Compatibilization and Characterization of Blends of Styrene–Maleic Anhydride Copolymer with Modified Polyethylenes

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ABSTRACT: Potentially reactive blends of styrene–maleic anhydride (SMAH) with ethylene/methyl acrylate/glycidyl methacrylate (E-MA-GMA) and nonreactive blends of SMAH with ethylene/methyl acrylate (E-MA) were produced in a Brabender batch mixer and in a corotating twin-screw extruder. The products were characterized in terms of rheology, morphology, and mechanical properties to understand the reaction characteristics between anhydride/epoxy functional groups. Storage modulus, G', loss modulus, G'' and complex viscosity, η^* of the reactive blends were higher than those of nonreactive ones. At 25% E-MA-GMA content, maximum in η^* was obtained for the reactive blends. The reactive blends showed finer morphology than the nonreactive ones at all concentrations studied. Mechanical characterization showed that reactive SMAH/E-MA-GMA blends had higher tensile strength, % strain at break, and tensile modulus than the nonreactive blends for all corresponding modified polyethylene contents. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 790–797, 2001

Key words: styrene–maleic anhydride; modified polyethylene blends; reactive processing; chain branching; compatibilization

INTRODUCTION

The development of useful polymeric products by reactive extrusion has been the subject of several investigations.[1–3] Polymer mixing processes involving chemical reactions between the functional groups of polymers create more stable and useful end products by improving the adhesion between blend components.[2] Compatibilization reactions that take place between functional groups require the correct selection of reactants to obtain the desired product. Common melt phase compatibilization reactions can occur between potentially reactive groups such as epoxy, alcohol, anhydride, amine, isocyanate, oxazoline,[3–7] and others.

There are various characterization techniques that can be employed to obtain more information on the properties of polymeric products, and also to understand the reaction characteristics between the functional groups of polymer blends. For example, measurements of rheological and mechanical properties are important characterization techniques conventionally applied.[8–12] Morphological (Scanning Electron Microscopy)

techniques are also important in confirming the occurrence of a reaction in a system and in supporting the other characterization methods.[13–15] By measuring viscoelastic properties such as storage modulus, G', loss modulus, G'', and complex viscosity, η^*, it is possible to obtain information on the effects of reactions on molecular weight (MW), molecular weight distribution (MWD), and chain branching.[8,9,16,17] Nakajima and Harrell[10] and Graessley[16] emphasized the effects of MW, MWD, and branching on the rheological properties of polymers due to the entanglements present in their systems. Mechanical properties such as tensile strength, percent strain at break, and tensile modulus are strongly affected by the morphology of the blend and the adhesive strength between the blend components.[18–21] Both of these factors are directly related to interfacial reactions that may take place in the system.

In this study, blends with anhydride/epoxy functionalized components were studied. The complex reactions of these groups, although documented for curing of epoxy resins, have not been extensively studied in polymer blends. The objectives of this study are to investigate the mixing/reaction characteristics of anhydride/epoxy-functionalized blends produced in a batch mixer and in a twin-screw extruder, and characterize the blends in terms of rheological, morphological, and mechanical properties. Two modified polyethylene polymers, namely ethylene/methyl acrylate/glycidyl methacrylate (E-MA-GMA) and ethylene/methyl acrylate (E-MA), which are similar in their rheological and mechanical properties but differ in the presence of the reactive epoxy functionality, were used. E-MA does not have epoxy functionality, and is denoted as polyethylene nonfunctionalized (PE-NF), whereas E-MA-GMA does, and is denoted as polyethylene functionalized (PE-F). In this manner, the effects of mismatched rheological and mechanical properties of the modified polyethylene component during dispersive mixing can be eliminated to a certain extent allowing for the analysis of the effects of the epoxy/anhydride reaction irrespective of the rheology of the blend components.

EXPERIMENTAL

Materials

SMAH (Dylark 232, Nova Chemicals) was used as the main component. The other materials used in this study were the terpolymer of ethylene/methyl acrylate/glycidyl methacrylate, E-MA-GMA (Lotader AX8900), and the copolymer of ethylene/methyl acrylate, E-MA (Lotryl 28 MA 07), both materials manufactured by Elf-Atochem. Hydrated zinc acetate ($ZnAc_2 \cdot 2H_2O$) was used as a potential catalyst for the reactive blend. The melt-flow index values of SMAH, E-MA-GMA (PE-F), and E-MA (PE-NF) are reported as 1.9, 6.5, and 6–8 g/10 min, respectively. GMA content of the PE-F was reported as 7.25 wt %.

In batch mixing experiments, 5, 10, 15, and 50 wt % of PE-F or PE-NF were mixed with SMAH in the presence of 1 wt % catalyst. The blends used in extrusion experiments contained 5, 25, and 50 wt % of PE-F or PE-NF with SMAH and 1 wt % of $ZnAc_2 \cdot 2H_2O$.

Processing Experiments

Batch mixing experiments were carried out in a Brabender Plasticorder (PL-2000). The processing conditions were: mixing temperature of 180°C, rotor speed of 60 rpm, and total mixing time of 20 min. Materials were added to the bowl in the following order: initially, SMAH, followed by PE-F or PE-NF after melting of SMAH at approximately 4 min, and finally hydrated zinc acetate right after PE-F or PE-NF addition. Nitrogen blanket was provided to prevent degradative oxidation.

Extrusion experiments were carried out in a 30-mm corotating twin-screw extruder (ZSK-30, Krupp Werner & Pfleiderer). The processing conditions were as follows: the temperature profile along the extruder was kept constant as 210°C. The screw speeds studied were 60, 150, and 220 rpm. By contrast to the batch mixer, the feed addition protocol involved premixed components that were fed to the hopper of the extruder.

Characterization Experiments

A rheometrics mechanical spectrometer, RMS 800, was used to measure the viscoelastic properties such as the storage modulus, G', the loss modulus, G'', and the complex viscosity, η^* at 180°C. Samples were prepared at 180°C by compression molding in the form of disks having a 25-mm diameter and 2-mm thickness. The fixtures used for the rheological experiments were parallel disks having a 25-mm diameter. In the oscillatory shear experiments, the frequency applied was in the range of 0.1 rad/s to 100 rad/s at a constant strain amplitude of 10%.
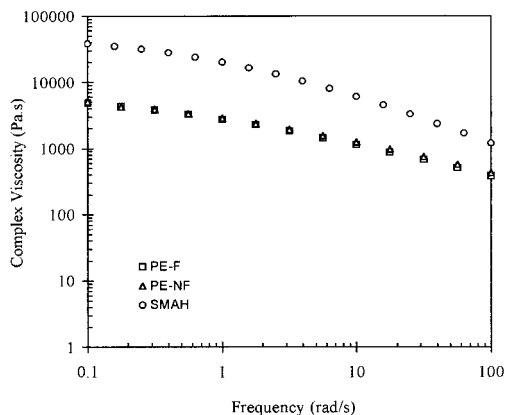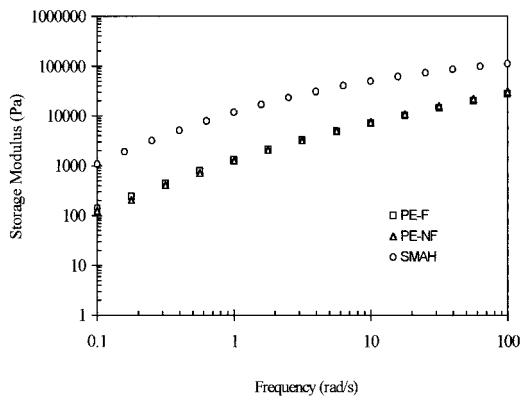
Figure 1 Complex viscosity of the blend components at 180°C.

Figure 3 Loss modulus of the blend components at 180°C.

Scanning Electron Microscopy (SEM) was used for morphological analysis. The materials were fractured at liquid nitrogen temperatures, and the surfaces of the fractured materials were analyzed by SEM (LEO 982).
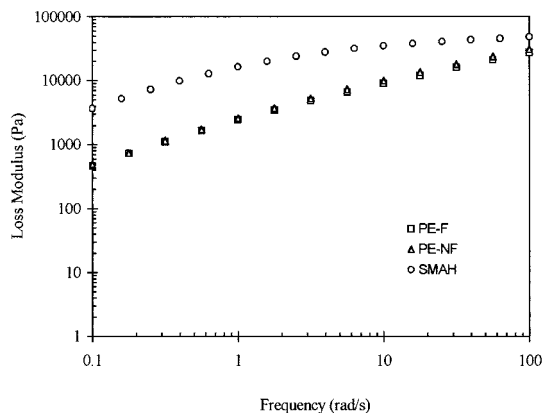
Tensile properties such as tensile strength, percent strain at break, and tensile modulus were measured by using a Tinius Olsen mechanical tester on five rectangular samples, approximately 0.5 mm thick, 1.27 cm wide, and 6.35 cm long. Samples were cut from compression-molded plaques prepared at 180°C for 1 min.

RESULTS AND DISCUSSION

Figures 1–3 show the complex viscosity, η^*, storage modulus, G', and loss modulus, G'', of PE-F, PE-NF, and SMAH, respectively. It is observed that SMAH has higher η^*, G', and G'' values than

either PE-F or PE-NF. The viscous and elastic properties of PE-F and PE-NF in the melt state are very similar to each other. The differences between the values of SMAH and modified polyethylenes are approximately an order of magnitude in the frequency range from 0.1 rad/s to 100 rad/s at 180°C.

In addition, the blend components were analyzed in the solid state, as shown in Figure 4. The solid-state storage modulus of PE-F and PE-NF also change similarly with respect to temperature. Thermal transitions occur at 120°C for SMAH and approximately at −25°C for PE-F and PE-NF. The storage modulus values of SMAH are higher than those of PE-NF and PE-F, whereas PE-NF and PE-F have similar storage modulus, even at the solid state.

In preliminary experiments, potentially reactive blends (SMAH/PE-F) and nonreactive blends

Figure 2 Storage modulus of the blend components at 180°C.
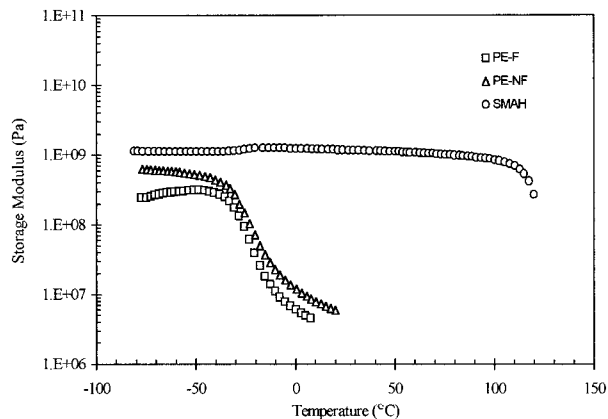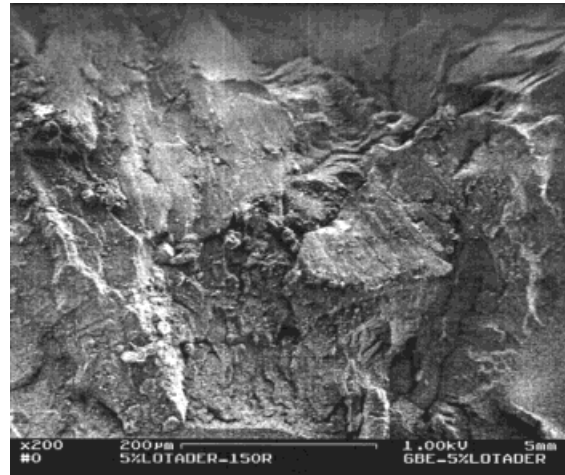

Figure 4 Solid-state storage modulus of the blend components.
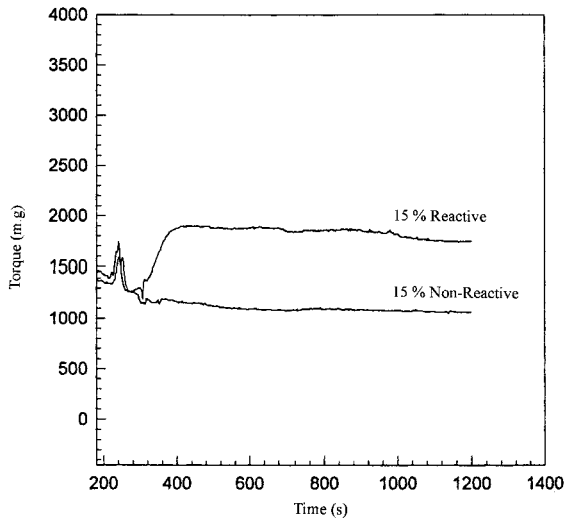
Figure 5 Torque vs. time behavior of batch mixed blends with 15% modified polyethylene content.

Figure 7 SEM of the blend with 5% PE-F. Magnification ×200.

(SMAH/PE-NF) in the presence of hydrated zinc acetate were prepared in a Brabender batch mixer to observe the viscosity changes due to reactions. Figure 5 shows the torque vs. time traces of the blends with 15% PE-F and 15% PE-NF. When PE-F is added to the SMAH melt, the torque values increase with respect to time, indicating that chain extension/branching reactions occur in the system, resulting in higher MW and viscosity. On the other hand, the addition of PE-NF to the SMAH melt at approximately 4 min does not significantly change the torque behavior of the system. In the reactive system, the main reaction is between the epoxy and the dicarboxy-

clic acid groups, the latter formed by opening of the MAH groups by water molecules either from the catalyst or from the environment, including moisture in the resin.

Several reaction possibilities make the reaction characteristics of the system very complex. The primary reaction occurs between the epoxy functional group and the anhydride or carboxyl functionality. Moreover, the reaction of epoxy with alcohol formed from the main reaction results in ether formation. The secondary alcohol could also react with carboxyl group to form esters.
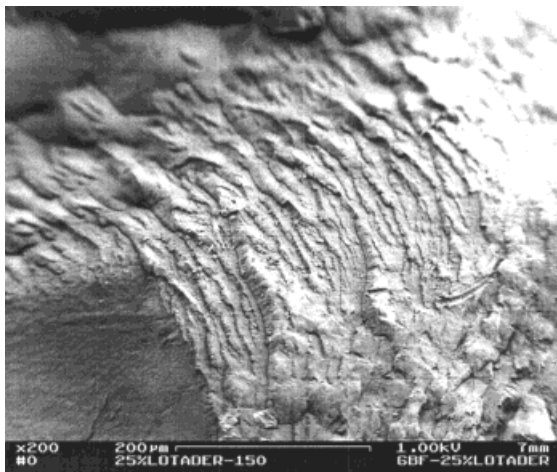
Figures 6–11 are the SEMs of extruded blends of 5, 25, and 50% PE-F or PE-NF with SMAH in
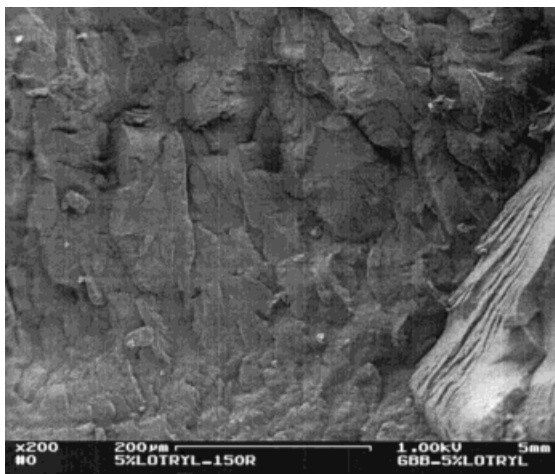
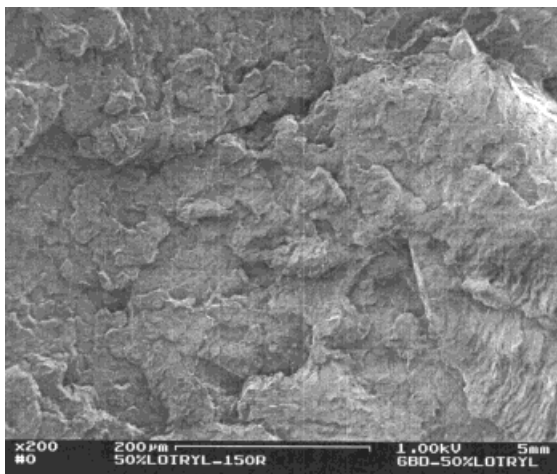**Figure 6** SEM of the blend with 5% PE-NF. Magnification ×200.
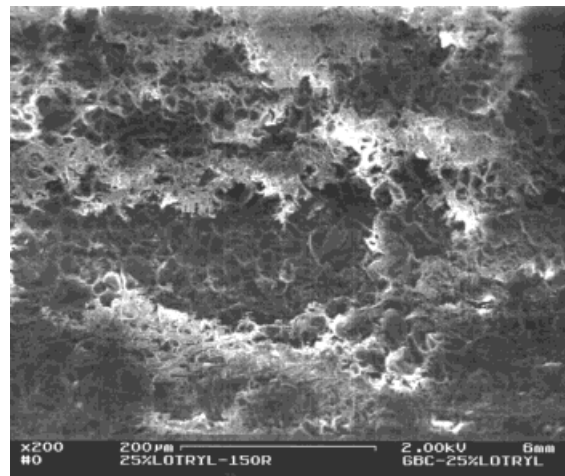
Figure 8 SEM of the blend with 25% PE-NF. Magnification ×200.

Figure 9   SEM of the blend with 25% PE-F. Magnification ×200.

Figure 11   SEM of the blend with 50% PE-F. Magnification ×200.

the presence of hydrated zinc acetate. As the amount of PE-F or PE-NF increases, two different morphologies are observed. For the reactive blends of SMAH/PE-F, the dispersion is fine at 5, 25, and 50% PE-F contents by contrast to the nonreactive blends containing PE-NF where larger domain sizes are observed. It is known that if the viscosity ratio of the blend components is high, then droplet breakup becomes difficult, and the final domain size becomes larger. This is true for both PE-F and PE-NF at the early stages of the extrusion, because $\eta^*_{SMAH}/\eta^*_{PE\text{-}F}$ and $\eta^*_{SMAH}/\eta^*_{PE\text{-}NF}$ are around 3 at a frequency of 100 rad/s, which can be seen in Figure 1. However, as the reaction proceeds, the viscosity of the modified

polyethylene interfacial domain in the systems with PE-F increases much more than the corresponding system with PE-NF. The viscosity of the PE-F/SMAH interface approaches the viscosity of SMAH, providing better mixing and droplet breakup. At the same time, the interfacial tension is reduced in the reactive blends. Thus, PE-F blends would have finer morphology than the PE-NFs. Also, as the amount of PE-F or PE-NF increases from 25 to 50%, the domain size decreases.

In all the micrographs of nonreactive blends, the dispersed phase is PE-NF and the continuous phase is SMAH. This conclusion is obtained from the phase inversion concept. It is known that the phase inversion occurs when $\phi_2/\phi_1 = \eta_1/\eta_2$, where

Figure 10   SEM of the blend with 50% PE-NF. Magnification ×200.

Figure 12   SEM of the blend with 25% PE-F. Magnification ×5000.
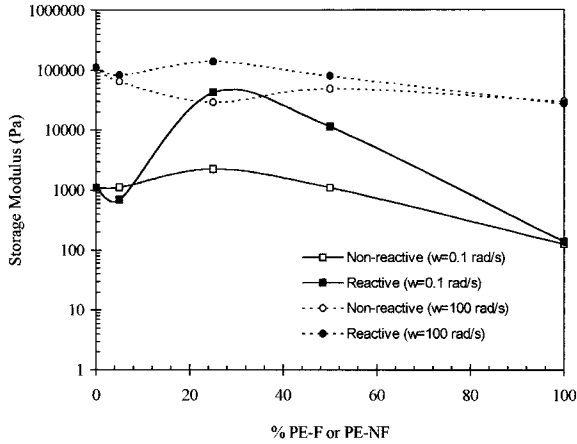
Figure 13 Storage modulus of the blends vs. percent modified polyethylene content.
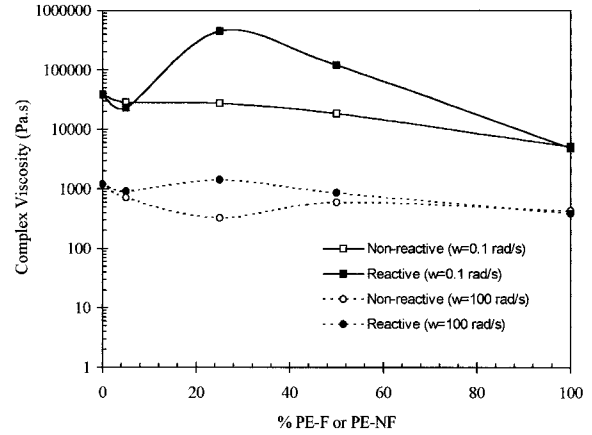

Figure 15 Complex viscosity of the blends vs. percent modified polyethylene content.

ϕ is the volume fraction, η is the viscosity, and 1 and 2 refer to the major and minor components, respectively.[22] At all concentrations of PE-NF studied, the viscosity ratio of the blend components, $\eta^*_{SMAH}/\eta^*_{PE-NF}$ is higher than ϕ_{PE-NF}/ϕ_{SMAH}, because the ratio of $\eta^*_{SMAH}/\eta^*_{PE-NF}$ is approximately 3 at 100 rad/s. Thus, SMAH should be the continuous phase, and PE-NF should be the dispersed phase in all the compositions studied.

High degrees of mixing are achieved at all concentrations of PE-F with SMAH. Figure 12 shows the maximum magnification studied for the 25% reactive blend. Even at this high magnification, the domains of PE-F are not visible, indicating high degrees of dispersive mixing.

Storage modulus, loss modulus, and complex viscosity of the blends with respect to modified polyethylene content are shown in Figures 13–15 at frequency values of 0.1 rad/s and 100 rad/s. At the low frequency value, reactive blends have higher G', G'', and η^* values than the nonreactive blends at 25 and 50% modified polyethylene contents. However, the nonreactive blend with 5% PE-NF has higher G', G'', and η^* values at low frequency than the blend with 5% PE-F. Blends with 5% polyethylene copolymer content show compatibility for both PE-F and PE-NF. At a high frequency value of 100 rad/s, the reactive blends have higher values of G', G'', and η^* for all concentrations of PE-F than the nonreactive counterparts, due to the reaction occurring in the system. In general, the additivity rule does not apply for G', G'', and η^* for reactive as well as nonreactive systems. At 25% PE-F content and 100 rad/s, the reactive blends show a maximum, whereas the nonreactive blends show a minimum in complex viscosity. At low PE-F contents, the complex vis-
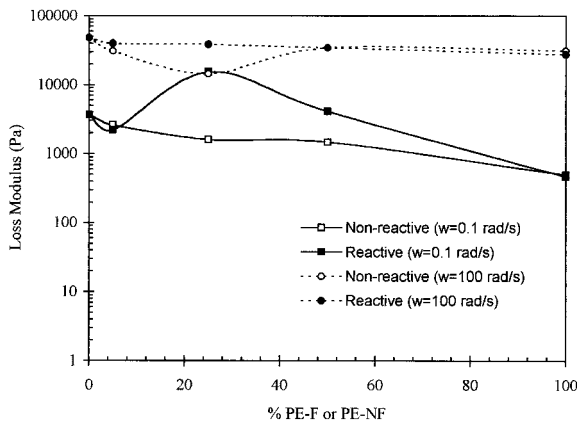
Figure 14 Loss modulus of the blends vs. % modified polyethylene content.
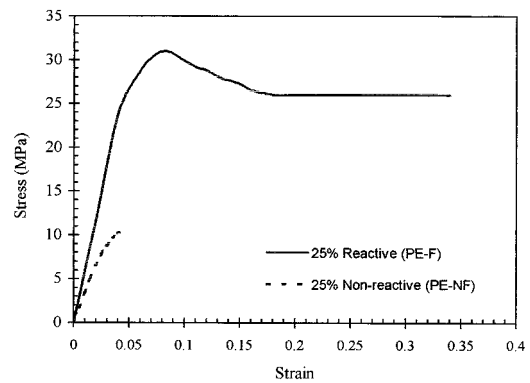
Figure 16 Stress–strain curve for 25% reactive and 25% nonreactive blends.
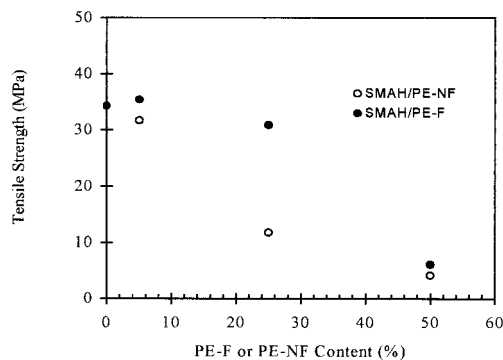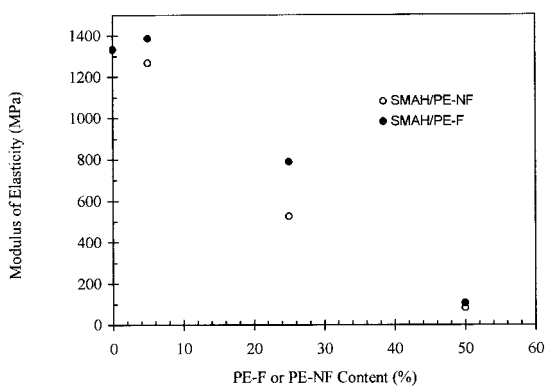
Figure 17 Tensile strength vs. percent modified polyethylene content.

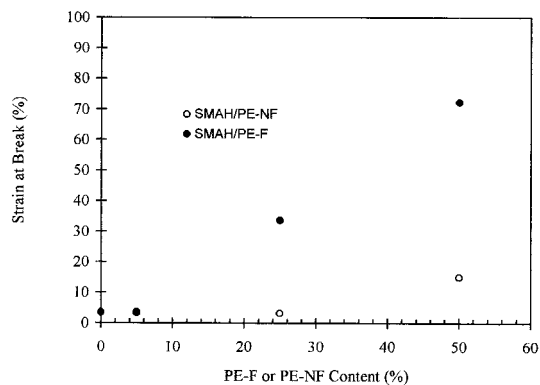**Figure 19** Percent strain at break vs. percent modified polyethylene content.

cosity is expected to increase with the PE-F content due to chain extension/branching reactions. However, at high PE-F contents, the complex viscosity is expected to decrease with the PE-F content, owing to the low complex viscosity of PE-F. The minimum in the nonreactive blend at 25% PE-NF may be due to the effect of interfacial slip in the system.

Figure 16 illustrates the stress–strain properties of blends containing 25% modified polyethylene. The reactive blend has higher tensile strength, percent strain at break, and modulus of elasticity than the nonreactive one. In addition, the 25% PE-F/SMAH blend shows ductility and a yield stress of 30.9 MPa. The significant improvement in mechanical properties is the result of enhanced adhesion due to interfacial reaction.

Figures 17–19 show the tensile properties of all SMAH/PE-F and SMAH/PE-NF blends. As the concentration of PE-F or PE-NF increases, tensile strength and modulus of elasticity decrease, but percent strain at break increases. Thus, the addi-

tion of polyethylene copolymers to SMAH provides toughness and improves the mechanical properties by overcoming the brittleness of SMAH. As expected, the results are more pronounced for the reactive system.

CONCLUSIONS

Reactive (SMAH/PE-F) and nonreactive blends (SMAH/PE-NF) with hydrated zinc acetate were produced in a Brabender batch mixer and in a twin-screw extruder. The blend components were analyzed in terms of their viscoelastic properties. PE-F and PE-NF have similar G', G'', and η^*, which are lower than those of pure SMAH. The blends were characterized in terms of morphology, viscoelastic, and mechanical properties. The reactive blends have finer morphology than the nonreactive ones at all concentrations of the modified polyethylene. The blends with 5% polyethylene copolymer exhibited compatibility for both PE-F and PE-NF. At 25 and 50% modified polyethylene contents, the reactive PE-F blends were considered compatible, whereas the nonreactive PE-NF blends were incompatible. In reactive blends, complex viscosity exhibited maximum at 25% PE-F content due to chain extension/branching reactions. However, the nonreactive blends did not exhibit such maxima. The reactive blends had higher modulus of elasticity, tensile strength, and strain at break than the nonreactive blends. The difference between the stress–strain behavior of the reactive and nonreactive system was most significant at 25% modified polyethylene content.

Figure 18 Modulus of elasticity vs. percent modified polyethylene content.

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