

The Phase Behavior, Mechanical, and Rheological Characteristics of Blends Containing Nitrile Polymers and Poly(Ethylene-co-Maleic Anhydride)

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SYNOPSIS

The phase behavior of binary blends of acrylonitrile/methyl acrylate/butadiene terpolymer (B210) and poly(ethylene-co-maleic anhydride) (PEMA) was examined based on thermal analysis and optical microscopy. Miscibility of these polymer blends was recognized over a wide range of compositions. The appearance of phase separation during subsequent heatings above the glass transition temperature (T_g) of these blends was associated with a lower critical solution temperature (LCST) behavior. Rheological characteristics such as shear storage modulus (G'), loss modulus (G'') and complex viscosity have been shown to depend on the amount of PEMA in the blend. Mechanical properties including the tensile strength and flexural modulus also were found to be related to the composition of the blend.

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INTRODUCTION

New plastic materials prepared via polymer blending offer an attractive alternative to the complex synthesis of completely new ones. The major goal in polymer-polymer blending is not to achieve a certain value of a single property, but a combination of characteristics such as maximum use temperature, toughness, ease of fabrication, resistance to chemicals, gas barrier properties, etc.

Mechanical, thermal, rheological, and other properties of a polymer blend depend strongly on its state of miscibility.¹ Blends of two or more different polymers may exist in a completely homogeneous state where their segments are mixed at the most intimate level or they may segregate into distinct phases. Mutual solubility among polymers is rare due to the limited (combinatorial) entropy of mixing. Occasionally, miscibility of two polymers is achieved through specific interchain interactions.²⁻⁵

The objective of this study is to investigate the thermal and rheological behavior as well as me-

chanical properties of blends consisting of acrylonitrile/methyl acrylate/butadiene terpolymer (Barex 210) and poly(ethylene-co-maleic anhydride) alternating copolymer (PEMA). Intermolecular interactions involving specific functional groups of the individual components of this system have been identified in a preliminary investigation.⁶ In this work, several compositions have been prepared and differential scanning calorimetry (DSC) measurements were used to determine the phase behavior of the resulting blend. Compression molded specimens of selected compositions have been tested for mechanical properties according to ASTM standards. The melt rheology under dynamic shear at 210°C was identified as a function of blend composition.

EXPERIMENTAL

Materials

The high nitrile polymer used in this study is a copolymer of acrylonitrile and methyl acrylate (75/25), grafted onto a rubbery copolymer of butadiene and acrylonitrile (70/30), and having a number of average molecular weight (\bar{M}_n) of about 50,000. This material is sold commercially under the trade name

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Table I DSC Data of B210/PEMA Blends

W_2^a	T_g (°C)	ΔC_{pexp} (cal g deg) $\times 10^2$	ΔC_{pcalc} (cal g deg) $\times 10^2$	$\Delta C_{pexp}/\Delta C_{pcalc}$
0.00	86.0	11.1	11.1	1.00
0.10	88.0	8.9	10.73	0.82
0.25	89.0	8.0	10.18	0.78
0.50	91.7 (T_{g1}) 141.9 (T_{g2})	5.5 (ΔC_{p1}) 2.3 (ΔC_{p2})	9.25	0.59 0.24
1.00	145.0	7.4	7.4	1.00

^a W_2 is the weight fraction of PEMA in the blend.

of Barex 210 by BP America, Inc., a subsidiary of British Petroleum Company. Poly(ethylene-co-maleic anhydride) (PEMA) was supplied by Monsanto Co. as EMA-1103 ($\bar{M}_n = 52,900$). Previous work⁶ carried out in our laboratory with PEMA obtained from other sources indicated there are some variations in the phase behavior of blends prepared from different materials. Prior to use, the pure components were carefully dried in a vacuum oven at 80°C for at least 48 h.

TECHNIQUES

A series of Barex 210/PEMA blends were prepared by melt mixing the polymer components in a Brabender Plasticorder. These binary blends were processed for 8 minutes at 185°C and slowly cooled to room temperature. The torque response monitored during mixing generally reached a steady value after 4 min. Sheets of the blends suitable for testing were prepared by heat pressing the sample in a Carver

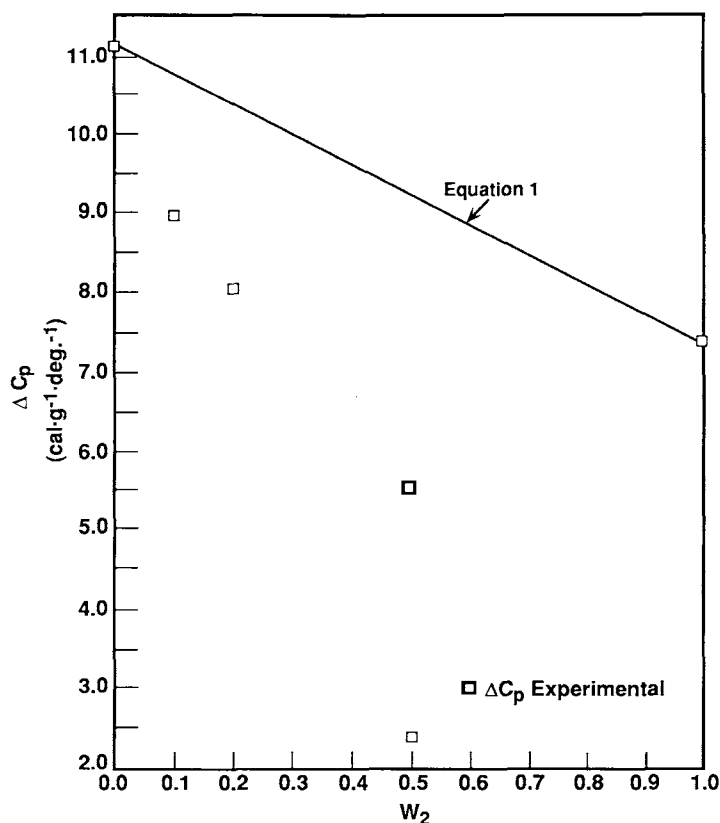


Figure 1 Variation of ΔC_{pcalc} and ΔC_{pexp} with the weight fraction (W_2) of PEMA.

press at 185°C for 3 min followed by slow cooling to room temperature. For comparative analysis, the pure components were subjected to the same thermal/processing history.

The differential scanning calorimetry study was performed on a Perkin-Elmer DSC-4 equipped with a TADS data station. Sample sizes ranged from 7 to 15 mg. Scans were done at a heating rate of 20°C/min. All samples were heated three times with subsequent quenching to ambient temperature. The T_g was defined as the midpoint of the heat capacity transition of the sample. Mechanical testing was performed on a Sintech instrument. Specimens were cut from the compression-molded plaques and subjected to flexural and tensile strength tests.

Thin films of blends were prepared for optical analysis by cutting off a representative portion of the material and placing it onto a circular, glass slide. The slide was then transferred into a chamber within LINKAN heating/cooling stage. The entire device was placed onto a Leitz, optical microscope system. The sample chamber was purged with a steady stream of dry nitrogen gas for about 30 min prior and during the analysis. The sample was imaged using transmitted light. The images were collected under cross-polarized light with a first-order red plate (full wave compensator).

Rheological properties were measured at 210°C on compression-molded plaques of about 2–3 mm in thickness using a computer controlled Rheometrics RMS 605 mechanical spectrometer equipped with a 25-mm diameter parallel plate test fixture set to gap a distance equal to the thickness of each sample plaque.

RESULTS AND DISCUSSION

Thermal Behavior of B210/PEMA Blend Systems

The thermal behavior of B210/PEMA blends was investigated and compared with that of B210 and PEMA. Three compositions: 90/10, 75/25, and 50/50 of B210/PEMA blend were analyzed. The DSC data for these blends are presented in Table I along with the data for individual polymeric components. The state of miscibility of the blends was judged based on the existence of a single glass transition temperature (T_g) or when the glass to rubbery transitions appeared shifted in comparison to those of the pure components. Table I shows the composition-dependent shifts of the glass transition temperature of the B210/PEMA system. The 90/10 and 75/25 B210/PEMA compositions exhibit distinc-

tive T_g 's which are intermediate between those ascribed to the pure components. The 50/50 B210/PEMA composition displays two glass transition temperatures. These two transitions are significantly shifted, indicating the presence of mixed phases. The phase characterized by a T_g at 92.7°C is a B210-rich phase while the one exhibiting a T_g at 141.3°C is a PEMA-rich phase.

The interpretation of the 50/50 B210/PEMA blend T_g data, however, is more complex. These data represent values obtained at the third heat. During the DSC study, it has been observed that the 50/50 B210/PEMA blend exhibits a single T_g at the first and second heat, but starts to show two T_g 's at subsequent heatings. This was an indication that the blend is susceptible to phase separation on heating. Therefore, it is important to follow the heat capacity changes of these blends at T_g . It is expected that if the blend composition is present as a single phase, the heat capacity change (ΔC_p) occurring through the transition should be a simple mass-weighted av-

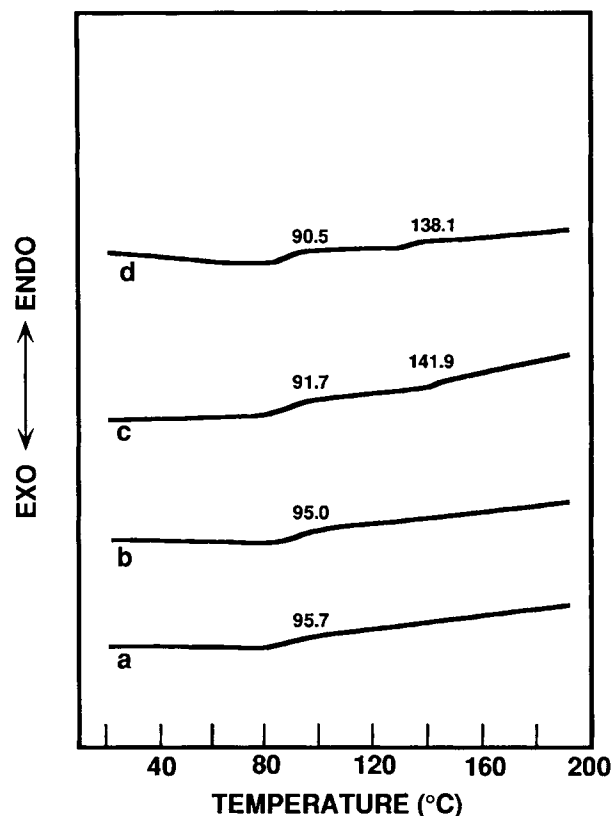


Figure 2 DSC traces of the 50/50 B210/PEMA composition at different heating cycles: (a) first heating scan; (b), (c) and (d), second, third, and fourth heating scan, respectively. Each time the sample was annealed at 180°C for 20 minutes and then quenched to room temperature.

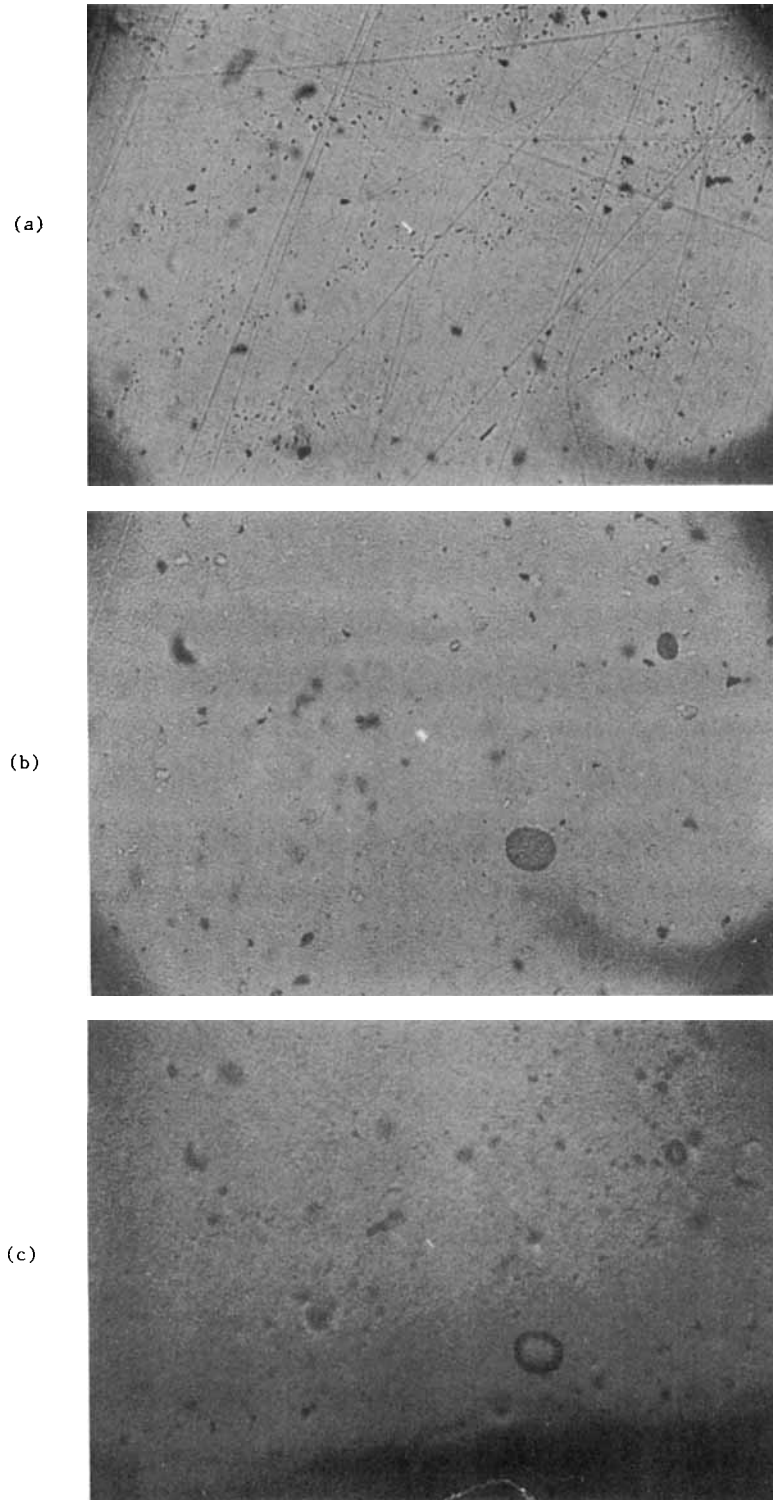
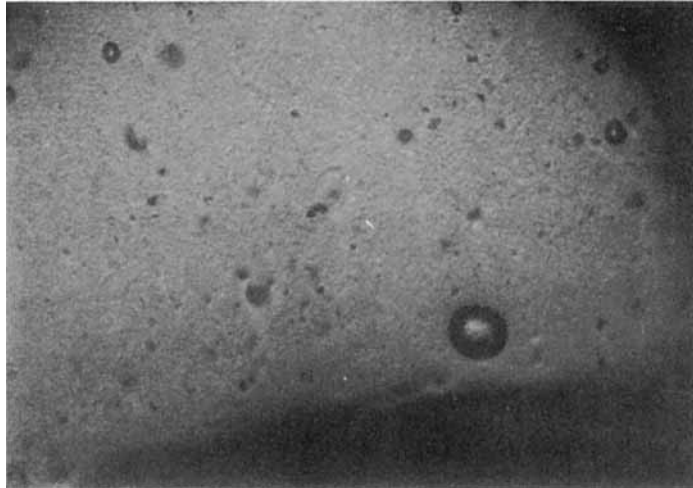
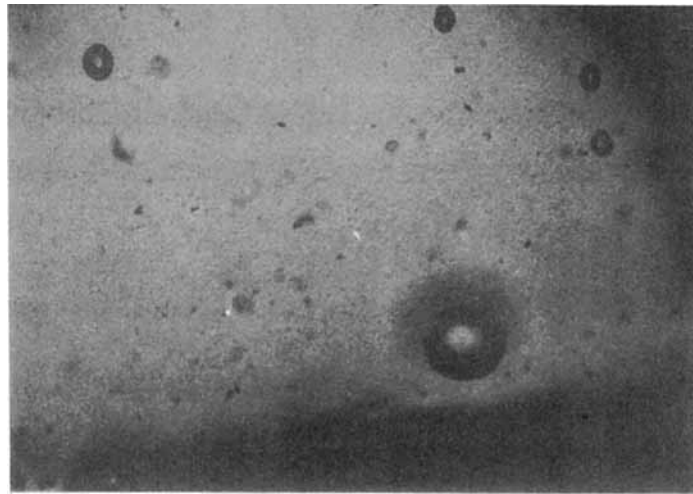


Figure 3 Morphology of the 50/50 B210/PEMA composition at different heating and cooling stages: (a) ambient temperature, (b) heated at 10°C/min to 130°C, (c) heated at 5°C/min to 180°C, (d) heated at 5°C/min to 200°C, (e) maintained at 200°C for 5 min (f) cooled at 5°C/min from 200°C to 50°C, (g) heated at 10°C/min from 50°C to 190°C, (h) heated at 10°C/min from 190°C to 210°C, (i) cooled at 10°C/min from 210°C to ambient temperature.

(d)



(e)



(f)

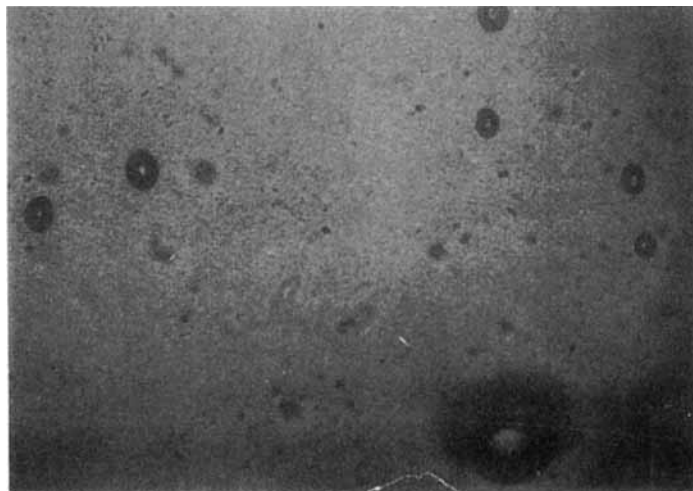
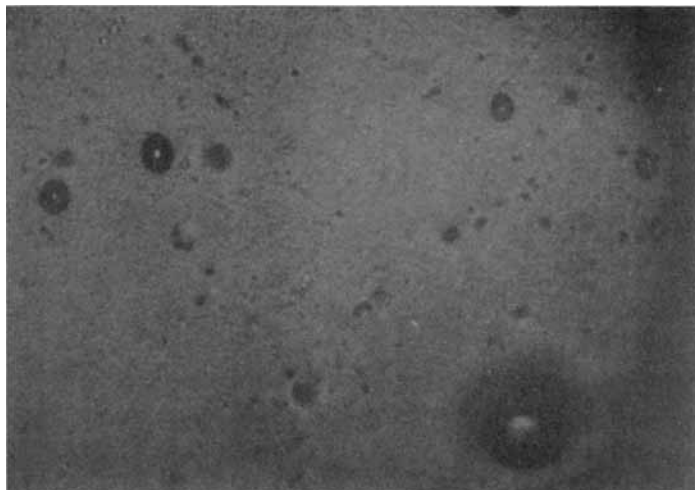
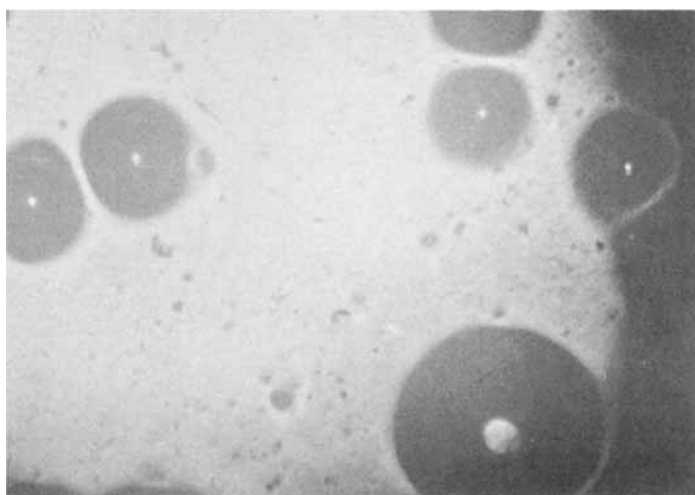


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(g)



(h)



(i)

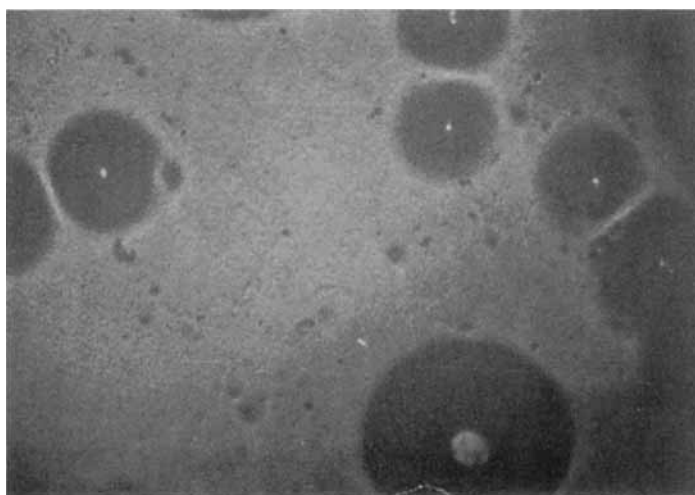


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erage of the components.⁷ The ΔC_p of the blend compositions was calculated from the following relationship:

$$\Delta C_p = W_1 \Delta C_{p1} + W_2 \Delta C_{p2} \quad (1)$$

where W_1 , and W_2 , ΔC_{p1} , and ΔC_{p2} are the weight fractions and heat capacity changes of B210 and PEMA, respectively. The calculated ΔC_p values for the blends are shown in Table I together with the corresponding values obtained experimentally.

A graphic representation of the variation of both $\Delta C_{p\text{calc}}$ and $\Delta C_{p\text{exp}}$ with the composition of the blend is illustrated in Figure 1. It should be noted that in miscible blends in which specific interactions exist,^{8,9} the experimentally determined T_g values and ΔC_p values, as well, are not necessarily identical with the calculated values assuming volume additivity of pure components. In our case, both the experimentally obtained T_g ⁶ and ΔC_p are lower than the calculated values. The decrease in ΔC_p is more pronounced as the composition of the blend reaches the 50/50 ratio. At this stage the blend becomes susceptible to phase separation and exhibits a dual-phase behavior. The ΔC_p experimentally measured for both phases is much below the calculated ΔC_p value which may indicate that not all the material is participating in these transitions. It can be speculated that at 50/50 B210/PEMA ratio the inter-phase mixing did not extend over the entire range of molecular weights present in the sample. On heating, demixing involving high-molecular weight molecules of the polydisperse components could occur easier since the thermodynamic restrictions for miscibility are more severe. In order to illustrate this phase separation at heating, typically defined as a lower critical solution temperature (LCST) phenomenon,¹⁰ a thermally induced phase separation experiment was conducted via DSC for the 50/50 B210/PEMA composition. The experiment consisted of heating the homogeneous 50/50 B210/PEMA blend at a rate of 20–180°C and maintaining it at this temperature for 20 minutes. This period was found to be long enough to attain a distinct phase separation in the sample without inducing degradation of either component at that temperature. After annealing, the sample was rapidly quenched to room temperature and subsequently scanned at 20°C/min. The results of quenching from 180°C and rerunning the thermograms of the 50/50 B210/PEMA blend sample are shown in Figure 2. By heating repeatedly the 50/50 B210/PEMA blend, the initial monophasic system exhibiting a single T_g starts to phase separate and the appearance

of two T_g 's can be observed. The broadness of these transitions suggests the existence of microheterogeneity due to the different segmental environments. At cooling, this composition does not return to its homogeneous state. This implies that the blend displays lower critical solution temperature (LCST) behavior. Further, this conclusion is substantiated from the results obtained from a hot stage optical polarized microscopy study.

Thermal Optical Microscopy of the 50/50 B210/PEMA Blend

Figure 3 (a) and (b) shows the morphological changes in the 50/50 B210/PEMA blend as it is heated from ambient temperature to 130°C at a rate of 10°C/min. It can be clearly observed that at room temperature, the morphology is characteristic for a homogeneous blend. As the temperature increases to 130°C the first sign of phase separation appears in the form of small circles dispersed throughout the entire system. Figure 3(c) represents the morphology of the blend further heated to 180°C at a rate of 5°C/min. No significant changes from the previous images can be observed. More small circles indicating the tendency of the system to phase separate are visible at this temperature. By increasing the temperature to 200°C the size of phase separated regions becomes visibly larger Figure 3(d). This is more evident when the sample is maintained for 5 minutes at 200°C Figure 3(e). At this latter stage of phase separation, the phase domain seemed to grow in size and developed in small spheres. The phase separation behavior induced by heating is not reversible under these kinetic conditions.

As Figure 3(f) indicates, the morphology of the blend remains unchanged by cooling the sample at 5°C/min from 200 to 50°C. The polymer blend sample was then heated again at 10°C/min to 210°C. Until the temperature reaches 190°C, the size of phase-separated domains remains approximately the same. At 190°C Figure 3(g) extension of these zones can be observed. This trend is further developed by increasing the temperature to 210°C. The formation of large spheres of one phase throughout the matrix can be observed in Figure 3(h). Again, once these spheres form they remain in the structure even after cooling to room temperature Figure 3(i).

Dynamic Shear Rheology of B210/PEMA Blends

Figure 4 illustrates the shear storage modulus G' of 90/10, 75/25, and 50/50 B210/PEMA blends as a

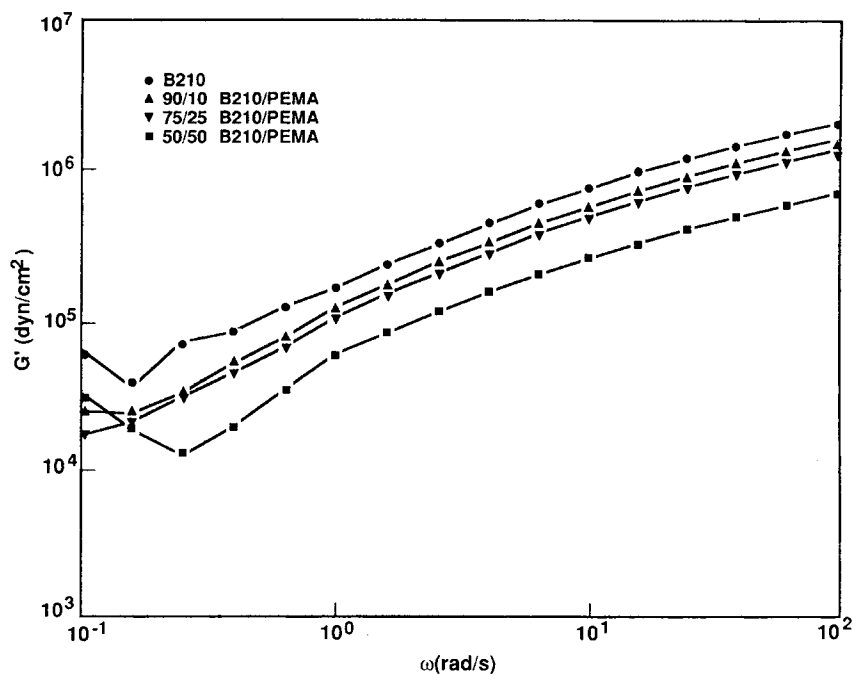


Figure 4 Log storage modulus (G') versus log frequency (ω) under oscillatory shear conditions at 210°C for B210 and 90/10, 75/25, and 50/50 B210/PEMA compositions.

function of frequency ω . The experiment was conducted at 210°C using a sinusoidal shear strain amplitude of 5% over a frequency range of 0.1–100 rads/s (0.016–15.9 cycles/s). It can be observed from

Figure 4 that the effect of increasing the PEMA level in the blend is to decrease G' at a given frequency.¹¹ In other words, the rigidity and the resistance to deformation of B210/PEMA blends are compo-

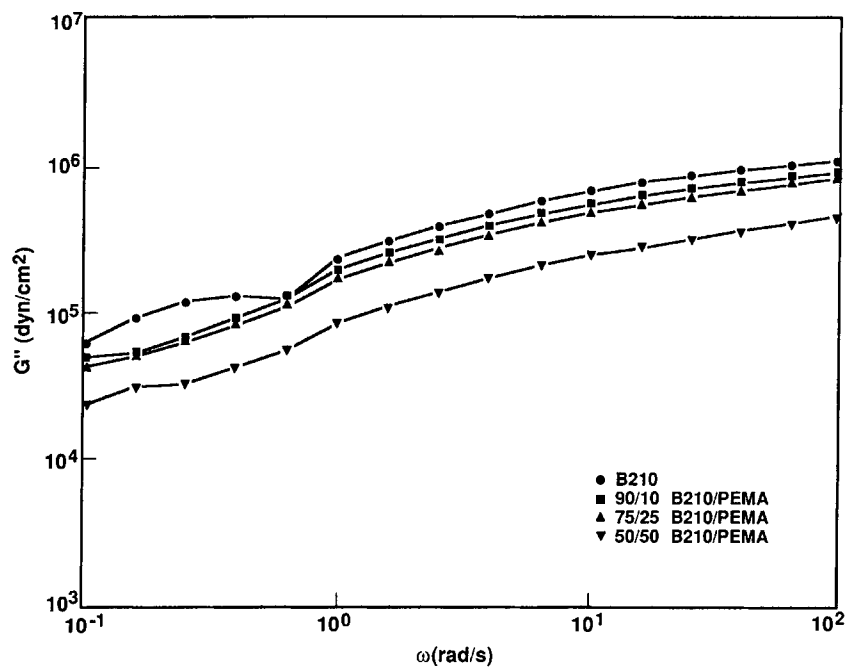


Figure 5 Log loss modulus (G'') vs. log frequency (ω) under oscillatory shear conditions at 210°C for B210 and 90/10, 75/25, and 50/50 B210/PEMA compositions.

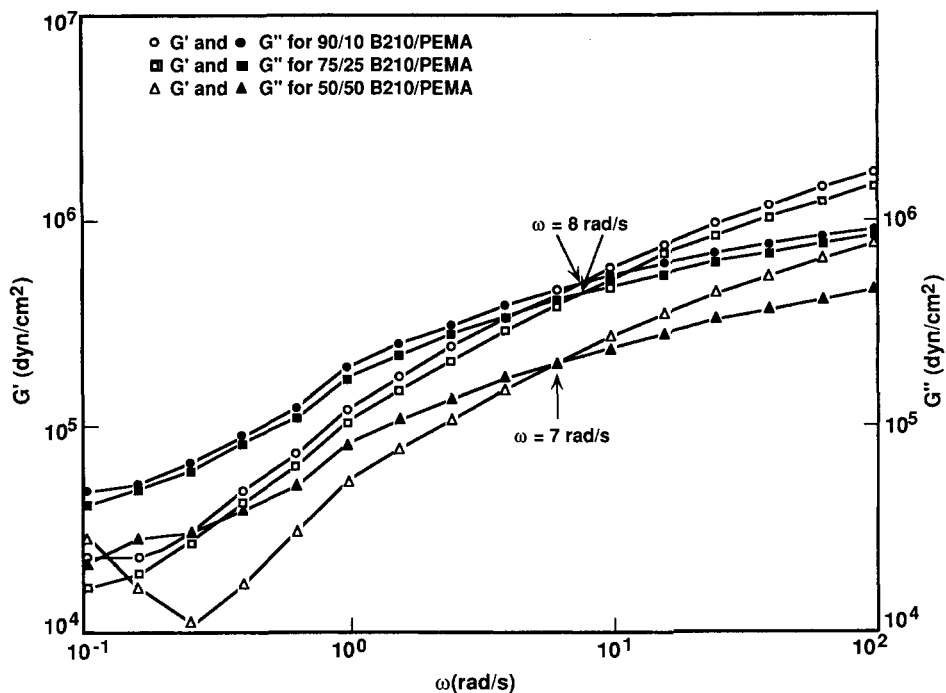


Figure 6 Log storage modulus (G') and log loss modulus (G'') vs. log frequency (ω) for 90/10, 75/25, and 50/50 B210/PEMA compositions.

tionally dependent, declining with increasing the level of PEMA. Figure 5 represents the loss modulus G'' as a function of ω under the same test conditions

as in Figure 4. Again, the effect of increasing the PEMA content is to reduce the magnitude of G'' at any given frequency.¹²⁻¹⁵ These data show that the

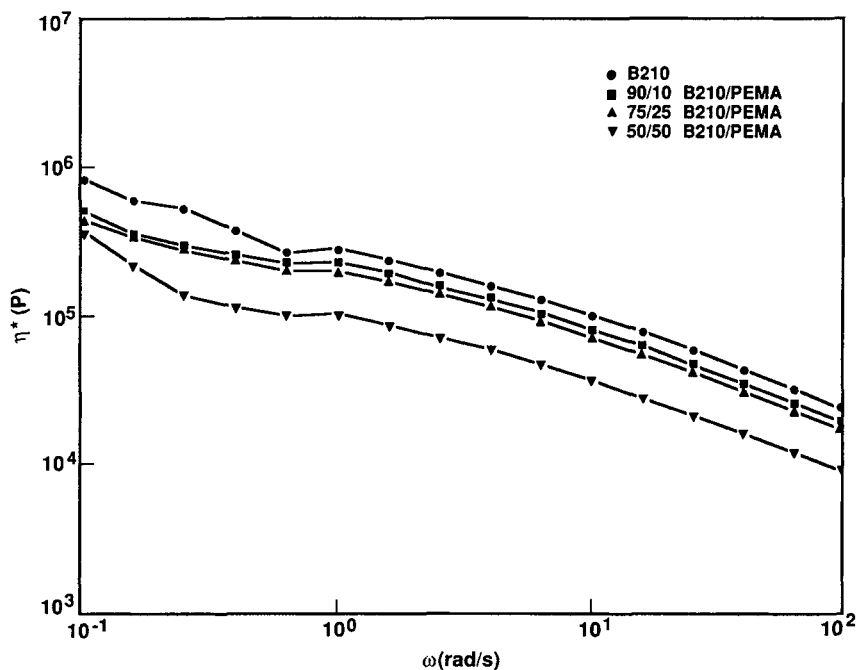


Figure 7 Log complex viscosity (η^*) as a function of log frequency (ω) for 90/10, 75/25, and 50/50 B210/PEMA compositions.

loss of useful mechanical energy through dissipation as heat reaches the lowest values when the blend contains 50% PEMA. The source of the dip observed at low frequencies cannot be explained at this time.

Figure 6 represents both storage modulus, G' and loss modulus G'' as a function of frequency for each composition studied. It can be observed that the transition to the deformation associated with long range forces is similar (8 rads/s) for both, 90/10 and 75/25 B210/PEMA blends. In contrast, 50/50 B210/PEMA composition exhibits this transition at 7 rads/s. Figure 7 illustrates a plot of the magnitude of the complex viscosity as a function of frequency. The influence of PEMA in decreasing the melt viscosity of B210 is clearly revealed for each blend composition. The molecular process associated with this behavior can be described in terms of reduced entanglement and increased mobility of B210 chains induced by the presence of miscible PEMA chains. This effect is more pronounced at higher levels of PEMA. The 75/25 B210/PEMA composition is almost two times less stiff and viscous in comparison with the blend containing 10% PEMA. The same trend is observed by going to 50/50 B210/PEMA blend which is significantly lower in stiffness and viscosity than the other compositions by approximately a factor of three.

Mechanical Properties of B210/PEMA Blends

The dependence of mechanical properties on the amount of components in the blend is shown in Table II. The flexural strength of B210 increases with a limited increase of the amount of PEMA in the blend and shows a maximum at about 25% of PEMA. For compositions containing higher levels of PEMA, no improvement in flexural strength is observed, and the blends reflect properties characteristic to PEMA individual component. The flexural strength of the 50/50 B210/PEMA composition is much below that of B210 constituent.

In contrast to the variation in flexural strength, the flexural modulus of B210/PEMA blends steadily

increases with the increase of the percentage of PEMA. The 75/25 B210/PEMA blend shows an improvement of 10% in comparison with B210 single component. This trend continues and a 20% improvement in flex modulus is observed at 50/50 ratio of the two partners.

Tensile strength shows a similar trend as the flexural strength. It is worth mentioning that the interesting synergism that has been observed for some B210/PEMA compositions for both strength and modulus also is reported for other miscible blends.¹⁶⁻¹⁸ This type of response is believed to be the result of the contraction of free volume or densification on mixing. For our blends, this assumption is supported by other experimental evidences, especially density measurements which show that the densities of B210/PEMA miscible blends are higher than calculated values based on volume additivity of the components.

CONCLUSIONS

The phase behavior of binary blends of acrylonitrile/methyl acrylate/butadiene terpolymer (B210) and ethylene-maleic anhydride alternating copolymer (PEMA) was investigated based on thermal analysis, optical microscopy, and mechanical testing. Miscibility of this polymer blend system was found over a wide range of compositions. A lower critical solution temperature (LCST) behavior was recognized. According to the DSC and thermal optical microscopy studies the B210/PEMA miscible blends are susceptible to phase separation when repeatedly heated above 180°C. Once the phase separation commences, it is maintained when the sample is quenched to room temperature. This LCST behavior is an important aspect which has to be taken into account when a blend is processed and is designed to be used for certain type of applications. These results show that blends of nitrile polymers and PEMA (at 50/50 ratio) phase separate on heating

Table II Some Mechanical Properties of B210/PEMA Blends

W_2^a	Flexural Strength (psi) $\times 10^{-2}$	Flexural Modulus (psi) $\times 10^{-3}$	Tensile Strength (psi) $\times 10^{-1}$
0.00	150.5	511.0	874.4
0.10	164.9	530.1	929.7
0.25	177.4	560.1	728.8
0.50	96.9	619.3	480.5

^a W_2 is the weight fraction of PEMA in the blend.

above 180°C which make melt processing difficult if a homogeneous mixture is desired. The data also indicate that this restriction is less stringent at lower levels of PEMA where a broader range of temperatures is available for processing.

The rheological characterization of B210/PEMA blends also indicates that the rigidity and the resistance to deformation of B210/PEMA blends are dependent on composition. Both the shear storage modulus (G') and the loss modulus (G'') are reduced at any given frequency with the increase of the PEMA content. The transition point to macroscopic deformation is the same for 90/10 and 75/25 B210/PEMA compositions while the 50/50 blend exhibits this transition at lower frequency.

The enhancement of some mechanical properties of blends containing low levels of PEMA has been observed. The composition dependence of the tensile strength and flex modulus for these blends exhibit characteristics of mechanical compatibility expected for miscible and partially miscible polymer systems.

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