

Blends of Nylon 6 with an Ethylene-Based Multifunctional Polymer.

I. Rheology-Structure Relationships

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Synopsis

An experimental study was conducted to investigate the rheological behavior of a heterogeneous polymer blend system consisting of nylon 6 and an ethylene-based multifunctional polymer (CXA 3101, DuPont Co.). For comparison purposes, we also investigated the rheological behavior of two additional blend systems, namely blends of nylon 6 with a chemically modified polyolefin (Plexar 3, Chemplex Co.) and blends of nylon 6 with ethylene-vinyl acetate copolymer (EVA). We have investigated the thermal and thermomechanical behavior of the blend systems, using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Also, we have attempted to identify the chemical structure of the functional groups present in the CXA 3101 and Plexar 3 resins, using infrared (IR) spectroscopy. This information has enabled us to interpret the observed rheological behavior. Furthermore, we have used both optical and scanning electron microscopies to investigate the state of dispersion of the constituent components in each of the blend systems. We have concluded that, during melt blending, chemical reactions have taken place between carboxyl or anhydride groups present in the CXA 3101 resin and the amino end groups of the nylon 6, forming a graft copolymer which then acted as an "interfacial agent."

INTRODUCTION

The polymer industry has been challenged to produce new polymeric materials by blending two or more homopolymers or copolymers, which are chemically incompatible. To meet the challenge, several attempts have been made by: (1) synthesizing new monomers, polymerizing them, and then blending them with existing polymers; (2) copolymerizing existing monomers and blending them with existing homopolymers; (3) modifying existing polymers by chemical and/or physical methods and blending them with existing homopolymers or copolymers; (4) synthesizing new compatibilizers that, when added to two incompatible polymers, can decrease the size of the dispersed domains and improve the interfacial properties or reactions, and thus the mechanical and/or physical properties desired.

There are some heterogeneous polymer blend systems that have met commercial success; for example, rubber-modified thermoplastics and thermoplastic elastomers. In such polymer systems, the matrix phase of rigid polymer contains the discrete phase of flexible polymer, consisting of globules with a certain size range. In the absence of any chemical reaction between the constituent components in a polymer blend system, it is generally understood today that success in improving physical/mechanical properties in heterogeneous polymer blend system depends on the control of

the domain size of the dispersed phase and on the ability to increase interfacial interactions.

Indeed, during the past decades, an approach has been taken to graft reactive molecules having functional groups onto one polymer (say, polymer A), which will then be melt-blended with another polymer (say, polymer B) that, also, contains functional groups. The rationale behind this approach lies in that, when polymers A and B are melt-blended, the functional groups present in the individual polymers may react chemically to form a graft copolymer. This newly formed graft copolymer would then play the role of an "interfacial agent" promoting adhesion between the matrix and the dispersed phase. A number of patents and scientific literature¹⁻¹¹ have reported such an approach.

More specifically, maleic anhydride was grafted onto polypropylene,^{1,2} polystyrene,³ polyethylene,⁴⁻⁸ or onto ethylene-propylene-diene terpolymer (EPDM rubber).⁹⁻¹¹ The grafted polymer was then blended with various polymers to improve the mechanical properties of the blends.

In recent years, multicomponent/multilayer films or sheets have been commercially produced by means of coextrusion processes.¹² The most important requirement for the production of multilayer constructions is the adhesion between the layers in the coextruded products. In general, two dissimilar thermoplastic resins that would possess, when coextruded, complementary physical and/or mechanical properties, have poor adhesion between the layers. The nylon 6/polyethylene system is one example that may be cited. Specifically stated, nylon 6 is strongly resistant to oils, but weak to moisture; on the other hand, polyethylene has good durability against moisture. Therefore, coextruded two-layer films would be ideal for packaging applications. However, very little adhesion exists between the layers of nylon 6 and polyethylene. To overcome this problem, serious attempts have been made in industry^{5,6,13} to chemically modify polyethylene. Such chemically modified polyolefins have been suggested for use as "tie layer" (or "glue layer") material for coextruding nylon 6 with polyethylene. Indeed, in one of our recent papers,¹⁴ we have reported the adhesion characteristics of coextruded films consisting of nylon 6 and a chemically modified polyolefin (e.g., Chemplex Plexar 3 or DuPont CXA 3095), and concluded that excellent adhesion was observed in the coextruded films.

The coextrusion processes for packaging films and blown containers are currently limited by high scrap rates. In order to make the coextrusion processes economical, one must reprocess the scraps, producing heterogeneous blends. This then requires a serious investigation into the fundamental aspects of the polymer blends produced from the recovery of such scraps. This has motivated us to conduct a fundamental investigation on the relationships that may exist between the rheological behavior and the structure of the constituent components, and between the mechanical properties and the morphology of heterogeneous polymer blend systems, which contain functional groups.

In these two-part papers, we shall present the results of our recent investigation into the rheology-structure relationships and property-morphology relationships, of blends of nylon 6 with an ethylene-based multifunctional polymer.

EXPERIMENTAL

Materials

Blends of nylon 6 with CXA 3101 were prepared, having the following five blend ratios (by weight) of nylon 6/CXA 3101: 80/20, 60/40, 50/50, 40/60, and 20/80. The nylon 6 used is a fiber-spinning grade, which was supplied to us by American Enka Co. The CXA 3101 resin used is known as ethylene-based multifunctional polymer, which was supplied to us by Du Pont de Nemours and Co. According to the resin manufacturer, the CXA 3101 resin, when coextruded, has good adhesion with a number of polymers, including nylon, polycarbonate, polyethylene, polypropylene, polystyrene, and high-impact polystyrene. In our laboratory, we indeed have verified that, when coextruded, the CXA 3101 has very good adhesion with those polymers.¹⁵ In other words, the CXA 3101 resin has been developed for use as the "tie layer" material for coextruding a pair of polymers having little or no adhesion. At present, however, the structure and composition of the CXA 3101 has not been disclosed.

For comparison purposes, two additional blend systems were prepared. They are: (1) blends of nylon 6 with ethylene-vinyl acetate (EVA) copolymer and (2) blends of nylon 6 with Plexar 3. The Plexar 3 (Chemplex Co.) used is known as a chemically modified polyolefin.^{5,13} In each blend system, five blends were prepared, having the same blend ratios as those for the nylon 6/CXA 3101 system. In all cases, a twin-screw compounding machine (Werner and Pfleiderer ZKS-30) was used to prepare the blends.

Thermal and Thermomechanical Analyses

In order to determine the melting behavior of the materials we used a DuPont 910 differential scanning calorimeter (DSC), and for measuring the thermomechanical behavior of the materials we used a DuPont 981 dynamic mechanical analyzer (DMA) in conjunction with a 1090 thermal analyzer. Before measurements were taken, the samples were dried in a vacuum oven at 65°C for 48 h, and measurements were carried out in a nitrogen atmosphere, and at a heating rate of 10°C/min for DSC measurement and 5°C/min for DMA.

Rheological Measurement

A cone-and-plate rheometer (a Weissenberg Model R-16 Rheogoniometer) was used to measure (1) steady shearing flow properties, namely, viscosity (η), shear stress (σ_{12}), and first normal stress difference (N_1), (2) oscillatory shearing flow properties, namely, dynamic viscosity (η'), storage modulus (G'), and loss modulus (G''). These quantities were determined using the expressions described in the literature.^{16,17}

RESULTS

Rheological Behavior

Figure 1 gives plots of first normal stress difference (N_1) vs. shear rate ($\dot{\gamma}$), and Figure 2 plots of storage modulus (G') vs. frequency (ω) at two

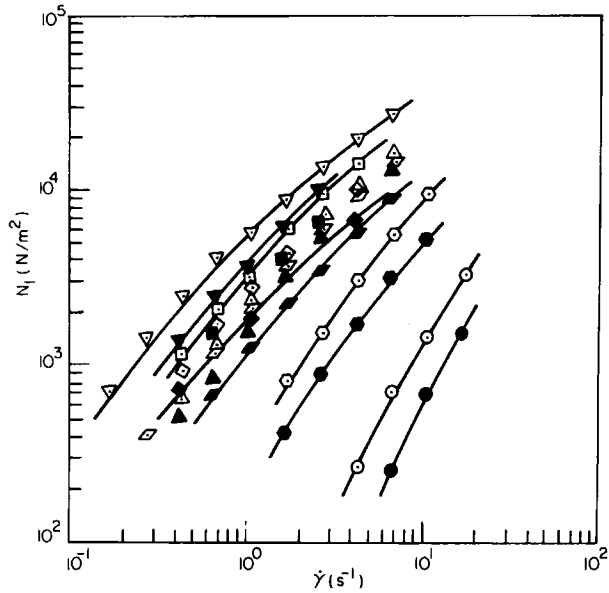


Fig. 1. N_1 vs. $\dot{\gamma}$ for the nylon 6/CXA 3101 blend system: (\odot, \bullet) nylon 6; ($\triangle, \blacktriangle$) CXA 3101; (\square, \blacksquare) nylon/CXA = 20/80; ($\nabla, \blacktriangledown$) nylon/CXA = 40/60; (\diamond, \blacklozenge) nylon/CXA = 50/50; (\square, \blacksquare) nylon/CXA = 60/40; (\odot, \bullet) nylon/CXA = 80/20. Open symbols for 230°C and closed symbols for 240°C.

different temperatures, for the nylon 6/CXA 3101 blend system. It is seen that N_1 and G' decrease with increasing melt temperature and that N_1 and G' of the CXA-rich blends are greater than those of the constituent components of the blends. However, when N_1 is plotted against shear stress

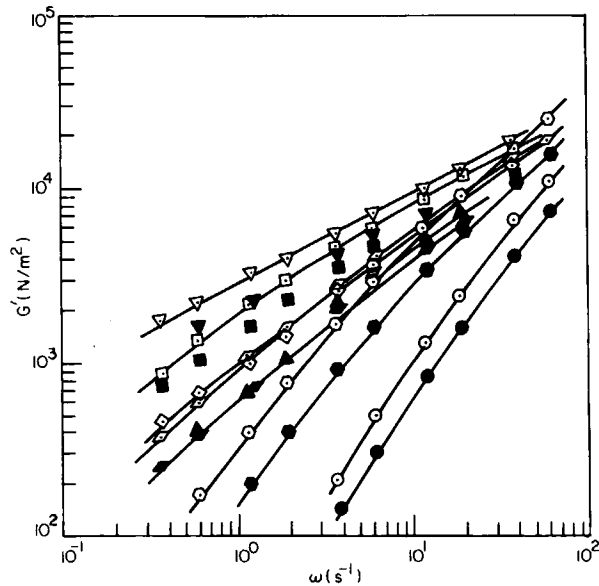


Fig. 2. G' vs. ω for the nylon 6/CXA 3101 blend system. Symbols are the same as in Figure 1.

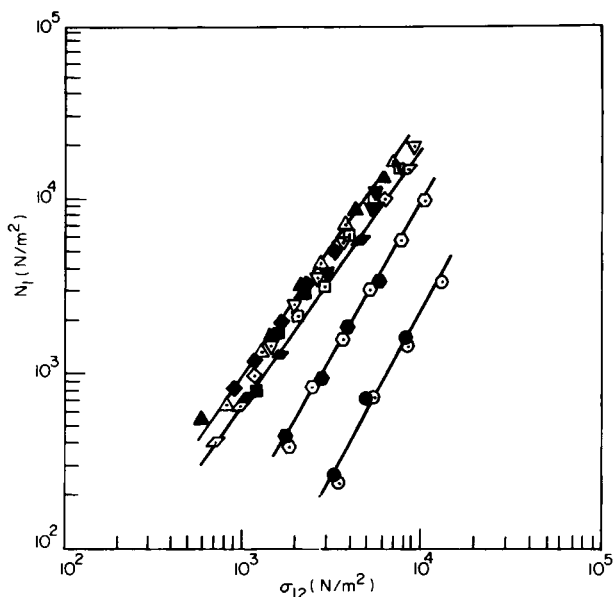


Fig. 3. N_1 vs. σ_{12} for the nylon 6/CXA 3101 blend system. Symbols are the same as in Figure 1.

(σ_{12}), and G' against loss modulus (G''), the dependence of N_1 and G' on temperature is suppressed, as may be seen in Figures 3 and 4. Similar observations, concerning N_1 vs. σ_{12} , have been reported earlier by Han and co-workers¹⁸⁻²⁵ starting over a decade ago, and more recently by White and co-workers.^{26,27} A phenomenological explanation, admittedly qualitative, has been presented in a recent paper by Han and Lem.²² It is worth pointing

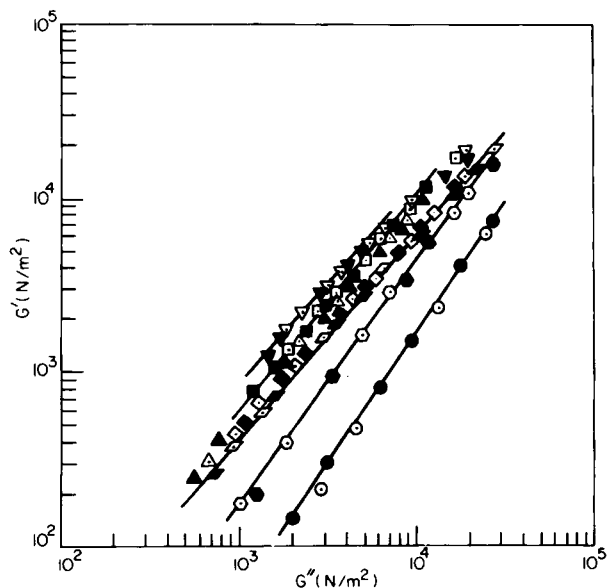


Fig. 4. G' vs. G'' for the nylon 6/CXA 3101 blend system. Symbols are the same as in Figure 1.

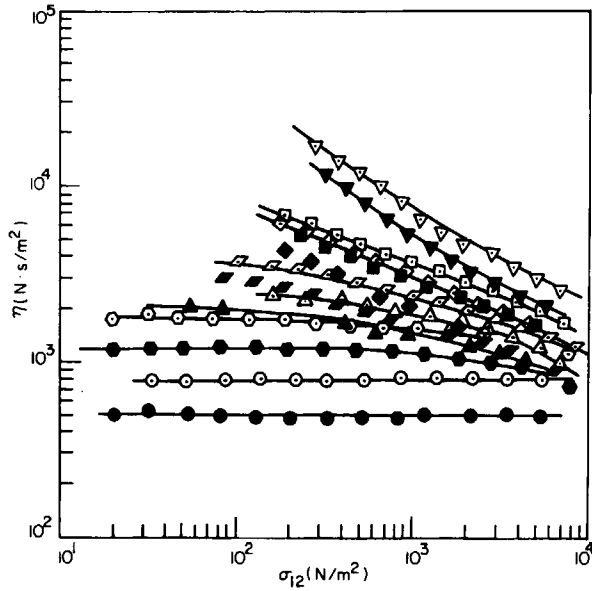


Fig. 5. η vs. σ_{12} for the nylon 6/CXA 3101 blend system. Symbols are the same as in Figure 1.

out, however, that the fact that plots of G' vs. G'' also become independent of temperature has been demonstrated only recently by Han and co-workers.^{22,25}

Note that plots of viscosity (η) vs. shear stress (σ_{12}) exhibit temperature dependency, as shown in Figure 5. As pointed out by Han,^{12,16} the use of

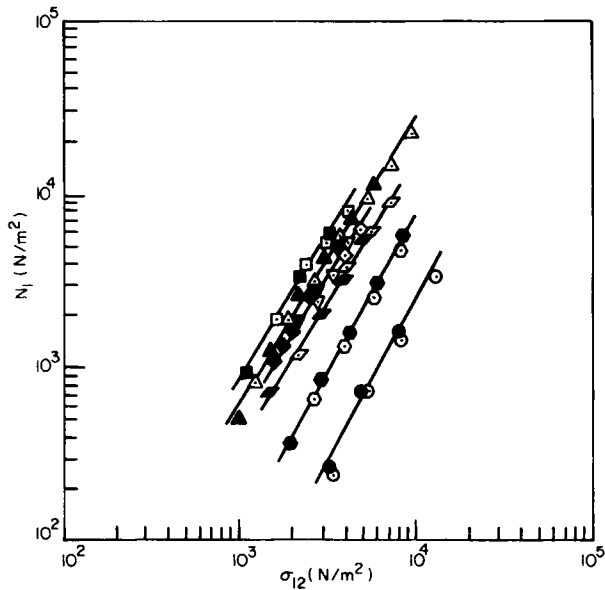


Fig. 6. N_{12} vs. σ_{12} for the nylon 6/Plexar 3 blend system: (\circ, \bullet) nylon 6; ($\triangle, \blacktriangle$) Plexar 3; (\square, \blacksquare) nylon/Plexar = 20/80; ($\nabla, \blacktriangledown$) nylon/Plexar = 40/60; (\diamond, \blacklozenge) nylon/Plexar = 50/50; (\square, \blacksquare) nylon/Plexar = 60/40; (\odot, \bullet) nylon/Plexar = 80/20. Open symbols for 230°C and closed symbols for 240°C.

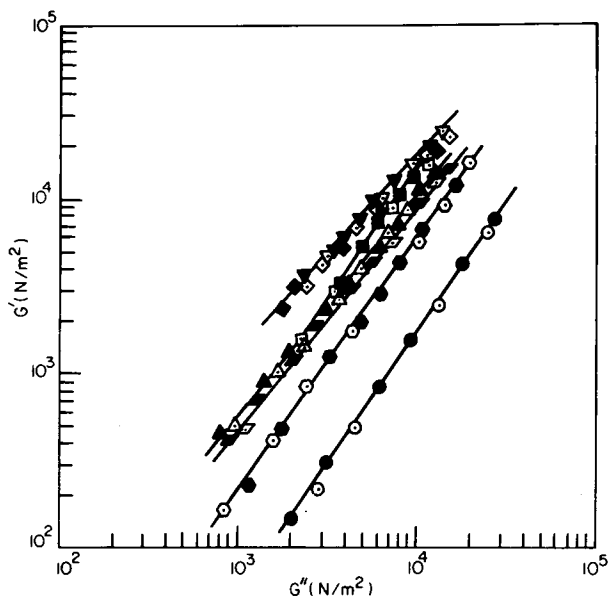


Fig. 7. G' vs. G'' for the nylon 6/Plexar 3 blend system. Symbols are the same as in Figure 6.

σ_{12} is appropriate for correlating the rheological properties of multiphase polymer systems.

Figure 6 gives plots of N_1 vs. σ_{12} , Figure 7 plots of G' vs. G'' , and Figure 8 plots of η vs. σ_{12} at two different temperatures, for the nylon 6/Plexar 3 blend system. Similar plots are displayed in Figures 9–11 for the nylon 6/EVA blend system.

Study of these plots elicits the following comments. First, the temperature

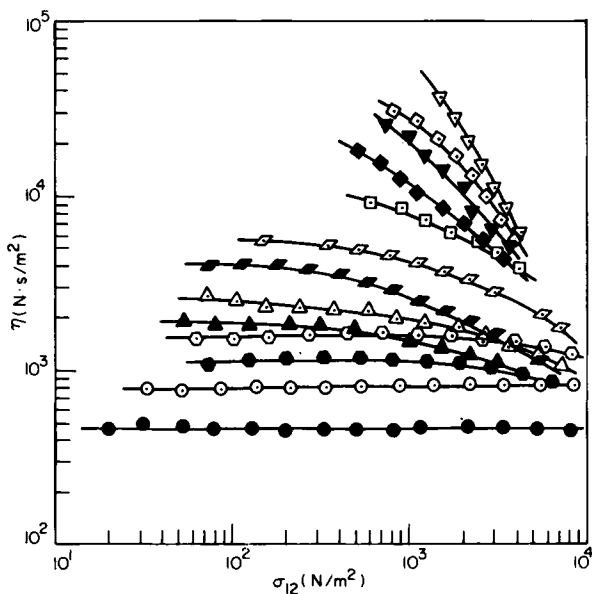


Fig. 8. η vs. σ_{12} for the nylon 6/Plexar 3 blend system. Symbols are the same as in Figure 6.

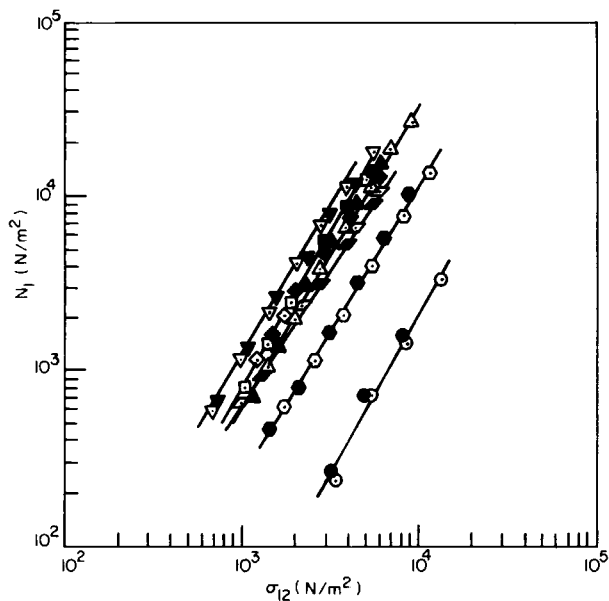


Fig. 9. N_1 vs. σ_{12} for the nylon 6/EVA blend system: (○,●) nylon 6; (△,▲) EVA; (□,■) nylon/EVA = 20/80; (▽,▼) nylon/EVA = 40/60; (◇,◆) nylon/EVA = 50/50; (◻,◼) nylon/EVA = 60/40; (◊,◈) nylon/EVA = 80/20. Open symbols for 230°C and closed symbols for 240°C.

independence of N_1 , when plotted against σ_{12} , and of G' , when plotted against G'' , is believed to be a universal feature of all viscoelastic fluids.^{12,16,18-25} Second, the dependence of N_1 on blend ratio is much stronger in the nylon 6/Plexar 3 and nylon 6/EVA blend systems than in the nylon 6/CXA 3101 blend system (compare Figs. 6 and 9 with Fig. 3). More spe-

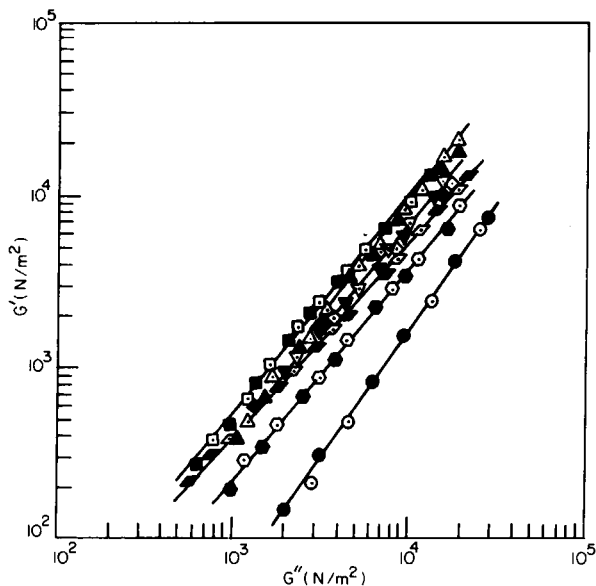


Fig. 10 G' vs. G'' for the nylon 6/EVA blend system. Symbols are the same as in Figure 9.

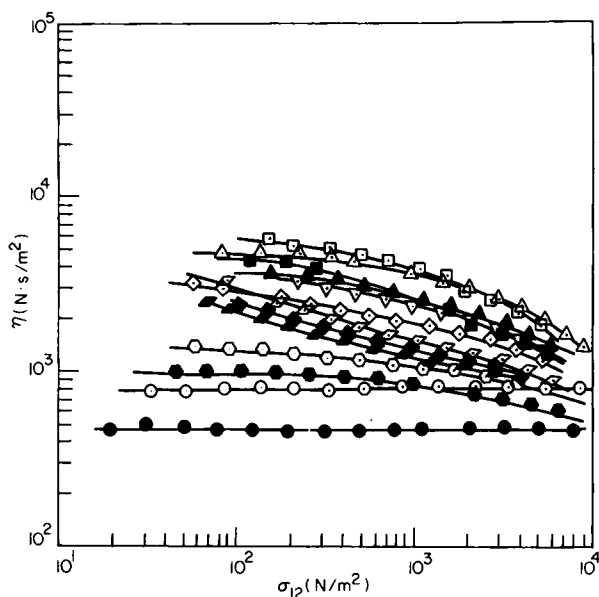


Fig. 11. η vs. σ_{12} for the nylon 6/EVA blend system. Symbols are the same as in Figure 9.

cifically, over the range of σ_{12} investigated, the nylon 6/Plexar 3 = 20/80 and 40/60 blends have N_1 values greater than Plexar 3 (see Fig. 6), and the nylon 6/EVA = 20/80, 40/60 and 50/50 blends have N_1 values greater than EVA (see Fig. 9). On the other hand, as may be seen in Fig. 3, N_1 values for the nylon 6/CXA 3101 blends lie between those of nylon 6 and CXA 3101.

Chemical Structures of CXA 3101 and Plexar 3

An attempt was made to characterize the structures of the CXA 3101, CXA 3095, and Plexar 3, using infrared (IR) spectroscopy. The results of our analysis of the vinyl acetate content and carboxylic acid groups are summarized in Table I. Note that, in our earlier publications,^{28,29} we have reported the rheological behavior, thermal and thermomechanical properties, melt drawability, and mechanical properties of the nylon 6/CXA 3095 blends.

It is seen in Table I that CXA 3095 and Plexar 3 have very similar chemical structures. According to the patent literature,^{5,6} both polymers appear to be blends of ethylene-vinyl acetate copolymer with a polyolefin (e.g., high-density polyethylene and polypropylene), onto which unsaturated carboxylic acids or anhydrides are grafted.

However, the structure of CXA 3101 appears to be quite different from

TABLE I
IR Analysis of CXA 3101, CXA 3095, and Plexar 3

	CXA 3101	CXA 3095	Plexar 3
Vinyl acetate (wt%)	18.1	6.9	6.5
-COOH groups (wt%)	2.1	0.1	0.1

that of Plexar 3 (or CXA 3095), in that CXA 3101 contains about three times as much vinyl acetate as Plexar 3 (or CXA 3095), and about 20 times as many —COOH groups as Plexar 3.

Thermal and Thermomechanical Behavior

Figure 12 displays DSC thermograms of the nylon 6/CXA 3101 blend system. It is seen that nylon 6 has a melting point of 221°C and CXA 3101 has a melting peak at about 88°C . Note that there is *no* noticeable depression of the melting point in this blend system.

Figure 13 shows the results of DMA runs, plots of loss modulus vs. temperature, for the nylon 6/CXA 3101 blend system. We observe three relaxation peaks in nylon 6: an α peak at 71°C , a β peak at -45°C , and a γ peak at -120°C , although the γ peak is not shown in Figure 13. The α peak is believed to be associated with the glass transition, the β peak is due to the segmental motion of the amide groups which are not bonded to other amide groups, and the γ peak is thought to be associated with the crankshaft rotation of the $\text{—(CH}_2)_n$ groups in the main chain of the polyamide.³⁰ The relaxation peaks observed in the nylon 6/CXA 3101 blend system are summarized in Table II.

The following observations are worth noting on Figure 13 and Table II: (1) In the nylon-rich blends, the glass transition temperature (T_g) of nylon 6 is little affected, whereas its β -transition (T_β) seems to have disappeared. Note in Figure 13 that strong shoulders are seen on the low temperature side of the peak and that the T_g of CXA 3101 is shifted toward lower

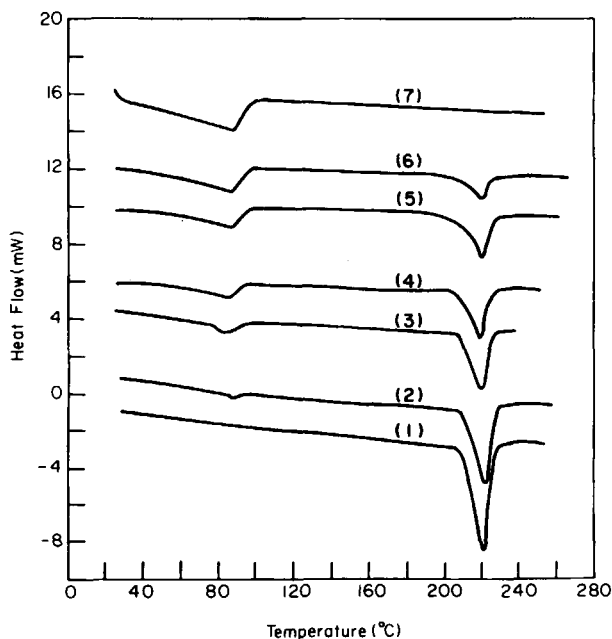


Fig. 12. DSC thermograms of the nylon 6/CXA 3101 blend system: (1) nylon 6; (2) nylon/CXA = 80/20; (3) nylon/CXA = 60/40; (4) nylon/CXA = 50/50; (5) nylon/CXA = 40/60; (6) nylon/CXA = 20/80; (7) CXA 3101.

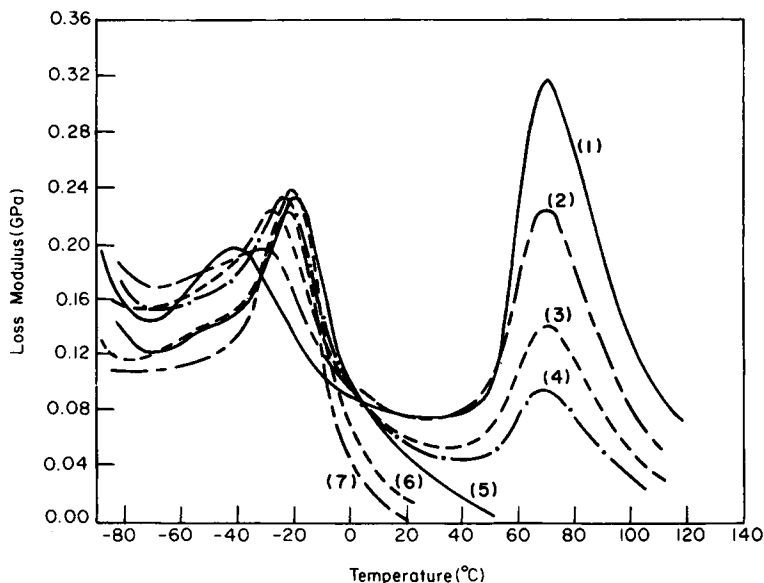


Fig. 13. Loss modulus vs. temperature for the nylon 6/CXA 3101 blend system: (1) nylon 6; (2) nylon/CXA = 80/20; (3) nylon/CXA = 60/40; (4) nylon/CXA = 50/50; (5) nylon/CXA = 40/60; (6) nylon/CXA = 20/80; (7) CXA 3101.

temperatures (-32 and -28°C in the nylon 6/CXA 3101 = 80/20 and 60/40 blends, respectively) and *no* peak representing the T_{β} of nylon 6 is seen; (2) in the CXA 3101-rich blends, *no* peak representing nylon 6 is seen, and the T_g of CXA 3101 (-23°C) is little affected by the presence of nylon 6.

We believe that, during the melt blending of nylon 6 and CXA 3101, chemical reactions have taken place between carboxyl or anhydride groups present in the CXA 3101 and amino end groups of nylon 6. We speculate that the chemical reactions made the β -transition of nylon 6 disappear in the nylon-rich blends. Note that the β -transition of nylon 6 is associated with the existence of polar groups forming hydrogen bonds.

In the beginning, we suspected that the observed disappearance of T_{β} of nylon 6 in the nylon-rich blends might have been due to the overlaps between the T_{β} (-45°C) of nylon and the T_g (-23°C) of CXA 3101. Note that, if a new relaxation peak were created from a shift of the two already existing peaks (i.e., transitions), we would expect to observe a splitting of the re-

TABLE II
Relaxation Peaks of the Nylon 6/CXA 3101 Blends

Blend composition (by weight)	Nylon 6		CXA 3101
	T_g ($^{\circ}\text{C}$)	T_{β} ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)
Nylon/CXA = 100/0	71	-45	—
Nylon/CXA = 80/20	70	—	-32
Nylon/CXA = 60/40	70	—	-28
Nylon/CXA = 50/50	68.5	—	-24
Nylon/CXA = 40/60	—	—	-20.5
Nylon/CXA = 20/80	—	—	-21
Nylon/CXA = 0/100	—	—	-23

laxation peak when the DMA runs were conducted at a lower heating rate. However, we confirmed later that different heating rates (2 and 10°C/min) in the DMA runs gave rise to the same results. Therefore, we have been convinced that possible overlaps between the T_{β} of nylon 6 and the T_g of CXA 3101 could *not* have caused the disappearance of the T_{β} of nylon 6.

Figure 14 displays DSC thermograms of the nylon 6/Plexar 3 blend system. It is seen that, in the nylon-rich blends, three melting peaks (two endotherms and one exotherm) of nylon 6 are observed, giving rise to two distinct melting points, 213 and 221°C. It has been reported³¹⁻³⁵ that nylon 6 has two crystalline structures, a monoclinic α -form crystalline structure having the melting point of 221°C and γ -form crystalline structure having the melting point of 213°C. In view of this, it is clear from Figure 14 that the presence of Plexar 3 has induced the γ -form crystalline structure of nylon 6 in the nylon-rich blends. (Note in Fig. 14 that Plexar 3 has two melting points, 127 and 98°C.) This is not surprising, because Plexar 3 is believed to be a blend of ethylene-vinyl acetate copolymer with a polyolefin onto which maleic anhydride is grafted.⁵ Note further in Figure 14 that the melting behavior of the Plexar-rich blends is little affected by the presence of nylon 6.

Figure 15 presents the results of DMA runs, plots of loss modulus vs. temperature, of the nylon 6/Plexar 3 blend system, and the relaxation peaks observed are summarized in Table III. It is seen that both T_g and T_{β} of nylon 6 are changed little in the nylon-rich blends, and that the T_g of Plexar 3 is changed little in the Plexar-rich blends. As will be shown below, in the nylon-rich blends, Plexar 3 forms the discrete phase and is dispersed in the continuous nylon phase and, in the Plexar-rich blends, nylon 6 forms the

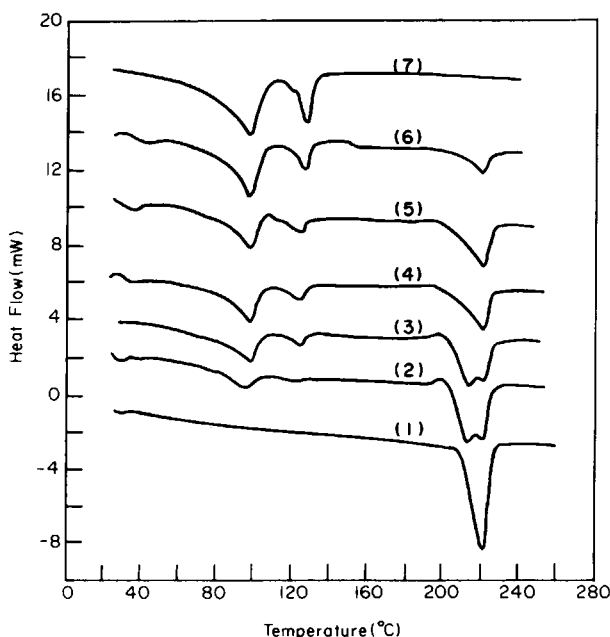


Fig. 14. DSC thermograms of the nylon 6/Plexar 3 blend system: (1) nylon 6; (2) nylon/Plexar = 80/20; (3) nylon/Plexar = 60/40; (4) nylon/Plexar = 50/50; (5) nylon/Plexar = 40/60; (6) nylon/Plexar = 20/80; (7) Plexar 3.

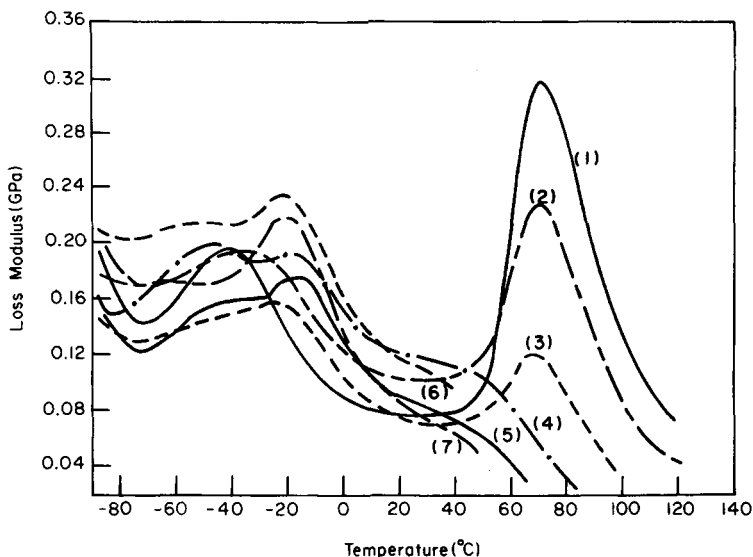


Fig. 15. Loss modulus vs. temperature for the nylon 6/Plexar 3 blend system: (1) nylon 6; (2) nylon/Plexar = 80/20; (3) nylon/Plexar = 60/40; (4) nylon/Plexar = 50/50; (5) nylon/Plexar = 40/60; (6) nylon/Plexar = 20/80; (7) Plexar 3.

discrete phase and is dispersed in the continuous Plexar phase. It is not clear from the DMA runs whether or not chemical reactions have taken place between nylon 6 and Plexar 3.

Figure 16 displays DSC thermograms, Figure 17 displays the results of DMA runs, and Table IV summarizes the relaxation peaks observed of the nylon 6/EVA blend system. It is seen in Figure 16 that *no* noticeable depression of the melting point occurred in this blend system. Figure 17 shows that T_g and T_β of nylon 6 are changed little in the nylon-rich blends in which EVA forms the discrete phase, and that T_g of EVA is changed little in the EVA-rich blends in which nylon 6 forms the discrete phase.

DISCUSSION

The State of Dispersion

Today it is a well-established fact that the state of dispersion in a heterogeneous polymer blend greatly influences its rheological behavior.^{12,16}

TABLE III
Relaxation Peaks of the Nylon 6/Plexar 3 Blends

Blend composition (by weight)	Nylon 6		Plexar 3
	T_g (°C)	T_β (°C)	T_g (°C)
Nylon/Plexar = 100/0	71	-45	—
Nylon/Plexar = 80/20	70	-36	—
Nylon/Plexar = 60/40	68	-41	-23
Nylon/Plexar = 50/50	—	-47	-20
Nylon/Plexar = 40/60	—	-41	-18.5
Nylon/Plexar = 20/80	—	-50	-20.5
Nylon/Plexar = 0/100	—	—	-21

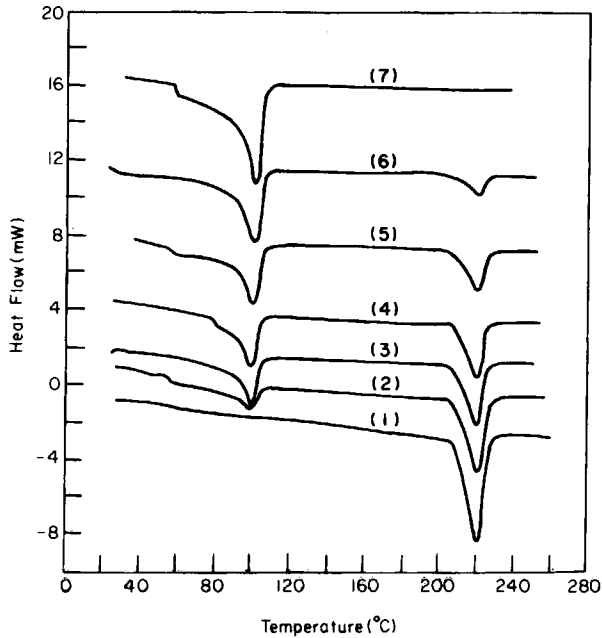


Fig. 16. DSC thermograms of the nylon 6/EVA blend system: (1) nylon 6; (2) nylon/EVA = 80/20; (3) nylon/EVA = 60/40; (4) nylon/EVA = 50/50; (5) nylon/EVA = 40/60; (6) nylon/EVA = 20/80; (7) EVA.

Therefore, it is meaningless to discuss the rheological behavior of heterogeneous polymer blends (or emulsions) without discussing the state of dispersion. It should be pointed out that the state of dispersion in a heterogeneous blend system is determined by the rheological properties of

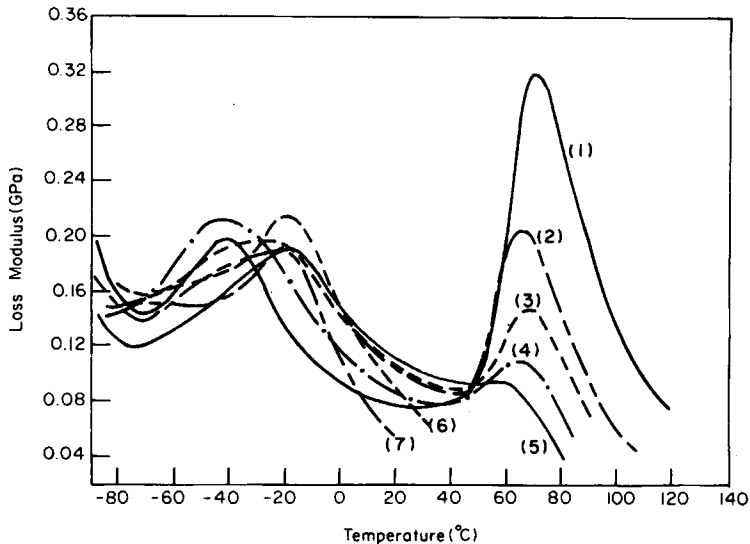


Fig. 17. Loss modulus vs. temperature for the nylon 6/EVA blend system: (1) nylon 6; (2) nylon/EVA = 80/20; (3) nylon/EVA = 60/40; (4) nylon/EVA = 50/50; (5) nylon/EVA = 40/60; (6) nylon/EVA = 20/80; (7) EVA.

TABLE IV
Relaxation Peaks of the Nylon 6/EVA Blends

Blend composition (by weight)	Nylon 6		EVA
	T_g (°C)	T_β (°C)	T_g (°C)
Nylon/EVA = 100/0	71	-45	—
Nylon/EVA = 80/20	67	-45	—
Nylon/EVA = 60/40	67	-42	-22
Nylon/EVA = 50/50	63.5	-42	-22
Nylon/EVA = 40/60	59	—	-20
Nylon/EVA = 20/80	—	—	-20
Nylon/EVA = 0/100	—	—	-22

the constituent components, the blend ratio, and the processing conditions under which the blends were prepared.^{12,16}

In order to investigate the state of dispersion of the three blend systems employed, we have used both optical and scanning electron microscopies. Figure 18 shows representative SEM micrographs of the cryogenically fractured surfaces of compression-molded specimens of nylon 6/CXA 3101 blends. Phase-contrast optical microscopy enabled us to distinguish which of the two constituent components forms the discrete, and which the continuous phase, because SEM was not effective for this purpose. The results of phase-contrast optical microscopy have given us the indication that, in the CXA-rich blends, nylon 6 forms the discrete phase dispersed in the continuous CXA 3101 phase and that, in the nylon-rich blends, CXA 3101 forms the discrete phase dispersed in the continuous nylon phase. In other words, the blend ratio appears to have played a predominant role in determining which of the two components forms the discrete and which the continuous phase.

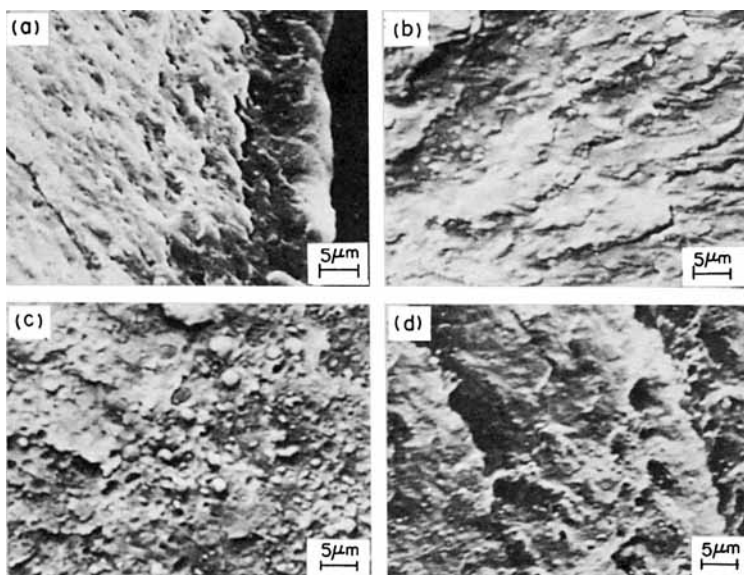


Fig. 18. SEM micrographs of the cryogenically fractured surface of the nylon 6/CXA 3101 blend system: (a) nylon/CXA = 20/80; (b) nylon/CXA = 40/60; (c) nylon/CXA = 60/40; (d) nylon/CXA = 80/20.

It is seen in Figure 18 that the domain size of the discrete phase is rather small (less than $1\ \mu\text{m}$ on the average) and is uniformly dispersed in the continuous matrix. Moreover, the discrete phase appears to have been anchored onto the continuous matrix. The fracture surface does not show sharp edges, indicating clearly that, during melt blending, chemical reactions have taken place between carboxyl or anhydride groups present in the CXA 3101 and amino end groups of nylon 6.

Figure 19 shows representative SEM micrographs of the cryogenically fractured surface of compression-molded specimens of nylon 6/Plexar 3 blends. Again, we found from phase-contrast optical microscopy that the blend ratio has determined which of the two components forms the discrete and which the continuous phase. A close examination of the micrographs in Figure 19 shows evidence that, during melt blending, chemical reactions have taken place between carboxyl or anhydride groups in the Plexar 3 and amino end groups of nylon 6.

Figure 20 shows representative SEM micrographs of the cryogenically fractured surfaces of compression-molded specimens of nylon 6/EVA blends. It is seen that the sizes of the dispersed particles (i.e., EVA particles in the nylon-rich blends, and nylon particles in the EVA-rich blends) are fairly large compared to those in the nylon 6/CXA 3101 blends (see Fig. 18) and nylon 6/Plexar 3 blends (see Fig. 19). It is also seen that, upon fracture, the particles were pulled off clean from the continuous phase, showing *no* evidence that any chemical reaction took place between nylon 6 and EVA. Note that the absence of any chemical reaction between the constituent components in nylon 6/EVA blends is also evident from the independent measurements of thermal and thermomechanical behavior (see Figs. 16 and 17 and Table IV).

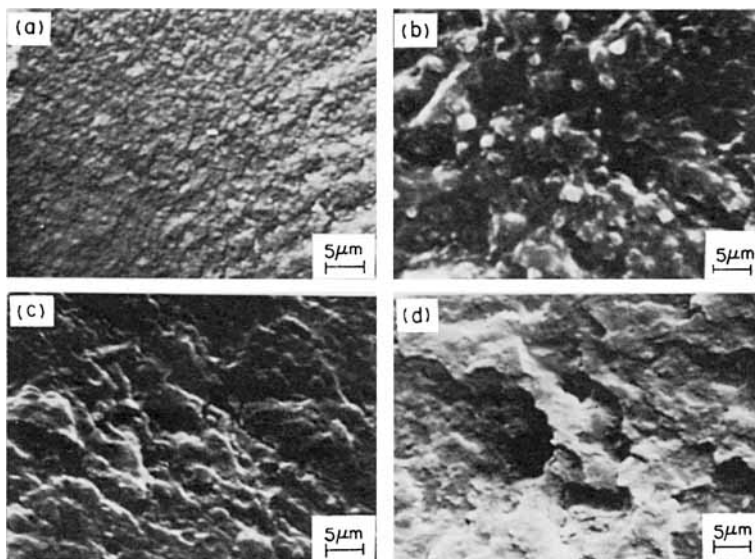


Fig. 19. SEM micrographs of the cryogenically fractured surface of the nylon 6/Plexar 3 blend system: (a) nylon/Plexar = 20/80; (b) nylon/Plexar = 40/60; (c) nylon/Plexar = 60/40; (d) nylon/Plexar = 80/20.

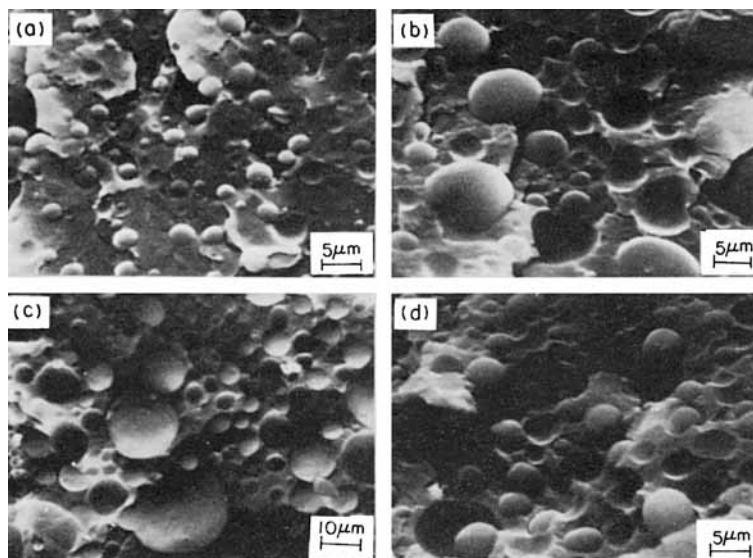


Fig. 20. SEM micrographs of the cryogenically fractured surface of the nylon 6/EVA blend system: (a) nylon/EVA = 20/80; (b) nylon/EVA = 40/60; (c) nylon/EVA = 60/40; (d) nylon/EVA = 80/20.

Compatibilizing Effects of a Graft Copolymer in the Nylon 6/CXA 3101 and Nylon 6/Plexar 3 Blends

It is clearly seen from Figure 20 that the boundaries of the discrete and continuous phases have very sharp interfaces, indicating that no chemical interaction took place, during melt blending, between EVA copolymer and nylon 6. On the other hand, a close examination of Figures 18 and 19 suggests that, in the nylon 6/CXA 3101 and nylon 6/Plexar 3 blends, a graft copolymer was formed and acted as an interfacial (i.e., compatibilizing) agent.

In our investigation, we also conducted a "Molau test"^{36,37} by mixing about 0.1 g of the 80/20 nylon 6/CXA 3101 blend with 5 mL of 80% formic acid. The mixture was first shaken thoroughly in a beaker and then left alone in a graduated test tube for a long period. We repeated the same procedure with blends of nylon 6/Plexar 3, nylon 6/CXA 3095, and nylon 6/EVA. Figure 21 gives the results of our Molau test.

Several hours after the preparation of the mixtures, we observed a phase separation in the 80/20 nylon 6/EVA blend, whereas turbidity persisted in the solution containing the 80/20 nylon 6/CXA 3101 blend, the 80/20 nylon 6/Plexar 3 blend, and the 80/20 nylon 6/CXA 3095 blend [see Fig. 21(b)]. As a matter of fact, turbidity lasted for several months, until we discarded the solutions. Note in Figure 21(b) that, for the nylon 6/EVA blend, the lower part of the test tube (the clear area) represents a solution consisting of formic acid and nylon 6, and the upper part of the same test tube (the dark area) represents a suspension of EVA particles. Note further in Figure 21(b) that, for the blends of nylon 6/CXA 3101, nylon/CXA 3095, and nylon 6/Plexar 3, the lower part of the test tube represents a suspension of CXA

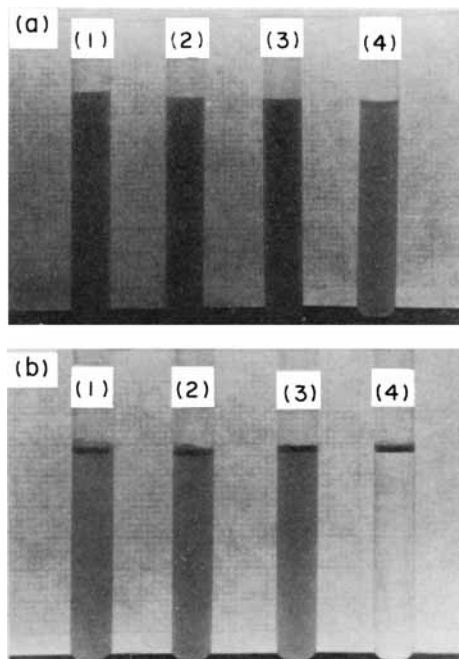


Fig. 21. Molau test solutions consisting of 80% formic acid and each of the following blend: (1) nylon/CXA 3095 = 80/20; (2) nylon/CXA 3101 = 80/20; (3) nylon/Plexar 3 = 80/20; (4) nylon/EVA = 80/20. (a) Right after the solution was prepared, and (b) 8 h after the solution was prepared.

3101 particles (or CXA 3095 or Plexar 3 particles) covered by a graft copolymer which was formed during melt blending.

Earlier, Molau^{36,37} and Illing⁷ conducted similar experiments, using solutions prepared with nylon/polyolefin blends with and without a graft copolymer.

Our Molau test confirms that, during the melt blending of nylon 6 and CXA 3101, chemical reactions have taken place between carboxylic or anhydride groups present in the CXA 3101 and amino end groups of nylon 6. Similar conclusions can be drawn for the nylon 6/Plexar 3 and nylon 6/CXA 3095 blends.

Rheology-Structure Relationships

Let us now examine the observed rheological behavior of the blend systems investigated, from the points of view of the state of dispersion and the chemical reactions taking place between the constituent components in the blends.

The effect of blend composition on η is given in Figure 22 for nylon 6/CXA 3101 blends, in Figure 23 for nylon 6/Plexar 3 blends, and in Figure 24 for nylon 6/EVA blends. These figures are prepared using the results in Figures 5, 8, and 11, respectively. It is seen that η goes through a maximum at a certain blend composition for the nylon 6/CXA 3101 and nylon 6/Plexar 3 blend systems (see Figs. 22 and 23), whereas η increases monotonically with blend composition for the nylon 6/EVA blend system (see

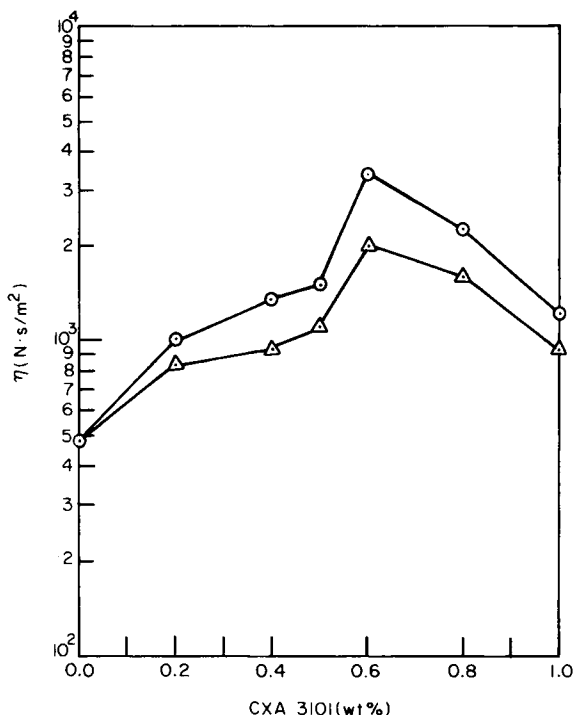


Fig. 22. The dependence of melt viscosity ($T = 240^{\circ}\text{C}$) on blend composition in the nylon 6/CXA 3101 blend system, at two different shear stresses (N/m²): (○) 2000; (△) 5000.

Fig. 24). It is seen that a blend system that underwent chemical reactions during melt blending (i.e., nylon 6/CXA 3101 and nylon 6/Plexar 3 blends) and a blend system that did not (i.e., nylon/EVA blends) differ strongly in their rheological behavior.

A close examination of Figures 5 and 8 reveals that, compared to 20/80 and 40/60 nylon 6/CXA 3101 blends, nylon 6/Plexar 3 blends having the same blend ratios show a very rapid decrease in η as σ_{12} increases. The observed strong dependence of η on σ_{12} is believed due primarily to the segregation of the discrete phase (i.e., nylon particles) suspended in the continuous medium. If the discrete phase were anchored strongly onto the continuous phase, one would not expect to observe such a rapid decrease of η with increasing σ_{12} .

In view of the fact that the number of carboxyl or anhydride groups present in the Plexar 3 is much fewer than in the CXA 3101 (see Table I), we would expect far less extensive chemical reactions and thus a very much weaker interfacial adhesion between the constituent components in the nylon 6/Plexar 3 blends than in the nylon 6/CXA 3101 blends.

The effect of blend composition on N_1 is shown in Figure 25 for the nylon 6/CXA 3101 blend system, in Figure 26 for the nylon 6/Plexar 3 blend system, and in Figure 27 for the nylon 6/EVA blend system. These figures are prepared using the results in Figures 3, 6, and 9, respectively. It is seen that N_1 increases monotonically with blend composition for the nylon 6/CXA 3101 blend system (see Fig. 25), whereas N_1 goes through a maximum

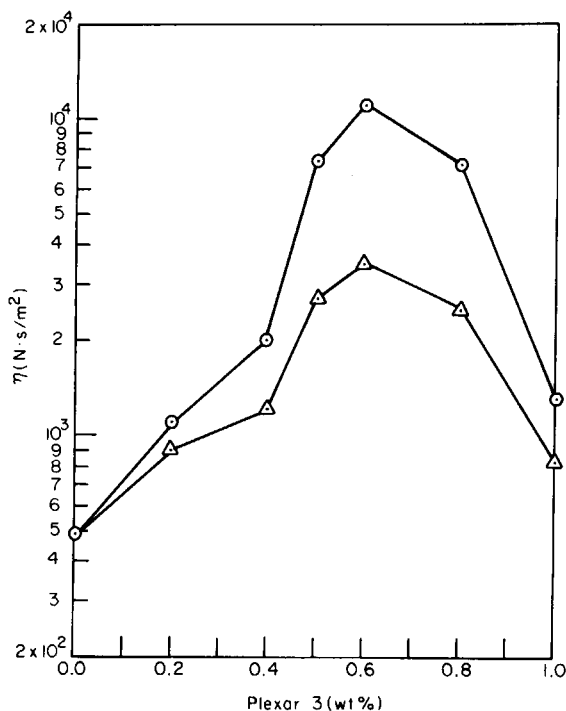


Fig. 23. The dependence of melt viscosity ($T = 240^{\circ}\text{C}$) on blend composition in the nylon 6/Plexar 3 blend system, at two different shear stresses (N/m^2): (○) 2000; (△) 5000.

at a certain blend composition for the nylon 6/Plexar 3 blend system (see Fig. 26) and nylon 6/EVA blend system (see Fig. 27). According to Han,^{12,16} in the absence of any chemical reaction between the discrete and continuous phases, the observed maximum in N_1 in a heterogeneous polymer blend system is attributable to the deformation of the discrete phase, when subjected to shear deformation. Note in Figure 20 that nylon 6/EVA blends contain large discrete phase particles. Note further that the force required to deform a droplet is approximately inversely proportional to its size, and, therefore, for a give external force (or at a given rate of deformation), the smaller the droplet size, the less likely the droplets will deform.

When the discrete phase is anchored onto the continuous phase, one would expect that the deformation of such particles would require much greater forces than those that are freely suspended. One would also expect that the greater the extent of chemical reactions between the discrete and continuous phases, the less likely it is that the discrete phase will deform. In view of the fact that the number of carboxyl or anhydride groups present in CXA 3101 is much greater than in Plexar 3 (see Table I), we would expect more extensive chemical reactions, and thus stronger interfacial adhesion, between the discrete and continuous phases in the nylon 6/CXA 3101 blend system than in the nylon 6/Plexar 3 blend system. We therefore conclude that the observed differences in the normal stress effects between the nylon 6/CXA 3101 blend system and the nylon 6/EVA (or nylon 6/Plexar 3) blend system are attributable, in part, to the differences in the size of the dispersed

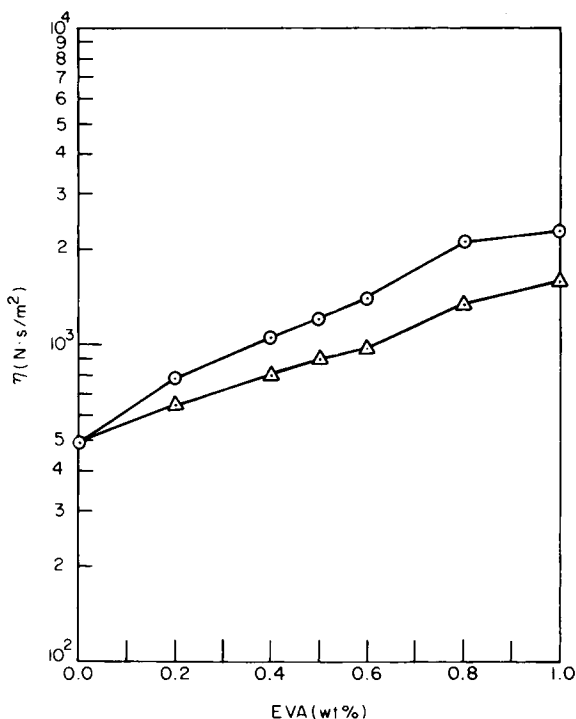


Fig. 24. The dependence of melt viscosity ($T = 240^{\circ}\text{C}$) on blend composition in the nylon 6/EVA blend system, at two different shear stresses (N/m^2): (○) 2000; (△) 5000.

particles in the respective blend systems and, to a great extent, to the differences in the extent (or lack) of chemical reactions that have taken place between the constituent components in the respective blend systems.

Dependence of the Rheological Properties on the Type of Shearing Flow

It is shown in Figures 3, 4, 6, 7, 9, and 10 that 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 shape of the discrete phase (i.e., droplets) greatly influence the rheological properties of heterogeneous polymer blends or emulsions.^{12,16}

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 the 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 affect the shape of the droplet only a little. However, when the droplet viscosity is very small compared to the

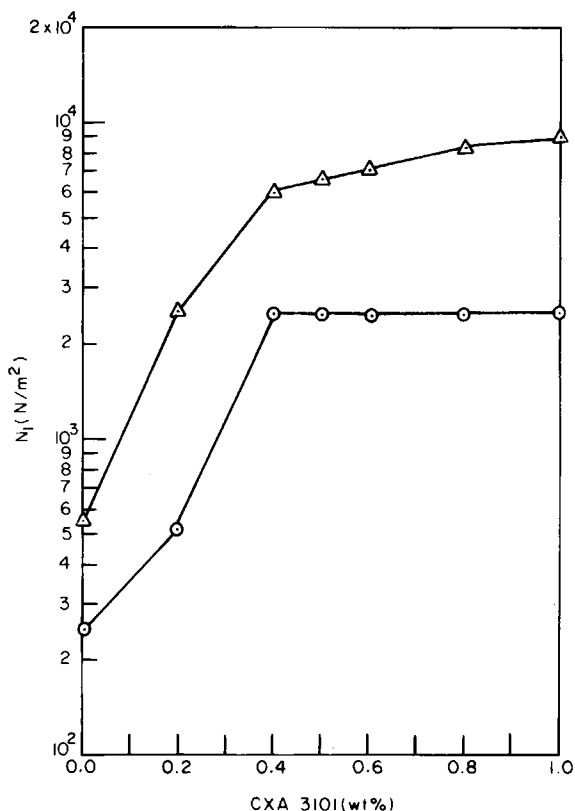


Fig. 25. The dependence of N_1 on blend composition in the nylon 6/CXA 3101 blend system, at two different shear stresses (N/m^2): (○) 2000; (△) 5000.

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 shearing flow properties (i.e., between N_1 and G') for heterogeneous polymer blends, especially when the discrete phase viscosity is small compared to the continuous phase viscosity.

At this juncture, it should be mentioned that, when dealing with heterogeneous polymer blends, the rheological properties, determined with a capillary rheometer, may *not* be correlatable to those obtained with a cone-and-plate rheometer. As pointed out by Han,^{25,38} taking pressure measurements in the reservoir section and making the entrance correction (i.e., the Bagley correction) with the data obtained in a plunger-type viscometer would *not* give correct information on the apparent viscosity of heterogeneous polymer blends, especially when the discrete phase viscosity is small compared to the continuous phase viscosity.

CONCLUDING REMARKS

It has been demonstrated above that blends of nylon 6 and CXA 3101 containing functional groups give rise to unique rheological behavior. The SEM micrographs of the cryogenically fractured surfaces of compression-

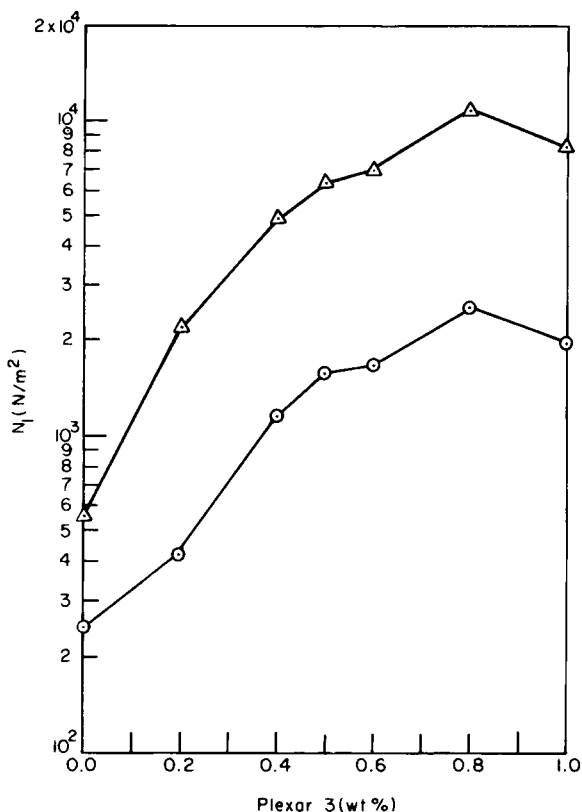


Fig. 26. The dependence of N_1 on blend composition in the nylon 6/Plexar 3 blend system, at two different shear stresses (N/m^2): (○) 2000; (△) 5000.

molded specimens indicate that compatibilizing effects exist at the interface between the discrete and continuous phases in nylon 6/CXA 3101 blends. This observation was confirmed by another experimental technique, the Molau test. The domain size of the discrete phase in the nylon 6/CXA 3101 blends was found to be much smaller than that in the nylon 6/EVA blends. This difference in the state of dispersion is reflected in the rheological properties measured independently. Phase-contrast optical microscopy has shown that blend ratio played a predominant role in determining which of the two constituent components forms the dispersed and which the continuous phase.

The unique rheological behavior and morphological state observed in the nylon 6/CXA 3101 blends are attributable to the chemical reactions that have taken place, during melt blending, between carboxylic or anhydride groups in CXA 3101 and amino end groups of nylon 6. On the basis of the rheological measurements shown in Figures 3 and 6 (and, also, in Figs. 25 and 26), we can conclude that nylon 6/CXA 3101 blends have stronger interfacial adhesion (thus greater compatibilizing effects) than nylon 6/Plexar 3 blends. We attribute this to the fact that CXA 3101 has much a greater number of $-\text{COOH}$ groups than Plexar 3 (see Table I).

The chemical reactions that have taken place between carboxyl or an-

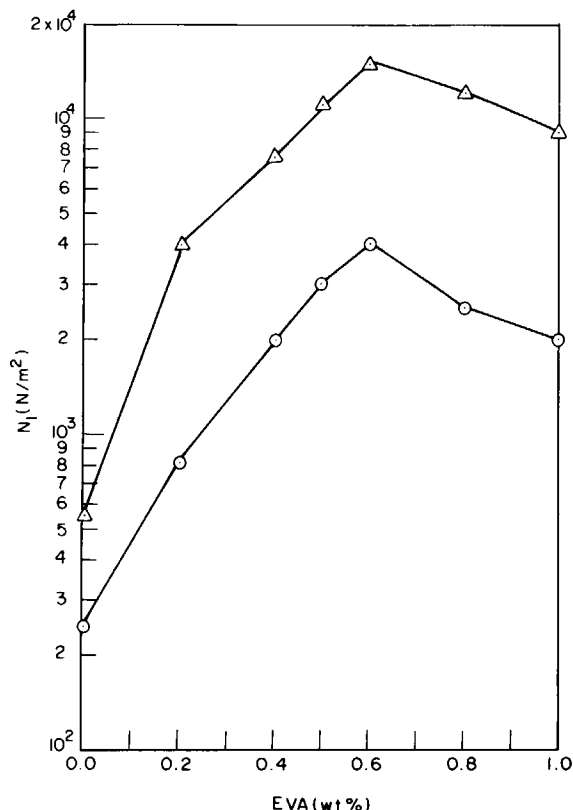


Fig. 27. The dependence of N_1 on blend composition in the nylon 6/EVA 3 blend system, at two different shear stresses (N/m^2): (○) 2000; (△) 5000.

hydride groups present in CXA 3101 and amino end groups of nylon 6 have enabled us to explain the same complex thermal and thermomechanical behavior observed in DSC and DMA runs, namely (1) the shifting of T_g of CXA 3101 toward a lower value and (2) the disappearance of T_β of nylon 6 in nylon 6/CXA 3101 blends (see Table II). It should be pointed out that this observation is very similar to that reported by Venkatesh et al.,³³ who investigated the chemical reactions between nylon 6 and poly(acrylic acid). According to Hoashi and Andrews,³⁹ the T_β peak of nylon 6 will disappear if the number of unbonded amide groups of nylon 6 is decreased, for instance, due to chemical reactions.

It should be pointed out that the disappearance of T_β of nylon 6 was not observed in the nylon 6/Plexar 3 blends (see Table III). We speculate that the number of $-\text{COOH}$ groups present in Plexar 3 is so small (see Table I) that they were not sufficient to affect the β -transition of nylon 6.

The authors wish to acknowledge that the Werner and Pfeleiderer Corp. prepared the blends employed in this study, the American Enka Co. supplied the nylon 6 resin, Du Pont Co. supplied the CXA3101 and EVA resins, and the Chemplex Co. supplied the Plexar 3 resin.

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Received August 17, 1984

Accepted October 4, 1984