

# Reactive Processing and Properties of Styrene–Maleic Anhydride and Poly(tetramethylene ether glycol)

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**ABSTRACT:** The anhydride/hydroxyl-functionalized blends of styrene–maleic anhydride (SMAH) with poly(tetramethylene ether glycol) (PTMEG) in the presence or absence of a hydrated zinc acetate catalyst were produced in a batch mixer and in a corotating twin-screw extruder. In batch mixing, torque values increased with time as a result of chain-extension/branching reactions. The reaction products were studied by thermal, mechanical, morphological, and spectroscopic characterization techniques. The glass transition temperature of SMAH was lowered by the addition of PTMEG into the system. Major morphological changes were observed at the initial stages of extrusion. The changes in the screw speed influenced the mechanical properties and morphology of the blends. SMAH/PTMEG blends were brittle due to the glassy nature of SMAH. FTIR analysis of the SMAH/PTMEG system showed carboxylic acid and ester formation in the extrusion experiments. Mechanical property data and FTIR spectra indicated that at 150 rpm chain-extension/branching reactions were maximized due to ester formation. However, at 220 rpm, a lower extent of ester formation was observed due to the lower residence time in the extruder. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2148–2156, 2002

**Key words:** reactive processing; compatibilization; morphology; branched; blending

## INTRODUCTION

Reactive processing is an effective way of obtaining new polymeric materials. This can be achieved by compatibilization of polymer blends that have some specific functional groups. Nogues<sup>1,2</sup> studied the reaction of carboxylic acid anhydride with compounds such as polyols, polyamines, polyepoxides, and polyisocyanates. In these studies, the reactions of maleic anhydride (MAH)-grafted polypropylene with polyol were

taken into consideration to produce new polymeric products. Similar condensation types of reactions were examined by Curry,<sup>3</sup> Maier and Lambla,<sup>4</sup> Hu and Lindt,<sup>5</sup> and Borve<sup>6</sup> in which the kinetics of the esterification reaction was studied and/or the reaction products were characterized in terms of their thermal, morphological, and mechanical properties and also in terms of spectroscopic analysis.

Characterization techniques are employed to obtain more information on the properties of polymeric products and to understand the reaction characteristics between the functional groups of polymer blends. Thermal, morphological, mechanical, and spectroscopic (FTIR) characterization techniques are conventionally used to confirm the occurrence of a reaction in a

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**Table I** Weight Percentage and Molar Amounts of Blend Components in Anhydride/Hydroxyl-Functionalized Blends Based on 100 g of the Mixture

Type of Experiment	Blend Component					
	SMAH		PTMEG		ZnAc <sub>2</sub> · 2H <sub>2</sub> O	
	Wt %	gmol MAH	Wt %	gmol PTMEG	Wt %	gmol Catalyst
Batch mixing	94	0.0767	5	0.0050	1	0.0046
	95	0.0776	5	0.0050	0	0
Extrusion	98.5	0.0804	0.5	0.0005	1	0.0046
	98	0.0800	1	0.0010	1	0.0046

polymeric system.<sup>7-9</sup> Characterization methods such as mechanical testing and morphological analysis should support each other.<sup>8-11</sup> Dagli and Kamdar<sup>8</sup> observed that favorable interactions between the functional groups provide good interfacial adhesion and result in better mechanical properties. Dagli and Kamdar<sup>8</sup> and Hu et al.<sup>9</sup> found that the mechanical properties depend on the morphology. The viscosity ratio of the blend components, blend composition, and processing parameters such as the screw speed, throughput, and temperature also influence the morphology.<sup>12</sup> Moreover, it is possible to control the morphology by using different mixers and by controlling the mixing characteristics.<sup>13</sup> Sundararaj et al.<sup>13</sup> determined that major morphological changes occurred during the initial softening stage of mixing. Besides determining the morphological and mechanical properties, FTIR analysis is also important in confirming the reactions in the system and supporting other characterization techniques.<sup>5,14,15</sup>

In this study, blends of styrene-MAH (SMAH) with poly(tetramethylene ether glycol) (PTMEG) with/without a hydrated zinc acetate catalyst were chosen because of the high degree of a reaction possibility between anhydride and hydroxyl functional groups. The major product of this reaction would be ester formation.<sup>16</sup> The reaction/mixing characteristics of the system were investigated in a batch mixer and in a corotating twin-screw extruder. After obtaining the reaction products, the blends were characterized in terms of thermal and mechanical properties and also by morphological and spectroscopic analysis in order to understand the effects of the reactions on the system.

## EXPERIMENTAL

### Materials

SMAH (Dylark 232), which is one of the blend components, was obtained from Nova Chemicals (Monaca, PA). The MAH content of the SMAH was reported as 8 wt % by the manufacturer. The other blend component, poly(tetramethylene ether glycol) (PTMEG; T1000) was procured from the DuPont Co. (Wilmington, DE). SMAH, which is a brittle material, has a glass transition temperature of 120.6°C. On the other hand, PTMEG (polyol) is a waxy material with a melt temperature ranging from 25 to 33°C and a hydroxyl number of 112. In this system, hydrated zinc acetate (ZnAc<sub>2</sub> · 2H<sub>2</sub>O), a well-known catalyst for esterification, was used as a potential catalyst.

The amount of materials used in each processing experiment was different. In batch-mixing experiments, 5 wt % of PTMEG was blended with SMAH in the presence or absence of a 1 wt % catalyst using a Brabender plasticorder. In continuous-mixing experiments, blends containing 0.5 and 1 wt % PTMEG were extruded in a corotating twin-screw extruder in the presence of 1 wt % hydrated zinc acetate. The corresponding molar amounts of materials in each process are given in Table I. It can be seen that the molar quantity of the MAH present is highly in excess of glycol and the H<sub>2</sub>O in the catalyst.

### Batch-mixing Experiments

A C.W. Brabender computerized plasticorder (PL-2000) was used for the batch-mixing experiments. The bowl capacity of the plasticorder is about 60 cm<sup>3</sup>. The experiments were performed at 80 % partial filling of the bowl capacity.

The processing conditions were as follows: 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 PTMEG, and, finally, hydrated zinc acetate. A nitrogen blanket was provided in order to have an inert environment and to prevent oxidation in the system. Torque versus time behavior was recorded for the blend compositions given in Table I.

### Continuous-mixing Experiments

Continuous-mixing experiments were conducted in a 30-mm intermeshing corotating twin-screw extruder (Krupp Werner & Pfeleiderer, Model ZSK 30) equipped with a sheet die. The temperature along the extruder was kept at 210°C. The temperature chosen for the extrusion was higher than the one used in batch mixing, since, at 180°C, the extruder was overloaded owing to a high torque. The screw speed was varied as 60, 150, and 220 rpm. The screw configuration used in this study can be seen in Figure 1, which also shows the morphology development discussed later. Screw elements are mainly responsible for conveying, kneading blocks are used mainly for both dispersive and distributive mixing, and, finally, the helical barrel rheometer section is used for both conveying and pressurization. In the helical barrel part, the grooves are on the barrel and the screw is shaped like a plain cylinder. The helical barrel section is equivalent to the melt-conveying zone. Feed addition was performed by premixing the components followed by the addition of premixed feed to the hopper of the extruder.

### Characterization Experiments

After the blends were produced by batch mixing or extrusion, the samples were prepared according to the standards of characterization techniques by compression molding at 180°C. Thermal transitions were studied using a differential scanning calorimeter (DSC-7). Two heating scans and one cooling scan were carried out at a rate of 20°C/min. The temperature range was changed from 40 to 180°C. The results reported here refer to the second heating scan. The morphological characterization was performed in the melt state at 180°C with hot-stage microscopy using a Q10 image analyzer.

Tensile properties such as tensile strength, percent strain at break, and tensile modulus were

measured using a Tinius Olsen mechanical tester. The test specimens were prepared according to ASTM standards. The thickness of the samples was approximately 0.5 mm. The samples were compression-molded to the desired thickness and then cut into slabs that were 1.27 cm in width and 6.35 cm in length. The speed of testing was 5 mm/min. For each run, the tensile properties of five samples were measured and the averages of five data points are reported.

FTIR analysis was performed using an FTIR spectrometer (Perkin–Elmer, Model 1760) within the wavelength range of 400 to 4000  $\text{cm}^{-1}$ . The thickness of the samples was not larger than 0.05 mm.

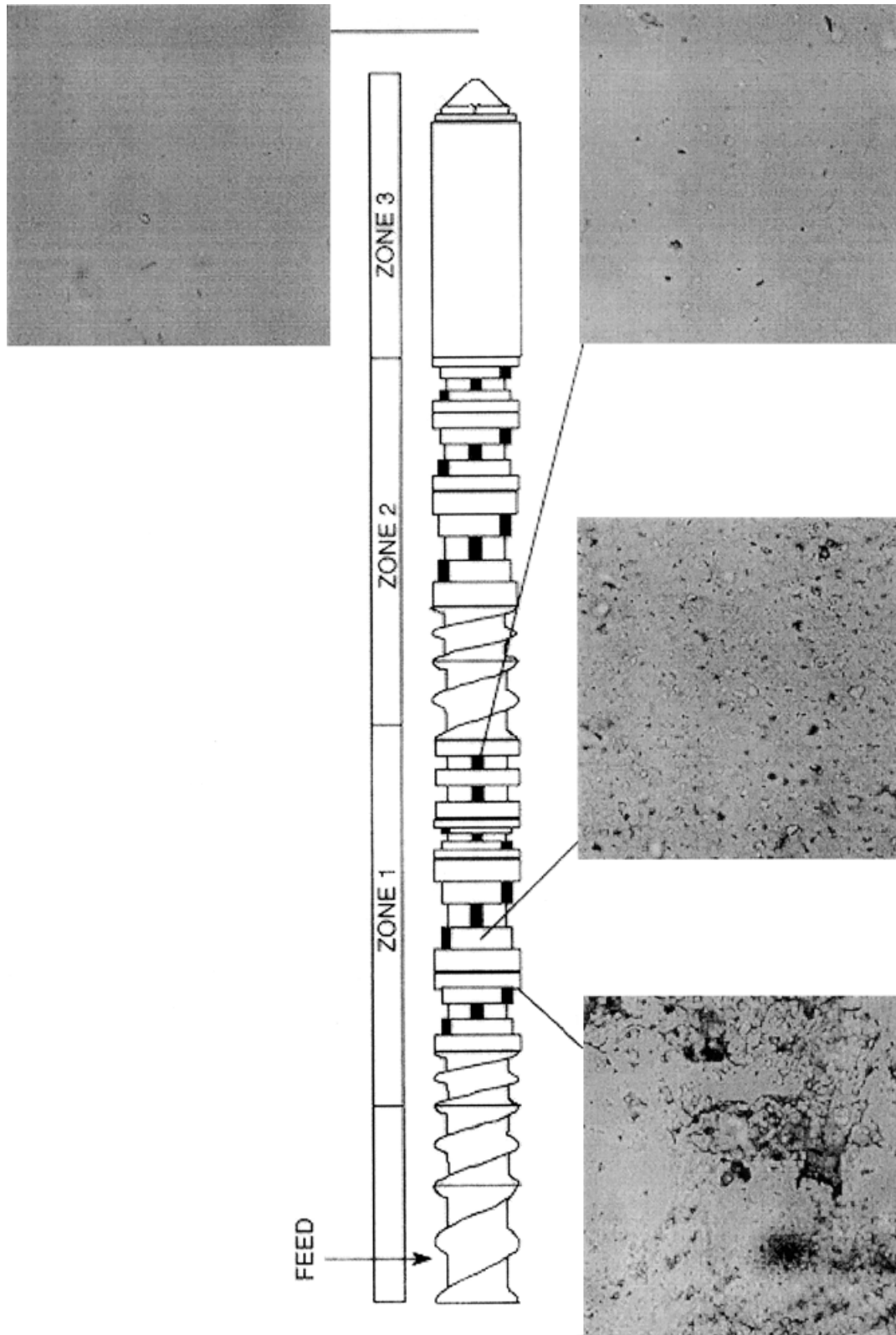
## RESULTS AND DISCUSSION

Two separate blends were prepared and analyzed in the mixer: One was 94% SMAH copolymer with 5% PTMEG in the presence of 1% hydrated zinc acetate and the other was 95% SMAH with 5% PTMEG in the absence of a catalyst. Figure 2 shows the torque versus time behavior of these two blends. SMAH and polyol were added sequentially into the mixer bowl. The torque started to increase with time, indicating that there are chain-extension/branching reactions in the system. The experiment with  $\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$ , which is a well-known esterification catalyst, resulted in a higher overall reactivity with a faster torque buildup and a higher final torque.

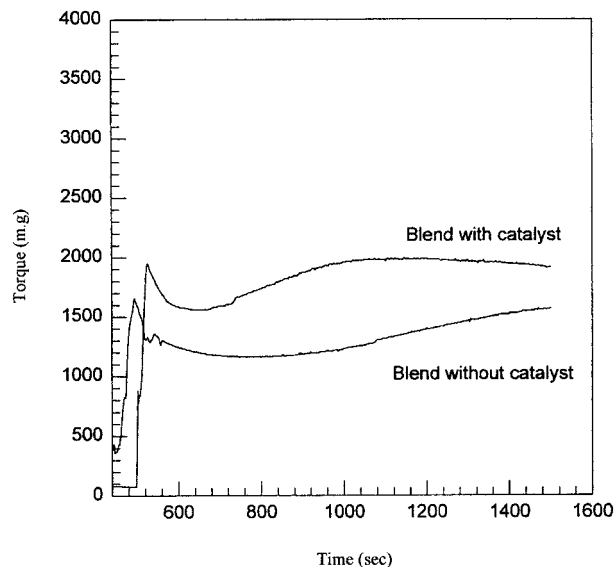
The reactions between anhydride and hydroxyl functional groups that cause an increase in torque in batch mixing may result from several possibilities, such as

- Opening of the anhydride ring with water;
- The reaction between opened MAH and PTMEG;
- The reaction between opened MAH and  $\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$ .

In addition to these reactions, transesterification, ester–ionomer interchange, and acidolysis are other types of reaction possibilities. Among these reactions, ester formation due to the hydroxyl and carboxylic acid functionalities has a higher degree of possibility. Carboxylic acid formation may take place with the opening of the anhydride by water that may come either from the environment or the catalyst. Carboxylic acid



**Figure 1** Screw configuration and morphology development for 1% PTMEG/SMAH/ $\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$  blend in the twin-screw extruder.



**Figure 2** Torque versus time traces of SMAH/PTMEG blends in the batch mixer.

groups formed can either react with hydroxyl groups of PTMEG to form an ester or with the catalyst to form an ionomer.

Here, in the batch-mixing experiment, taking a basis of 100 g of the mixture, 0.0767 gmol of MAH exists compared to 0.005 gmol of PTMEG (corresponding to 0.01 gmol of OH) and 0.0046 gmol of the catalyst (Table I). Thus, there is an excess amount of MAH in the system. The molar quantity of MAH is also much more than that of H<sub>2</sub>O in the catalyst, which is 0.0092 gmol. This indicates that, even if all the water was used to open the MAH groups, there would be an excess amount of MAH.

Extrusion experiments were performed with lower concentrations of polyol in the presence of 1% ZnAc<sub>2</sub> · 2H<sub>2</sub>O as seen in Table I. The amount of MAH is much more in excess than in the batch mixing. The reaction possibilities given before are also valid again in the case of extrusion.

Table II shows the glass transition temperature of the pure SMAH and batch-mixed and extruded SMAH/PTMEG blends in the presence or absence of hydrated zinc acetate. The experiments with 5% of PTMEG refer to batch mixing. It is seen that the addition of PTMEG to SMAH lowers the  $T_g$  of SMAH. The decrease in the glass transition temperature may be attributed to the low molecular weight of PTMEG, which causes plasticization in the system.

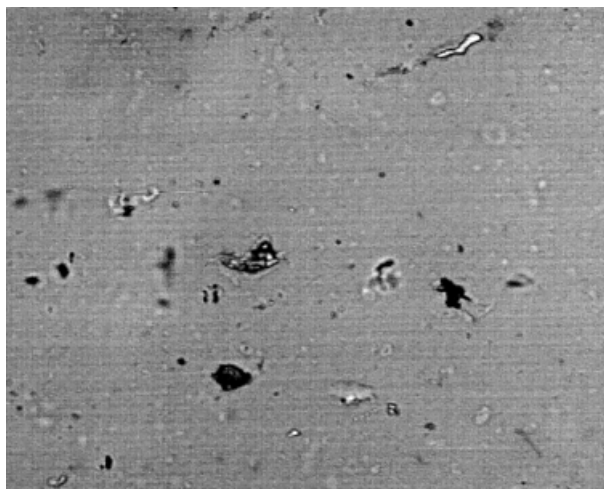
For the extrusion cases (0.5 and 1% PTMEG), the  $T_g$  of the blends is again lowered by the addition of PTMEG. However, the decrease in  $T_g$  of the batch-mixed samples is much more than that of the extruded samples, owing to the higher quantities of PTMEG (i.e., 5%) used in batch mixing compared to 0.5 and 1% of PTMEG in the extruded samples. Chain-extension/branching reactions take place in both systems, which may be expected to increase the  $T_g$  due to higher molecular weight and branching. However, even when there is a chain-extension/branching reaction, the ether bond in PTMEG introduces mobility to the system. Thus, it lowers the  $T_g$  of the blend.

It is also interesting to note that in batch mixing the blend with the ZnAc<sub>2</sub> · 2H<sub>2</sub>O catalyst has a lower  $T_g$  than that of its counterpart without the catalyst. This could be due to an additional amount of impurity (i.e., catalyst) introduced to the system. The ester bond introduced through zinc acetate also imparts mobility to the system. In addition, formation of carboxylic acid by opening of the MAH ring reduces the steric hindrance and therefore increases the mobility of the main chain. Overall, the plasticization and impurity introduced as PTMEG and the catalyst dominate the effects of chain extension/branching.

Figure 1 shows the morphology development during the extrusion of a 1% PTMEG/SMAH blend in the presence of hydrated zinc acetate at 150 rpm in the twin-screw extruder. This figure is obtained by stopping the extrusion and solidifying

**Table II** Glass Transition Temperatures of Pure SMAH and Batch-mixed and Extruded SMAH/PTMEG Blends in the Presence or Absence of ZnAc<sub>2</sub> · 2H<sub>2</sub>O

Material	Process	PTMEG Content (%)	ZnAc <sub>2</sub> · 2H <sub>2</sub> O Content (%)	$T_g$ (°C)
SMAH	Batch	0	0	120.6
SMAH/PTMEG	Batch	5	0	112.3
SMAH/PTMEG/ZnAc <sub>2</sub> · 2H <sub>2</sub> O	Batch	5	1	110.3
SMAH/PTMEG/ZnAc <sub>2</sub> · 2H <sub>2</sub> O	Extrusion	0.5	1	119.1
SMAH/PTMEG/ZnAc <sub>2</sub> · 2H <sub>2</sub> O	Extrusion	1	1	118.5

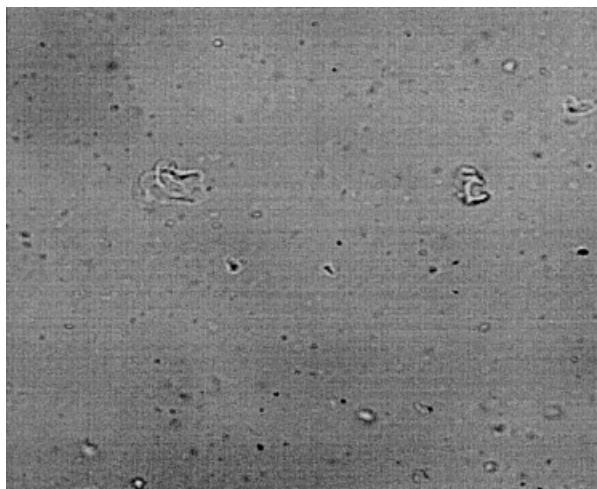


**Figure 3** Hot-stage micrograph of 0.5% PTMEG/SMAH blend at 60 rpm.

the mixture, followed by hot-stage microscopy of the carcass. Since polyol is the low viscosity component, it is not easily miscible with the high-viscosity SMAH component and is formed into spherical shapes in the early stages of the extrusion. Then, these spherical shapes slowly disappear through the reaction and mixing, and, finally, a homogeneous well-mixed product is taken from the die as seen in Figure 1. The irregular spots in the hot-stage micrograph of the PTMEG/SMAH blend could be either the polyol or the catalyst which is not consumed.

In the system studied, the viscosity ratio of the blend components,  $\eta_2/\eta_1$ , is very low due to the large difference between the viscosity of SMAH,  $\eta_1$ , and polyol,  $\eta_2$ ; thus, the breakup of PTMEG droplets is difficult, but it is still observed. In all the blends, SMAH is the continuous phase and polyol is the dispersed phase, which can be seen as droplets in the micrograph.

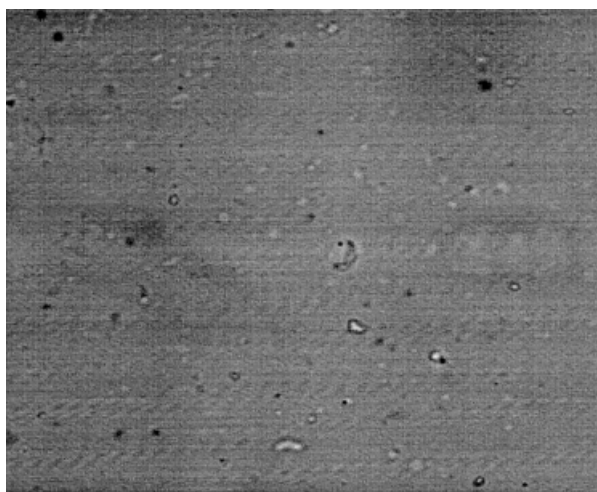
Figures 3–5 show hot-stage micrographs of a 0.5% PTMEG/SMAH blend product in the presence of a catalyst at screw speeds of 60, 150, and 220 rpm. As the screw speed increases, the domain sizes of polyol and zinc acetate become smaller and the interfacial surface area increases. The reason for the reduction in the domain size may be attributed to higher shear stresses provided by the rotation of the screws at high screw speeds. In addition to this, the domain size should also decrease due to the reaction occurring between the polyol and SMAH. However, at a constant feed rate, the residence time and, hence, the reaction time decrease with increasing screw



**Figure 4** Hot-stage micrograph of 0.5% PTMEG/SMAH blend at 150 rpm.

speed. Thus, there are two opposing factors for the extent of the reactions, and a maximum in the extent of the reactions could be expected at an intermediate screw speed. This is, in fact, observed at 150 rpm as discussed in the analysis of the mechanical properties. At the speed of 220 rpm, since the residence time in the extruder is small, the extent of chain-extension/branching reactions is not as high as in the case of 150 rpm.

The tensile properties of pure SMAH and 0.5 and 1% PTMEG-functionalized SMAH blends in the presence of hydrated zinc acetate extruded at 150 rpm can be compared using Table III. The addition of polyol to the system causes slight



**Figure 5** Hot-stage micrograph of 0.5% PTMEG/SMAH blend at 220 rpm.

**Table III** Effects of Processing Parameters and PTMEG Content on PTMEG/SMAH Extruded Blends with 1% Catalyst

% PTMEG	Screw Speed	Tensile Strength (MPa)	Elongation at Break (%)	Modulus of Elasticity (MPa)
0	150	26	1.9	1490
0.5	60	27	2.3	1532
	150	24	1.8	1655
	220	26	2.2	1414
1	60	29	2.9	1320
	150	27	2.4	1372
	220	30	3.3	1268

changes in the mechanical behavior of the system. For example, the addition of 0.5% polyol to SMAH decreases the tensile strength and percent strain at break, but increases the tensile modulus of SMAH, indicating that branching may be dominant in the presence 0.5% PTMEG. When the PTMEG content is increased to 1%, the opposite behavior in the tensile properties is obtained. This may be attributed to the unreacted polyol that would be responsible for plasticization in the system.

Since SMAH is a glassy material, the motions of the molecules are very restricted. On the other side, PTMEG is a low molecular weight polymer with low viscosity. It is expected that chain extension/branching would restrict the molecular motions further and decrease the tensile strength and strain at break and increase the tensile modulus. On the other hand, further addition of low molecular weight PTMEG would increase the molecular mobility, giving rise to the opposite effect.

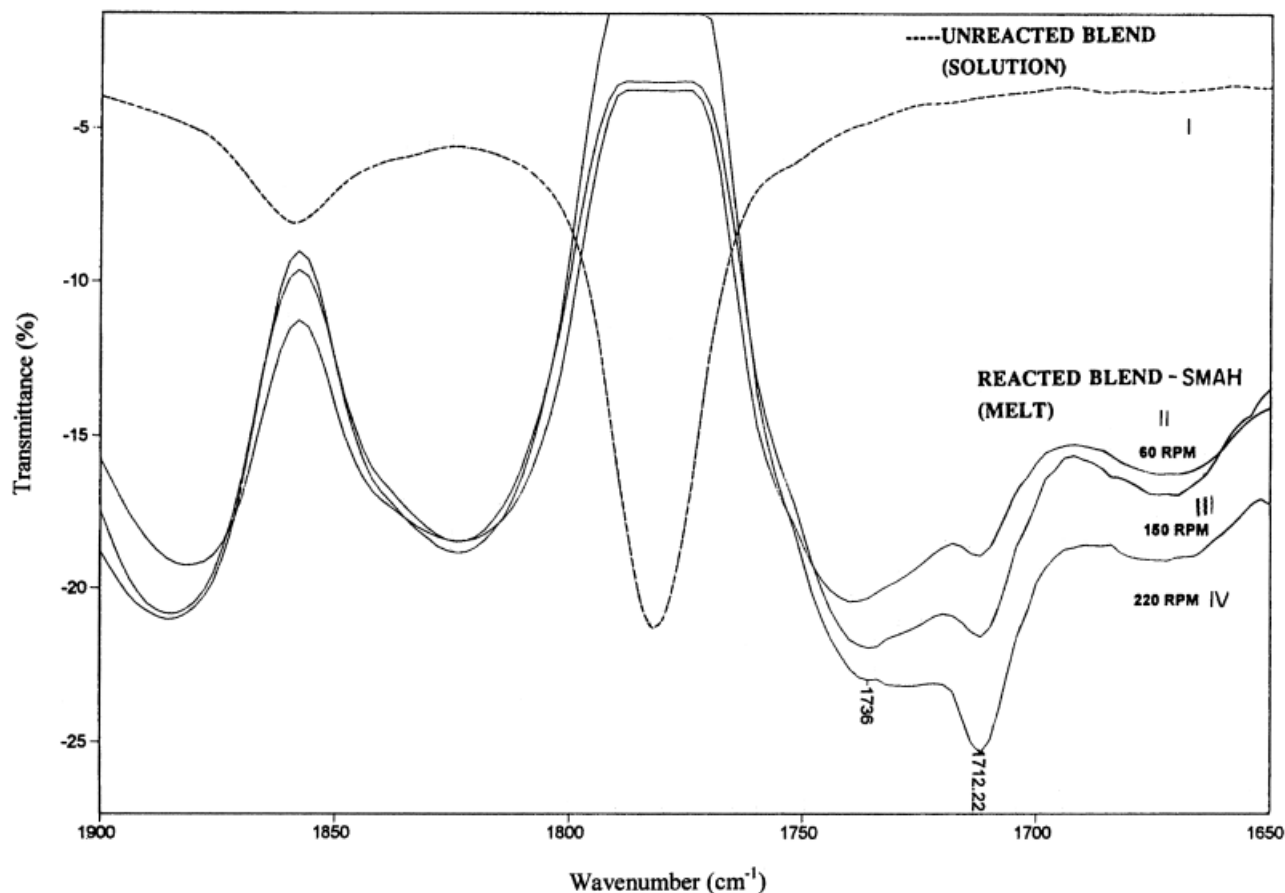
The effects of processing parameters on the PTMEG/SMAH blends can be observed from Table III. At both concentrations of PTMEG, the tensile strength and strain at break decrease slightly and the modulus of elasticity increases when the screw speed is increased from 60 to 150 rpm. However, with further increase in the screw speed to 220 rpm, the opposite is observed, that is, the tensile strength and strain at break increase and the modulus decreases. This indicates that the chain-extension/branching reactions are maximized at 150 rpm among the screw speeds studied. At low rpm (60), mixing is not vigorous; thus, the reaction rates are low. At high rpm (220), mixing is vigorous; however, now the residence time is low. By increasing the screw speed from 60 to 150 rpm, a higher reaction rate is observed due to a larger surface area and better mixing, but by

increasing the screw speed from 150 to 220 rpm, a lower extent of the reaction is observed due to the low residence time in the extruder.

The occurrence of reactions was analyzed by taking the FTIR spectra of the extruded blends and an unreacted blend, which was prepared as a solution at room temperature. Figure 6 shows the FTIR spectra of the unreacted (solution) blend as I and also the difference in the FTIR spectra of the extruded (i.e., reacted) blend and pure SMAH as II, III, and IV at various screw speeds. The unreacted solution blend does not show any ester (at  $1736\text{ cm}^{-1}$ ) or carboxylic acid (at  $1712\text{ cm}^{-1}$ ) peaks as expected. However, in the extruded blends, the formation of both an ester (at  $1736\text{ cm}^{-1}$ ) and a carboxylic acid group (at  $1712\text{ cm}^{-1}$ ) are observed. Carboxylic acid formation is due to the opening of the MAH ring. Different overall reactions are possible depending on the process time and conditions in the processing equipment. The formation of carboxylic acid is more dominant than is the ester formation, especially at high rpm, since the residence time decreases with increasing screw speed. As seen from Figure 6, at 220 rpm, most of the carboxylic acid groups formed by hydrolysis cannot react with the polyol to form ester groups. Thus, FTIR data support the observations on the thermal, mechanical, and morphological properties.

## CONCLUSIONS

SMAH/PTMEG blends were prepared in an intensive batch mixer and in a twin-screw extruder. The increase in torque behavior in batch mixing indicated that chain-extension/branching reactions occurred in the system. The blends with the catalyst exhibited higher torque buildup and



**Figure 6** FTIR spectra of the solution mixture and the difference in the FTIR spectra of the extruded blends and neat SMAH at various screw speeds.

faster reactions. The addition of PTMEG to SMAH lowered the  $T_g$  of SMAH in both batch mixing and in extrusion experiments, because the ether bond in PTMEG introduced mobility to the system. In the hot-stage microscopy analysis of the extruded 0.5 % PTMEG/SMAH/ $ZnAc_2 \cdot 2H_2O$  system, reduction in the domain size was observed with increasing screw speeds of 60, 150, and 220 rpm. In the mechanical characterization, addition of 0.5 % PTMEG into the system resulted in lower tensile strength and percent strain at break and a higher tensile modulus in comparison to SMAH. Further addition of 0.5 % PTMEG into the system (total of 1% PTMEG) resulted in opposite trends in the tensile properties due to the plasticization effect of the unreacted polyol in the system. The mechanical properties indicate that, among the screw speeds studied, 150 rpm produced the highest extent of chain-extension/branching reactions. In the FTIR analysis of the 0.5% PTMEG/SMAH extruded blend, both the

formation of ester and carboxylic acid groups were observed. However, at 220 rpm, most of the carboxylic acid groups could not react further to form an ester, owing to the lower residence time at high rpm.

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