Rheological Behavior of Styrene-Maleic Anhydride/Polyol Blends Obtained through Reactive Processing

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ABSTRACT: The condensation reaction of styrene-maleic anhydride copolymer (SMAH) with polytetramethylene ether glycol (PTMEG) in the presence or absence of a hydrated zinc acetate catalyst was studied in a batch mixer. As a control, pure SMAH and an SMAH/catalyst blend were also subjected to the same processing conditions. The reaction characteristics of the blends were investigated by Fourier transform infrared spectroscopy (FTIR) and thermal and rheological analysis. FTIR analysis of the SMAH/PTMEG blend indicated ester formation. The addition of zinc acetate and/or PTMEG to SMAH decreased the glass transition temperature of pure SMAH. Oscillatory shear properties of storage modulus, G', loss modulus, G'', and complex viscosity, η^*, were measured. The SMAH/PTMEG/zinc acetate blend had higher G', G'', and η^* than the blend without the zinc acetate catalyst. The parameters of the relaxation spectra were calculated by using the experimental oscillatory data and the generalized Maxwell model. Zero shear viscosity and the mean relaxation time increased with addition of zinc acetate and/or PTMEG to SMAH as a result of chain extension/branching reactions. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2615–2623, 2002

Key words: styrene-maleic anhydride; polyol; viscoelastic properties; relaxation spectra; reactive processing; FTIR spectra

INTRODUCTION

There have been several studies on using condensation-type reactions to create new grafted copolymers or cross-linked structures[1–4] and on understanding the kinetics of these reactions by means of various characterization techniques.[5,6] Borve[1] examined the reaction between maleic anhydride grafted polypropylene and the hydroxyl groups of thermoplastic phenol-formaldehyde resin and discussed the kinetics of the reaction. Hu and Lindt[5] investigated the kinetics of the monoesterification reaction of maleic anhydride with aliphatic alcohol in ethyl benzene solution. Alcohols such as 1-octanol and 1-hexanol were reacted with two styrene maleic anhydride resins having different maleic anhydride contents. The authors searched for efficient catalysts and also studied the reversibility of the reaction. Maier and Lambla[6] focused on grafting small molecules of nonylphenylethoxylate onto a previously maleated ethylene-propylene. The kinetics of the reaction was studied by using Fourier transform infrared (FTIR) spectroscopy. Conversion along the extruder

Table I Weight Percentage and Molar Amounts of the Blend Components Based on 100 g of the Mixture

| | Blend Component[a] | | | | | |
| | SMAH | | PTMEG | | $ZnAc_2 \cdot 2H_2O$ | |
	wt %	gmole MAH	wt %	gmole PTMEG	wt %	gmole Catalyst
SMAH/$ZnAc_2 \cdot 2H_2O$ (Blend A)	99	0.0808	0	0	1	0.0046
SMAH/PTMEG (Blend B)	95	0.0776	5	0.0050	0	0
SMAH/PTMEG/$ZnAc_2 \cdot 2H_2O$ (Blend C)	94	0.0767	5	0.0050	1	0.0046

[a] SMAH = styrene-maleic anhydride copolymer; PTMEG = poly tetramethylene ether glycol.

length was predicted, and the residence time distribution was determined at various locations along the barrel. All of these studies were mainly focused on the reaction kinetics of anhydride/hydroxyl functional blend components. Either FTIR analysis or morphological, thermal, or rheological characterization techniques were used to obtain information on the kinetics of the condensation reactions. However, the use of rheological analysis to characterize anhydride/hydroxyl functional blends has been relatively limited.

As chemical reactions affect flow properties during reactive processing, rheological data can be used to study the reactions occurring in a variety of systems. Such data can be related to changes in molecular weight (MW), molecular weight distribution (MWD), and long-chain branching.[7] Bouilloux et al.,[8] Cassagnau et al.,[9] and Ishida and Smith[10] investigated chain growth and cross-linking reactions using rheological characterization.

Cole–Cole plots have been used as an analytical tool to study the viscoelastic behavior of polymeric systems, providing information on their elasticity and the effects of MW, MWD, and branching resulting from chemical reactions that may occur between functional groups.[11–13] Calculation of the Maxwell model parameters, such as the relaxation strength versus relaxation time has been useful in correlating rheological data with molecular interpretations.[14] Application of the Maxwell model on the rheological properties of polymer melts has resulted in good agreement with experimental oscillatory shear data.[15,16]

The objectives of this study are to produce anhydride/hydroxyl functionalized blends in a Brabender batch mixer; to investigate the condensation reaction through thermal, spectroscopic, and rheological analysis; and finally, to relate the structural changes occurring in the system to their rheological properties.

EXPERIMENTAL

Materials and Processing

Styrene Maleic Anhydride copolymer, SMAH (Dylark 232) with 8 wt% maleic anhydride content was supplied by Nova Chemicals (Monaca, PA). We measured the glass transition temperature (T_g) at 120.6°C. Polytetramethylene ether glycol, PTMEG (Terathane T1000), was obtained from Dupont de Nemours Company (Wilmington, DE). PTMEG has a hydroxyl number of 112 and melt temperature ranging from 25° to 33°C. In this study, hydrated zinc acetate ($ZnAc_2 \cdot 2H_2O$) was used as an esterification catalyst.

Blends with the compositions indicated in Table I were prepared by using a Brabender Computerized Plasticorder (PL 2000). A mixing temperature of 180°C, a rotor speed of 60 rpm, and a total mixing time of 20 min under a nitrogen blanket were applied as processing conditions. Essentially, two binary blends and a ternary blend were prepared: blend A contained SMAH and zinc acetate; blend B contained SMAH and PTMEG; and the ternary blend C contained SMAH, zinc acetate, and PTMEG. Although the main purpose of the study was to investigate blends B and C, blend A was also studied as the quantity of the catalyst zinc acetate used was significant in comparison with that of PTMEG. Pure SMAH was also subjected to the same processing conditions as the control. In the preparation of blends B and C, the addition sequence to the bowl of the mixer was SMAH followed by PTMEG, SMAH, PTMEG, and hydrated zinc acetate, respectively.

For FTIR analysis, an unreacted blend was also prepared as a solution cast film at room temperature by dissolving 5% polyol and 95% SMAH mixture in methyl ethyl ketone.
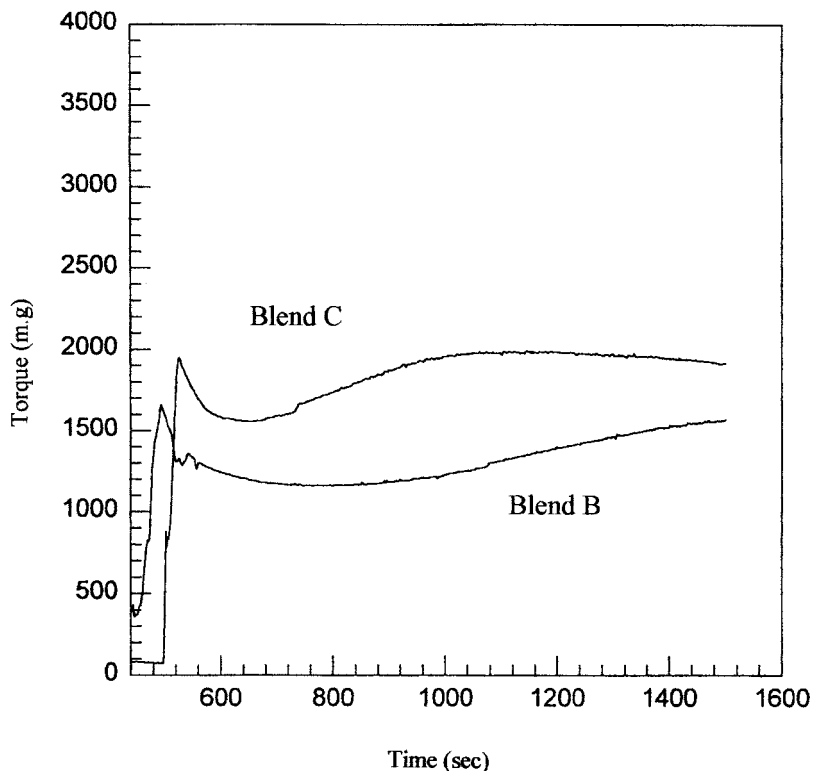
Figure 1 Torque versus time traces for the blends with or without catalyst.

Characterization

Samples for characterization experiments were prepared by compression molding at 180°C. FTIR analysis was performed on either compression-molded or solution-cast films by a Perkin Elmer FTIR spectrophotometer (Model Paragon1760) using "spectrum" software within the wavelength range of 400 cm^{-1} to 4000 cm^{-1}. A differential scanning calorimeter (Perkin-Elmer DSC-7) was used for thermal analysis at a heating rate of 20°C/min. Rheological properties were measured by a Rheometrics mechanical spectrometer (RMS 800) at 180°C using parallel disks with a 25-mm diameter. Strain amplitude was kept constant at 10%. Applied frequency ranged from 0.1 rad/s to 100 rad/s.

RESULTS AND DISCUSSION

Figure 1 shows the torque versus time behavior of blends B and C containing PTMEG. The torque started to increase with time, indicating the occurrence of chain extension/branching reactions. The experiment with the $ZnAc_2 \cdot 2H_2O$ catalyst

resulted in a higher overall reactivity with a faster torque buildup and a higher final torque, indicating the effectiveness of the catalyst. The reactions between anhydride and hydroxyl functional groups that cause an increase in torque in batch mixing may result from several possibilities, such as the opening of the anhydride ring with water, the reaction between opened maleic anhydride (MAH) and PTMEG forming ester and half ester, and the reaction between opened MAH and $ZnAc_2 \cdot 2H_2O$ forming an ionomer.

In addition to these reactions, transesterification, ester–ionomer interchange, and acidolysis are other possibilities. Among these reactions, ester formation resulting from the hydroxyl and carboxylic acid functionalities is more possible. Carboxylic acid formation may take place through the opening of the anhydride by water that may come either from the environment or the $ZnAc_2 \cdot 2H_2O$ catalyst. Carboxylic acid groups formed can then react either with the hydroxyl groups of PTMEG to form an ester or with the catalyst to form an ionomer. In the case of blend A, which contained SMAH and zinc acetate, carboxylic acid formation followed by ionomer forma-
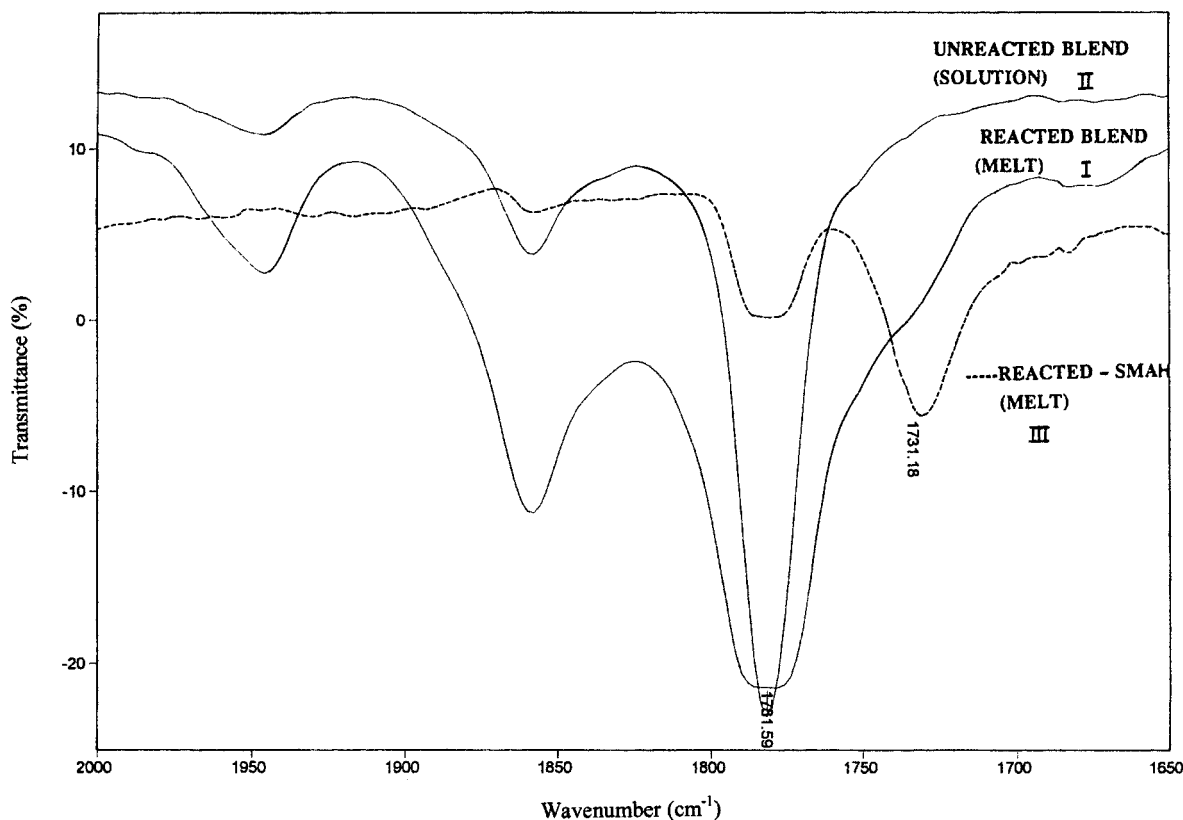
Figure 2 Fourier transform infrared (FTIR) spectra of the reacted blend (I), the solution mixture (II), and the difference in the FTIR spectra (III) of the reacted blend (I) and neat styrene-maleic anhydride copolymer.

tion are among the reaction possibilities; this system was run separately in the batch mixer.

In blend C, taking a base of 100 g of mixture, 0.0767 mol of MAH exists in comparison with 0.005 mol of PTMEG (corresponding to 0.01 mol of OH) and 0.0046 mol of catalyst (Table I). Thus, there is an excess amount of MAH in the system in comparison with the hydroxyl groups. The molar quantity of MAH is also much higher than that of H_2O in the catalyst, which is 0.0092 mol. Therefore, it would be expected that in blend C, not all anhydride groups could react. Similarly, in blend B, the molar quantity of MAH is much higher than that of the hydroxyl in PTMEG.

The occurrence of reactions, even in the absence of catalyst, was confirmed using the FTIR spectrum of blend B containing 5% PTMEG. Figure 2 shows the FTIR spectrum of the batch mixed blend B (shown as I) and also the FTIR spectrum of a mixture that has the same composition as blend B but that is prepared from a solution at room temperature (shown as II). Methyl ethyl ketone is used as a solvent. For this solution, it is assumed that no reaction occurs in the mixture under these conditions. The FTIR spectrum of pure SMAH was also obtained, and the difference between the FTIR spectrum of the melt reacted blend B (I) and pure SMAH is shown as III. In the FTIR spectrum of the reactive blend, I, there is a shoulder at around 1730 cm^{-1} that does not exist in the spectrum of the unreacted blend, II. When the difference in the FTIR spectra of the batch-mixed blend B and pure SMAH is obtained as III, the ester peak at 1731.8 cm^{-1} is clearly observed. Thus, it could be concluded that blending of 5% PTMEG and 95% SMAH at 180°C in the batch mixer for 20 min results in ester formation.

T_g of pure SMAH and the batch-mixed blends are shown in Table II. In blend A, the addition of zinc acetate to SMAH slightly lowers T_g. Carboxyl acid and ionomer formation reactions are expected in this blend. Although ionomer formation would restrict chain mobility and increase T_g, there are three potential reasons for the reduction of T_g that are apparently dominant: (1) the ester bond introduced through zinc acetate imparts mobility to the system; (2) formation of carboxylic

Table II   Glass Transition Temperature of Pure Styrene-Maleic Anhydride Copolymer and the Blends[a]

Material	PTMEG Content (wt%)	$ZnAc_2 \cdot 2H_2O$ Content (wt%)	T_g (°C)
SMAH	0	0	120.6
SMAH/ZnAc$_2$ · 2H$_2$O (Blend A)	0	1	119.2
SMAH/PTMEG (Blend B)	5	0	112.3
SMAH/PTMEG/ZnAc$_2$ · 2H$_2$O (Blend C)	5	1	110.3

[a] PTMEG = polytetramethylene ether glycol.

acid by opening of maleic anhydride ring reduces steric hindrance and therefore increases the mobility of the main chain; (3) any unreacted zinc acetate decreases T_g by acting as an impurity.

In blend B, the addition of PTMEG to SMAH lowers T_g relative to that of pure SMAH in spite of the chain extension/ branching reactions that took place. This may be a result of the plasticization effect of the low–molecular weight polyol and the ether bond introduced to the system by the addition of PTMEG. The catalyzed blend (blend C) has slightly lower T_g than the uncatalyzed one (blend B). This may be attributed to the same three reasons put forward for the reduction of T_g in blend A.

Rheological Characterization

Figures 3–5 illustrate the behavior of storage modulus, G', loss modulus, G'', and complex vis-cosity, η^*, with respect to frequency for pure SMAH and the blends. Blend A has higher storage modulus, loss modulus, and complex viscosity than pure SMAH, blend B, and blend C, mainly resulting from ionomer formation, resulting in higher effective molecular weight, higher molecular weight distribution, and branching.

In blends B and C, the low–molecular weight PTMEG component would have the tendency to decrease the storage modulus, loss modulus, and complex viscosity if there had not been any reactions. However, the reaction between PTMEG and SMAH results in a higher molecular weight, higher molecular weight distribution, and higher degree of branching. Thus, the values of G', G'', and η^* are higher for the catalyzed blend C in comparison with the corresponding properties of the uncatalyzed blend B and pure SMAH, especially at low frequencies.
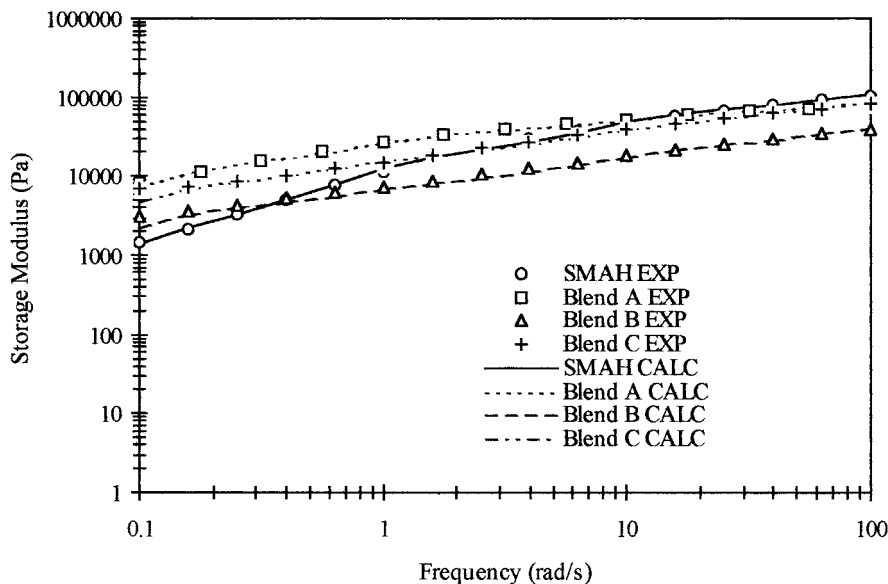

Figure 3   Storage modulus of styrene-maleic anhydride copolymer and the blends as a function of frequency.
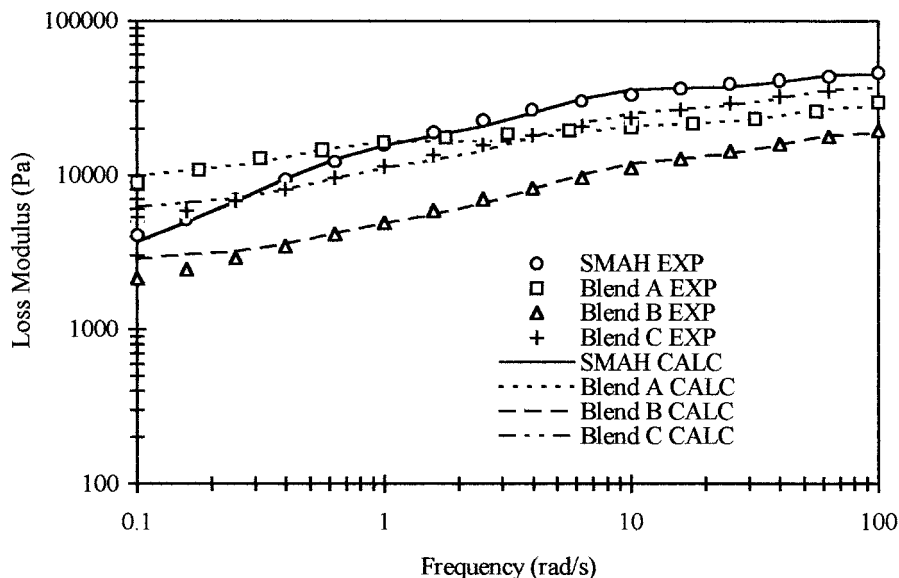
Figure 4 Loss modulus of styrene-maleic anhydride copolymer and the blends as a function of frequency.

All of these molecular factors also result in a high negative slope in the complex viscosity vs. in the frequency curve of blend C.[7] For example, there exist crossovers in Figure 5 between the complex viscosities of SMAH and blends A and C. At low frequencies, the complex viscosity of pure SMAH is higher than the complex viscosity of the uncatalyzed blend B. The blend with the catalyst (blend C) has higher viscosity than pure SMAH at low frequencies, as the effect of entanglements is greater at low frequencies. However, at higher frequencies, the decreasing influence of entanglements results in a lower viscosity for the blends. This argument is also valid for the comparison of the complex viscosities of blend A and pure SMAH with respect to the frequency.

Crossovers exist in Figure 3 between the storage moduli of all the blends and the storage modulus of SMAH. In Figure 4, the loss modulus of SMAH crosses the loss moduli of blends A and C.
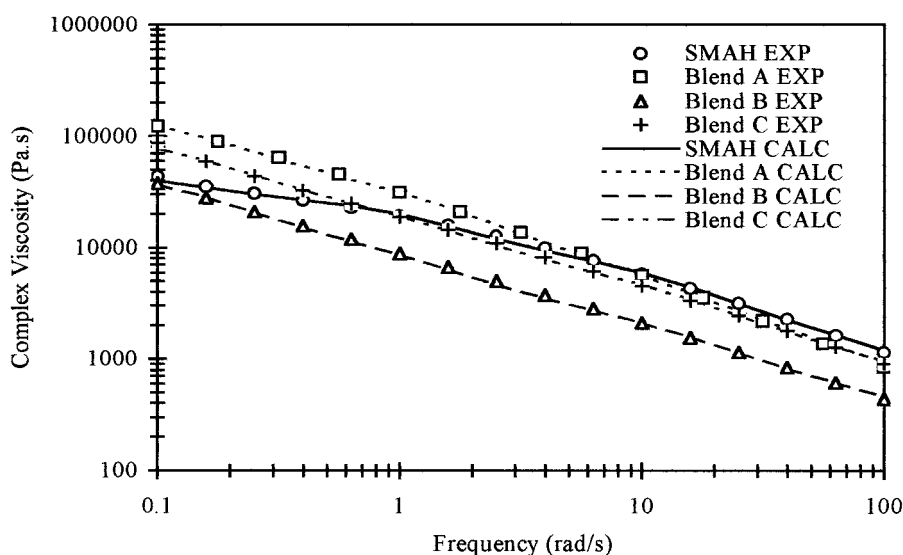

Figure 5 Complex viscosity of styrene-maleic anhydride copolymer and the blends as a function of frequency.
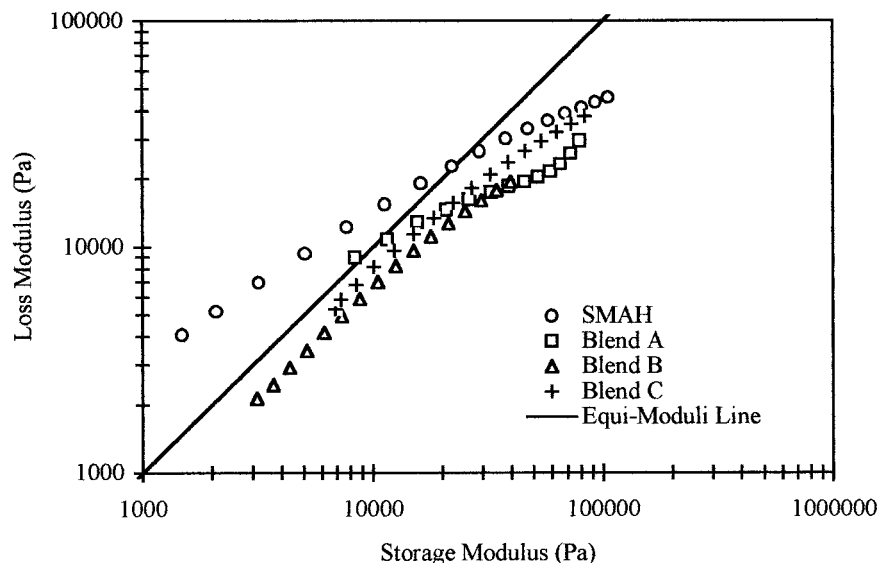
Figure 6 Cole–Cole plot for styrene-maleic anhydride copolymer and the blends.

At low frequencies, the slope of the moduli for pure SMAH is higher than those of the blends. However, at high frequencies, the opposite is observed as a result of higher MW, higher MWD, and a higher degree of branching in the blends.[11,12]

This fact can be expressed mathematically through the dependency of G', G'', and η^* on the frequency. Eq. (1) indicates that the complex viscosity is directly proportional to G' and G'' and inversely proportional to the frequency:

$$\eta^* = [(G'/\omega)^2 + (G''/\omega)^2]^{0.5} \qquad (1)$$

In the blends, G' and G'' are less sensitive to the frequency; thus, the complex viscosity of the blends should decrease in a more sensitive manner than the complex viscosity of pure SMAH.

The use of a Cole–Cole plot can also explain the behavior of these systems, as seen in Figure 6. The equi-moduli line representing $G' = G''$ is important in terms of the position of the data with respect to this line. If the behavior of the material, as seen for the blends in Figure 6, is on the right-hand side of the equi-moduli line, it means that these systems show a higher degree of elastic behavior. The data on the left side of the line show a higher degree of viscous behavior. Here, all the blends exhibit elastic behavior resulting from the long-chain branching, high molecular weight, and large molecular weight distribution resulting from the chemical reaction between the carboxyl

and polyol functional groups as well as ionomer formation.

Linear viscoelastic properties of polymer solutions and melts can be described by using the generalized Maxwell model,[17] which has the parameters of relaxation strength, G_i, and relaxation time, λ_i. One can determine the parameters of the relaxation spectra by using experimental oscillatory shear data and the following functions of the Maxwell model:

$$G'(\omega_j) = \sum_{i=1}^{N} G_i \frac{(\omega_j \lambda_i)^2}{1 + (\omega_j \lambda_i)^2} ; \qquad (2)$$

$$G''(\omega_j) = \sum_{i=1}^{N} G_i \frac{(\omega_j \lambda_i)}{1 + (\omega_j \lambda_i)^2} , \qquad (3)$$

where ω_j refers to the experimental frequency.

In this study, the linear least square principle was applied to determine the parameters of the relaxation spectrum.[15] A numerical technique, singular value decomposition (SVD) was used to solve the equations formed as matrices from linear regression.

After finding the relaxation strength versus the relaxation time, the values of G' and G'' were calculated by using eqs. (2) and (3). Then the complex viscosity was obtained from eq. (1). The curves in Figures 3–5 represent the values calcu-
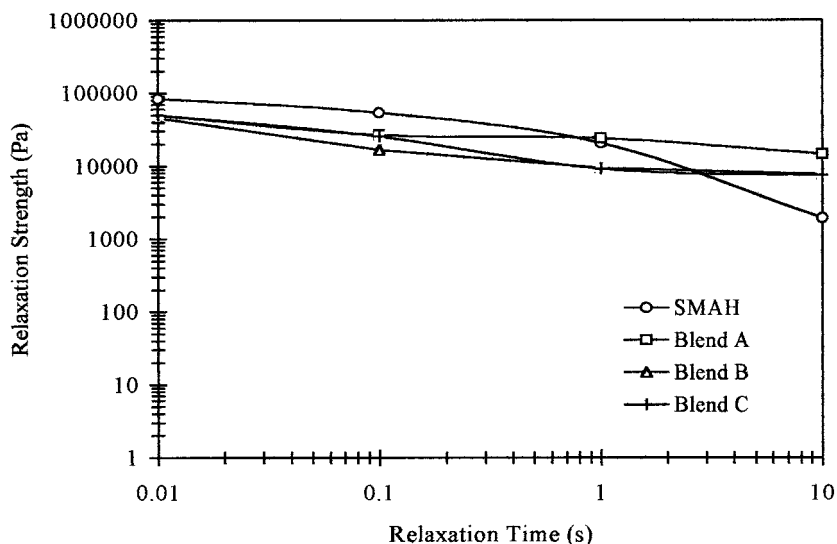
Figure 7 Relaxation strength versus relaxation time for styrene-maleic anhydride copolymer and the blends.

lated from the constitutive equations of the corresponding materials. The agreement between the experimental and the calculated values is good; thus, it is possible to describe the linear viscoelastic behavior of SMAH and the blends for various deformations.

In Figure 7, the relaxation strength versus the relaxation time calculated from oscillatory shear data are shown for SMAH and the blends. The relaxation strength of pure SMAH decreases with increasing relaxation time. However, G_i values for blends B and C decrease up to a value of $\lambda_i = 1$ sec; after this point, G_i remains relatively constant. The relaxation strengths of blend A are also higher in comparison with those of SMAH at long relaxation times. In all the blends, a higher degree of chain extension/branching and entanglement result in higher relaxation strengths at long relaxation times in comparison with the behavior observed in pure SMAH. For the same reason, at

small frequencies, the blends exhibit higher G' and G'' than does pure SMAH.

It is possible to calculate certain viscoelastic parameters by using the relaxation spectra values (G_i, λ_i) calculated. These parameters and their corresponding equations are as follows:[14] zero shear viscosity, η_0, defined as the limiting value of the viscosity at low shear rates:

$$\eta_0 = \sum \lambda_i G_i \qquad (4)$$

mean relaxation time, $<\lambda>$, defined as the average time for stress to relax or decay from its initial value at a constant strain:

$$\langle \lambda \rangle = \left(\sum \lambda_i^2 G_i \right) \Big/ \left(\sum \lambda_i G_i \right) \qquad (5)$$

Table III summarizes the values of zero shear

Table III   Calculated Viscoelastic Characteristics of Pure Styrene-Maleic Anhydride Copolymer and the Blends[a]

Material Parameters	Pure SMAH	Blend A (SMAH + 1% Catalyst)	Blend B (SMAH + 5% PTMEG)	Blend C (SMAH + 5% PTMEG + 1% Catalyst)
η_0 (Pa.s) $* 10^{-4}$	4.63	17.2	8.89	8.63
$\langle \lambda \rangle$ (s)	4.64	8.56	8.82	8.70

[a] PTMEG = polytetramethylene ether glycol.

viscosity and mean relaxation time. The blends exhibit a higher degree of melt elasticity in comparison with pure SMAH owing to higher MW, higher MWD, and higher long-chain branching. Thus, the blends have longer mean relaxation times as seen in Table III. Moreover, zero shear viscosities of the blends are higher than that of pure SMAH.

CONCLUSIONS

SMAH and PTMEG were blended with or without hydrated zinc acetate in a batch mixer. As a control, pure SMAH and SMAH/catalyst blends were also subjected to the same processing conditions. The reaction characteristics and structure of the systems were investigated by FTIR, thermal, and rheological analysis. In the FTIR analysis of the 5% PTMEG/SMAH blend, ester formation was observed at 1731.8 cm^{-1}. In thermal analysis, it was observed that the addition of polyol or zinc acetate to the system lowered the T_g of pure SMAH. Rheological properties such as the storage modulus, loss modulus, and complex viscosity of the blends were in the following order: blend A > blend C > blend B. Properties of catalyzed blend C were higher than those of the uncatalyzed blend B because of a higher degree of chain extension/branching reactions in the catalyzed blends. Cole–Cole plots indicated that the blends exhibited a higher degree of melt elasticity than did SMAH. Good agreement between the experimental and calculated values of rheological properties was obtained using the relaxation spectra (G_i, λ_i) determined. The relaxation strengths of the blends at long relaxation times were higher in comparison with those of pure SMAH. The mean relaxation time and zero shear viscosity of the blends were also higher in comparison with those of pure SMAH.

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