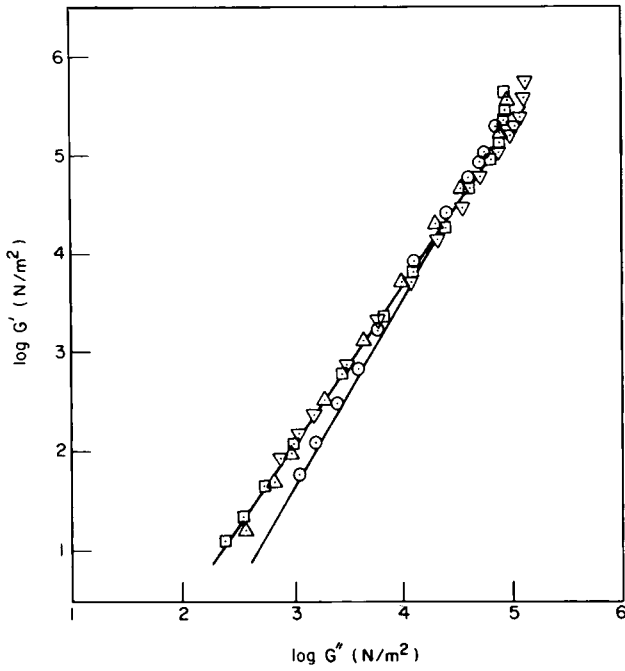


Fig. 14. $\log G'$ vs. $\log G''$ for PPO/PS blends with the weight fraction of PPO: (○) 0.0; (△) 0.049; (□) 0.192; (▽) 0.403.

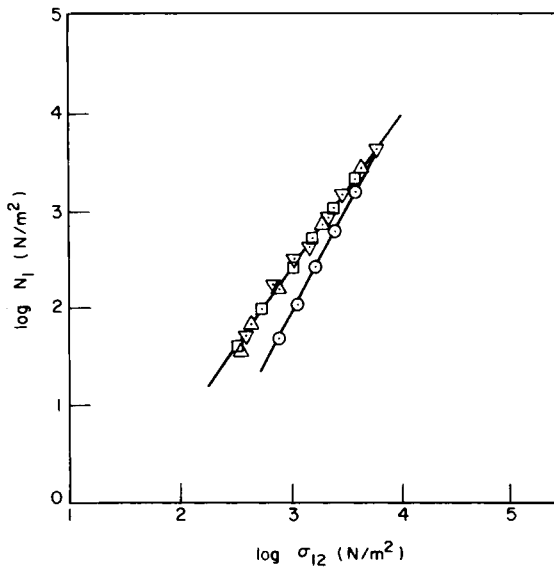


Fig. 15. $\log N_1$ vs. $\log \sigma_{12}$ for PPO/PS blends. Symbols are the same as in Figure 14.

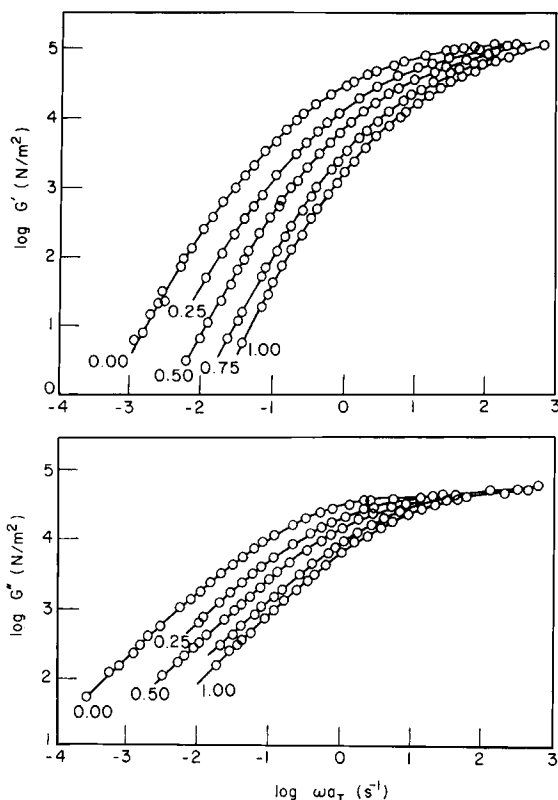


Fig. 16. $\log G'$ and $\log G''$ vs. $\log \omega_T$ for SAN/SMA blends.⁸ The numerical values shown in the figure represent the weight fraction of SAN.

3101 forms the discrete phase dispersed in the continuous nylon phase. It is seen that this blend system forms two phases.

As may be seen in Figure 20, N_1 values of certain blend compositions of the nylon 6/EVA blend system are greater than those of the constituent components. The observed difference in N_1 - σ_{12} correlation between the nylon 6/CXA 3101 blend system and the nylon 6/EVA blend system is attributable to the fact that the average domain size of the discrete phase in nylon 6/CXA 3101 blends is much smaller than in nylon 6/EVA blends, as may be seen from the photomicrographs given in Figures 26 and 27. The observed small domain size in nylon 6/CXA 3101 blends has been achieved by the presence of an "interfacial agent" (or "compatibilizing agent"), which is believed to be a graft copolymer formed from the chemical reactions between nylon 6 and CXA 3101. Note that the smaller the domain size, the more difficult it will be to deform the discrete phase subjected to a shearing flow field.

A close examination of Figure 24, plotted for nylon 6/CXA 3101 blends of various compositions, reveals that, with the exception of the 80/20 nylon 6/CXA blend, all such blends behave almost like a compatible blend system, in that they give rise to a N_1 - σ_{12} correlation almost independent of blend composition (see, for instance, Figs. 11 and 15).

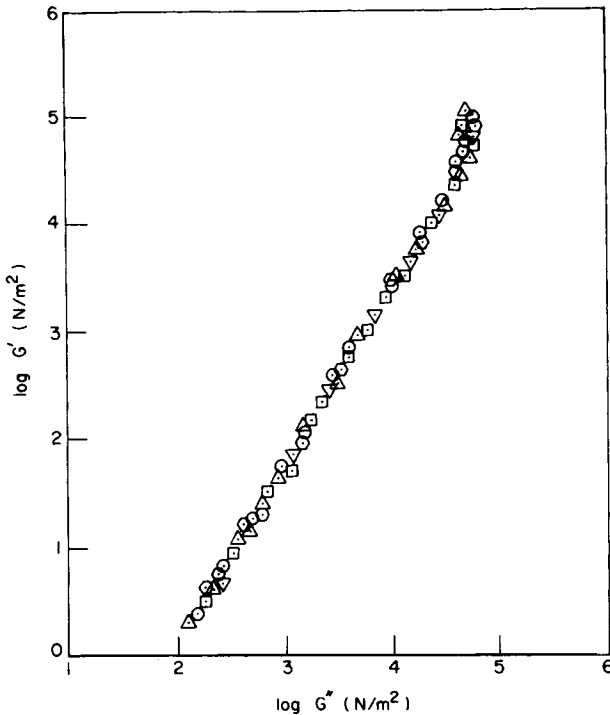


Fig. 17. $\log G'$ vs. $\log G''$ for SAN/SMA blends with the weight fraction of SAN: (○) 0.0; (△) 0.25; (□) 0.50; (▽) 0.75; (⊙) 1.0.

Photomicrographs given in Figure 27 clearly show evidence of the existence of a graft copolymer covering the surface of the dispersed particles. Note that the nylon particles dispersed in the continuous CXA 3101 phase do not show sharp edges at the boundaries of the tensile fracture surface. By contrast, one can observe in Figure 26 the dislodgment of dispersed particles on the tensile fracture surfaces of nylon 6/EVA blends.

The presence of a graft copolymer as "interfacial agent" in nylon 6/CXA 3101 blends would make the deformation of dispersed particles much more difficult than those that are freely suspended in the nylon 6/EVA blends. We can therefore conclude that heterogeneous polymer blends having extensive chemical interactions between the constituent components can give rise to a N_1 - σ_{12} correlation which becomes independent of (or weakly dependent upon) blend composition, behavior typical of compatible polymer blends.

Correlation between N_1 - σ_{12} and G' - G'' Plots in Heterogeneous Polymer Blends

Comparison of Figure 20 with Figure 21, and Figure 24 with Figure 25, indicates that, in heterogeneous polymer blends, the dependence of N_1 on blend composition, when plotted against σ_{12} , is different from the dependence of G' on blend composition, when plotted against G'' . This may be understood if one realizes that the state of dispersion and, specifically, the

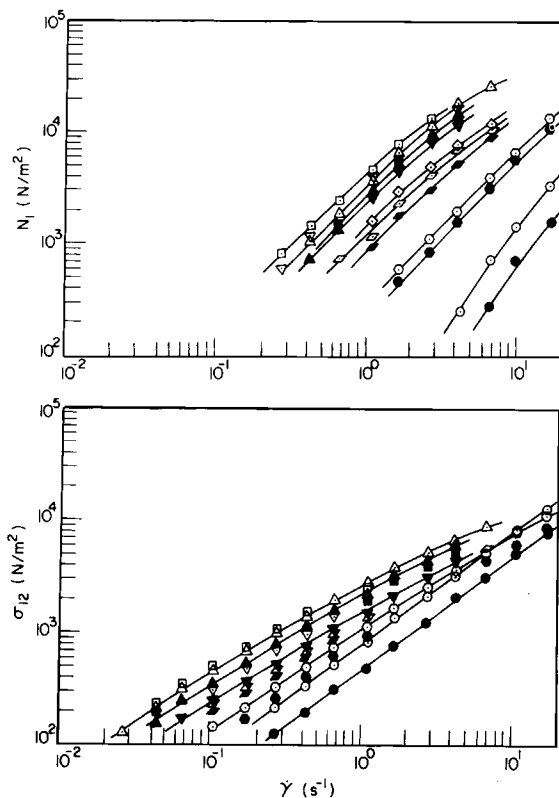


Fig. 18. N_1 and σ_{12} vs. $\dot{\gamma}$ for nylon 6/EVA blends: (○, ●) nylon; (□, ■) nylon/EVA = 20/80; (▽, ▼) nylon/EVA = 40/60; (◇, ◆) nylon/EVA = 50/50; (◇, ◆) nylon/EVA = 60/40; (○, ●) nylon/EVA = 80/20; (△, ▲) EVA. Open symbols at 230°C and closed symbols at 240°C.

state of dispersion and, specifically, the shape of the dispersed phase greatly influence the rheological properties of heterogeneous blends.^{4,5}

Consider a spherical droplet suspended in a continuous medium, which is subjected to either a steady shearing flow or an oscillatory shearing flow. Under the steady shearing flow, the droplet is deformed in the direction of the shearing plane, and the greater the shear rate, the longer the droplet will be stretched. On the other hand, under oscillatory shearing flow, the shape of the droplet will also oscillate, commensurate with the frequency of the oscillation imposed on the fluid. When the droplet phase viscosity is very large compared to the medium viscosity, the oscillatory motion of the cone (or plate) of the rheometer may have only a small effect on the shape of the droplet; but when the droplet viscosity is very small compared to the medium viscosity, the shape of the droplet will oscillate greatly. Therefore, one must not expect any correlation between the steady shearing flow properties and the oscillatory flow properties (e.g., between N_1 and G') for heterogeneous blends.

CONCLUDING REMARKS

It has been demonstrated in this paper that plotting N_1 against $\dot{\gamma}$, and G' against ω , cannot distinguish whether a polymer blend system is compatible or not. Both N_1 - $\dot{\gamma}$ and G' - ω plots show the dependency of N_1 and

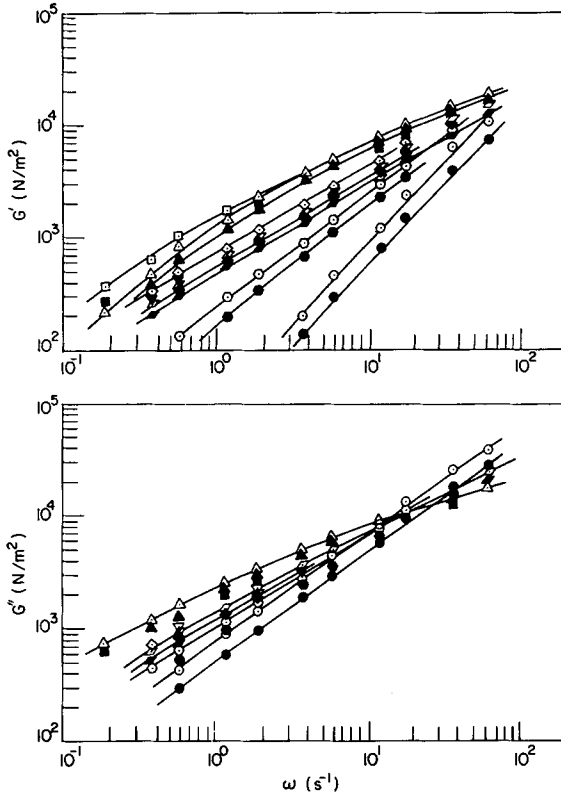


Fig. 19. G' and G'' vs. ω for nylon 6/EVA blends. Symbols are the same as in Figure 18.

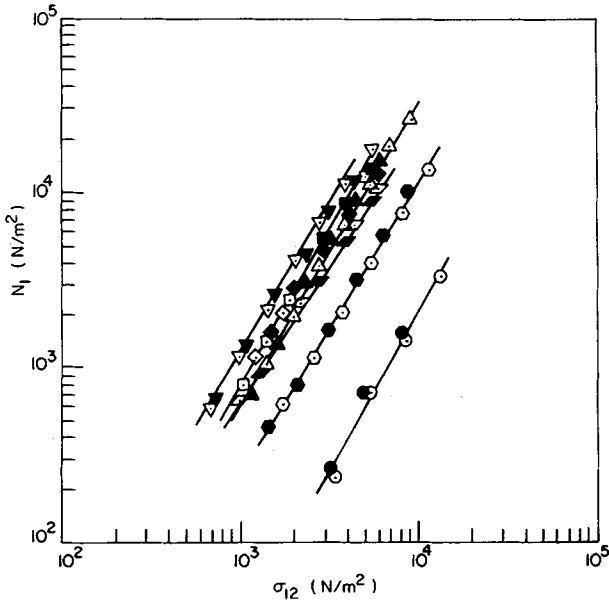


Fig. 20. N_1 vs. σ_{12} for nylon 6/EVA blends. Symbols are the same as in Figure 18.

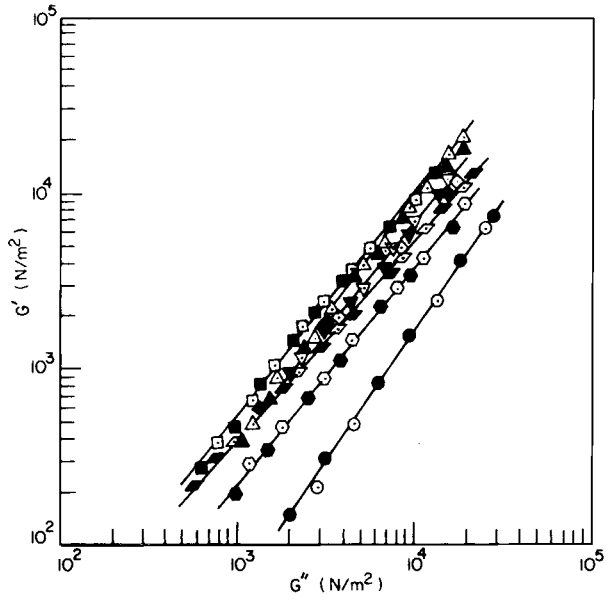


Fig. 21. G' vs. G'' for nylon 6/EVA blends. Symbols are the same as in Figure 18.

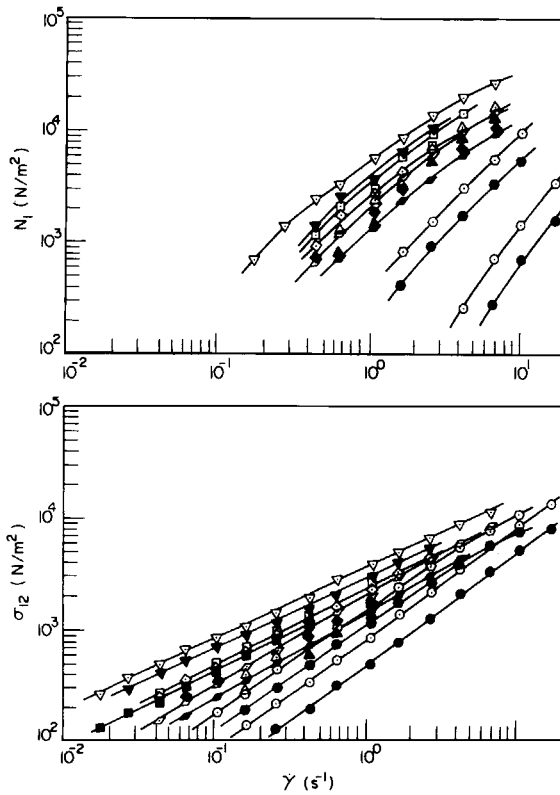


Fig. 22. N_1 and σ_{12} vs. $\dot{\gamma}$ for nylon 6/CXA 3101 blends: (\odot, \bullet) nylon; (\square, \blacksquare) nylon/CXA 3101 = 20/80; ($\nabla, \blacktriangledown$) nylon/CXA 3101 = 40/60; (\diamond, \blacklozenge) nylon/CXA 3101 = 50/50; (\square, \blacksquare) nylon/CXA 3101 = 60/40; (\circ, \bullet) nylon/CXA 3101 = 80/20; ($\triangle, \blacktriangle$) nylon/CXA 3101. Open symbols at 230°C and closed symbols at 240°C.

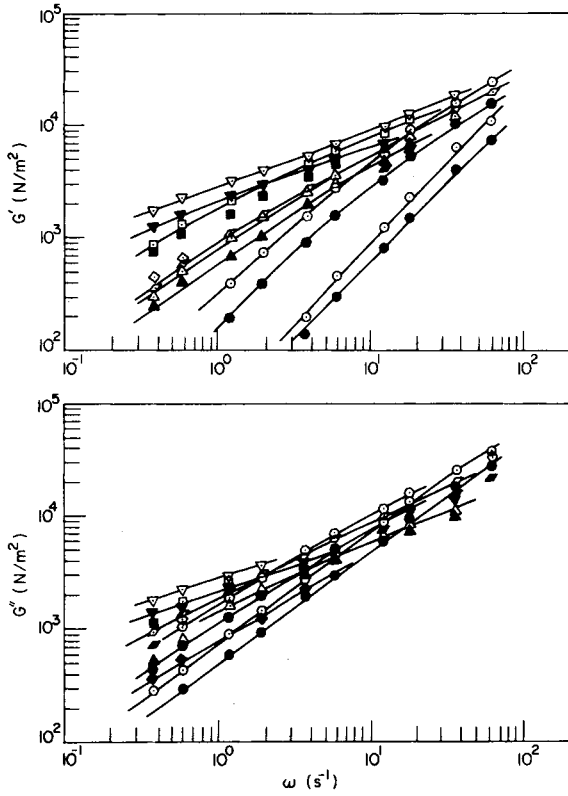


Fig. 23. G' and G'' vs. ω for nylon 6/CXA 3101 blends. Symbols are the same as in Figure 22.

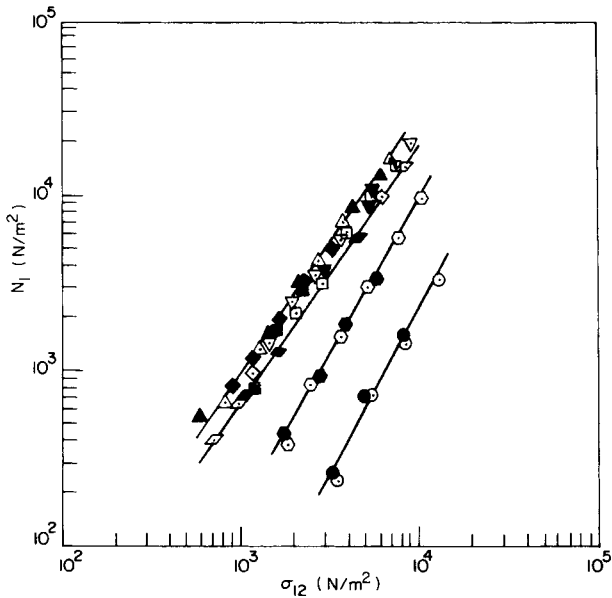


Fig. 24. N_1 vs. σ_{12} for nylon 6/CXA 3101 blends. Symbols are the same as in Figure 22.

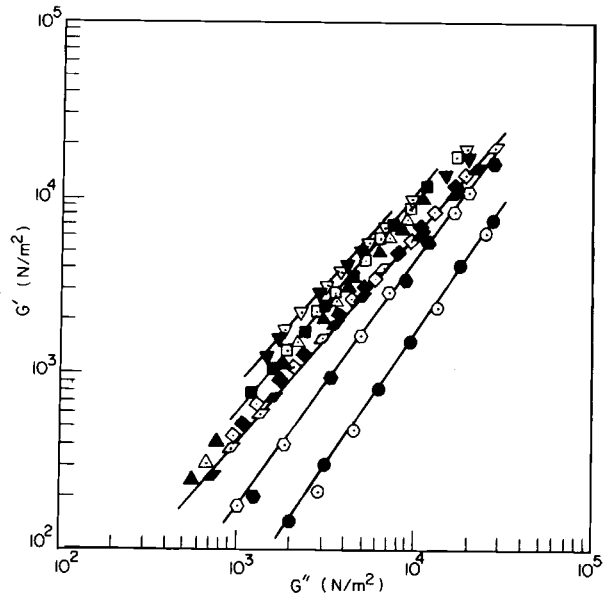


Fig. 25. G' vs. G'' for nylon 6/CXA 3101 blends. Symbols are the same as in Figure 22.

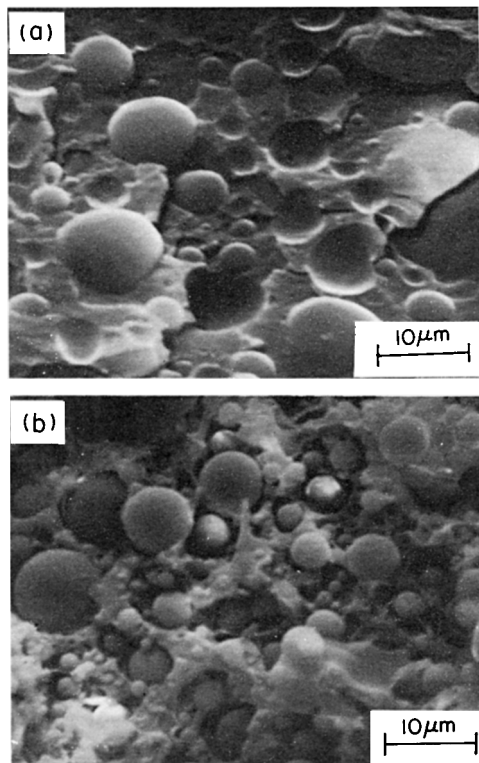


Fig. 26. SEM micrographs of the fracture surface: (a) nylon/EVA = 20/80; (b) nylon/EVA = 60/40.

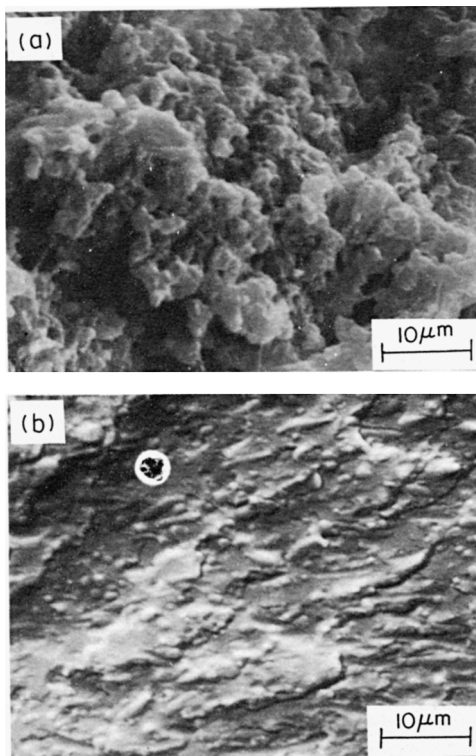


Fig. 27. SEM micrographs of the fracture surface: (a) nylon/CXA 3101 = 20/80; (b) nylon/CXA 3101 = 60/40.

G' on blend composition, regardless of whether a blend system is compatible or not. Moreover, such plots show the dependency of N_1 and G' on temperature.

However, plotting N_1 against σ_{12} , and G' against G'' , give rise to correlations which may become independent of blend composition for compatible blend systems, but dependent upon blend composition for incompatible blend systems. Such plots also yield temperature-independent correlations, regardless of whether a blend system is compatible or not. We therefore suggest that N_1 - σ_{12} and G' - G'' plots be used for determining the rheological compatibility of polymer blend systems.

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