

Syntheses and Characterization of Maleic Anhydride–Styrene–Allyl Propionate Terpolymer Ester Derivatives

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ABSTRACT: In this study, maleic anhydride (MA)–styrene (St)–allyl propionate (AP) was produced with MA, St, and AP. It was then reacted with *n*-propyl alcohol (Pr), *n*-butyl alcohol (Bu), *n*-pentyl alcohol (Pn), and benzyl alcohol (Bz) under certain conditions to produce ester derivatives of the terpolymer. These ester derivatives were designated alkyl maleate terpolymers (PrMA–St–AP, BuMA–St–AP, PnMA–St–AP, and BzMA–St–AP). The polymers were investigated by solubility and viscosity experiments, with

the number of ester groups in the polymers determined by chemical analysis. They were also characterized by Fourier transform infrared spectroscopy, with thermomechanical properties measured via stress–strain curves. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 296–299, 2003

Key words: modification; mechanical properties; synthesis; stress; strain

INTRODUCTION

In the recent years, the chemical modification of polymers for synthesizing polymers with required characteristics and their utilization in various areas have often been studied. Among these studies, the synthesis of polymers in which more than one monomer was formed has been very important. The existence of functional groups in the synthesized polymers increases their utilization. The synthesis of polymers involving functional groups in greater numbers provides a facile means for the production of graft polymers.¹ Maleic anhydride (MA) is a reactive monomer, and the copolymers or terpolymers of MA are called reactive polymers because of the existence of MA units in the main chain. During the polymerization, anhydride units provide a reaction tendency, and these units form the active regions during graft and modification.^{2–4}

Because of these characteristics, MA has been used in the synthesis of many copolymers and terpolymers.^{5–7} These polymers have been used in a number of areas for various purposes. In one study, the polyesterification of poly(ethylene glycol) with different atomic masses,⁸ MA copolymers were used to obtain compatible polymer mixtures.^{9–12} Studies on increasing the number of copolymers involving MA units

have continued in a great number of usage areas because of the fact that MA is a functional monomer.¹³

In this study, the functionality of MA units benefited from the MA unit involving terpolymer maleate ester derivatives obtained from alcohols with different chain lengths, one of which was benzyl alcohol (Bz). From an examination of the changes in the characteristics of the ester derivatives, we saw that they had different properties. We believed this was related to the structure of the alcohols used in the ester formation.

Bz was chosen because of its aromatic composition. The thermomechanical characteristics of the ester derivatives from different alcohols were similar, whereas those of the ester obtained from Bz were significantly different. The differences in the thermomechanical properties between of the alkyl and benzyl esters suggested that they were related to the ring structures.

EXPERIMENTAL

Materials

Allyl propionate (AP) and styrene (St; Merck) were distilled before use. They had the following characteristics: AP boiling point (BP) = 122°C; St BP = 138°C. MA (Sigma) was purified before use by recrystallization from anhydrous benzene and by sublimation under vacuum. Azobisisobutyronitrile (AIBN) was purified by recrystallization twice from a chloroform solution. *n*-Propyl alcohol (Pr), *n*-butyl alcohol (Bu), *n*-pentyl alcohol (Pn), and Bz (Merck) were distilled before use.

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TABLE I
Solubilities, Colors, $[\eta]$ values, Number of Esters of MASMMA and *n*-Alkyl Maleate in Different Solvents

Polymer	THF	A	SH	DMF	T	Water	Color	$[\eta]$	Numbers of esters
MA-St-AP	+	+	+	+	-	-	White	1.35	705
PrMA-St-AP	+	+	+	+	-	-	Yellow	1.10	728
BuMA-St-AP	+	+	+	+	-	-	Yellow	0.65	750
PnMA-St-AP	+	+	+	+	-	-	Brown	1.02	773
BzMA-St-AP	+	+	+	+	-	-	Yellow	0.91	762

Synthesis of the terpolymer and ester derivatives

In this study, the terpolymer was initially produced with MA, St, and AP with molar proportions of 2:1:1 in the methyl ethyl ketone solvent in the presence of AIBN as an initiator at 70°C. The ester derivatives of this terpolymer were then obtained. Pr, Bu, Pn, and Bz were used to obtain the terpolymer ester derivatives. We produced the ester derivatives by keeping the terpolymer alcohol ratio at 1:4 in separate tubes without an initiator at a constant temperature of 150°C for 4 h. A PerkinElmer 1600 Fourier transform infrared spectrometer was used for the spectroscopic characterization of the samples.

Various solvents were used to determine the solubility of the polymer samples. In addition, the unit viscosity factor and the ester number of each polymer were determined.

For the determination of thermomechanical properties, 1 g of each of the polymer samples was put into a film form with tetrahydrofuran (THF). A Shimadzu TMA-50 was used to record the stress-strain curves of the films.

RESULTS

The colors and physical situations of the produced terpolymer and ester derivatives were visually inspected initially. All of the MA terpolymer was in the form of white powder, whereas the *n*-alkyl maleate terpolymers were hard, resin-like structures with different colors.

The solubilities of the terpolymer and the ester derivatives were observed in THF, toluene (T), cyclohexanone (SH), dimethylformamide (DMF), acetone (A), and water. In addition, viscosimetric analyses of the polymers in 0.1 g dL⁻¹ of solution were performed with the one-point measure method. The limit viscosity number ($[\eta]$) of the Mark-Houwink relationship of each polymer was calculated with the Solomon-Ciuta equation:¹⁴

$$[\eta] = \frac{1.414}{C}(\eta_{sp} - \ln \eta_r) \quad (1)$$

where η_{sp} is the specific viscosity number in the Huggins relationship, η_r is the relative viscosity number in the Creamer relationship, and *C* is the molarity. The solubility information and viscosity values are given in Table I.

Based on the results, no changes occurred in the solubility of the terpolymer or of their ester derivatives. A change of the MA structure into an alkyl maleate may be thought contribute to the solubility of the ester derivatives because this change would increase the number of ester subgroups occurring in the main chain. However, when the $[\eta]$ values of the terpolymer and ester derivatives were compared, it was not clear that a smooth increase or decrease occurred with the carbon number in the alcohol.

The difference between the chemical structure of the MA terpolymer and the alkyl maleate terpolymers was the anhydride unit. The differences in the Fourier transform infrared (FTIR) spectra between the terpolymer and ester derivatives are shown in Figure 1. The MA peaks, seen at 1785, 1790, 1855, and 1020 cm⁻¹ in the terpolymer, were not observed in the ester derivatives.^{15,16} This was an important observation, proving that the anhydride chains changed into esters.

Shown in Scheme 1 is a possible mechanism for the esterification of the MA-St-AP terpolymer with alcohol, obtained as a result of chain opening among MA and the alcohols. The PrMA-St-AP reaction is given as an example. The chemical formulas for the other ester derivatives are given in Schemes 2-4.

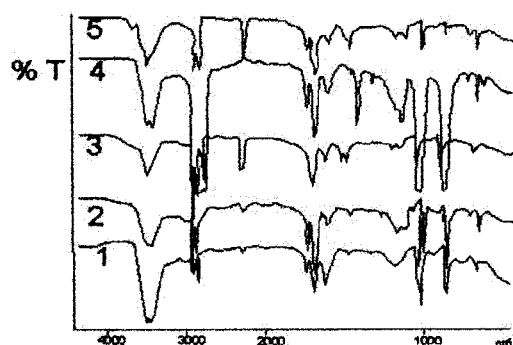
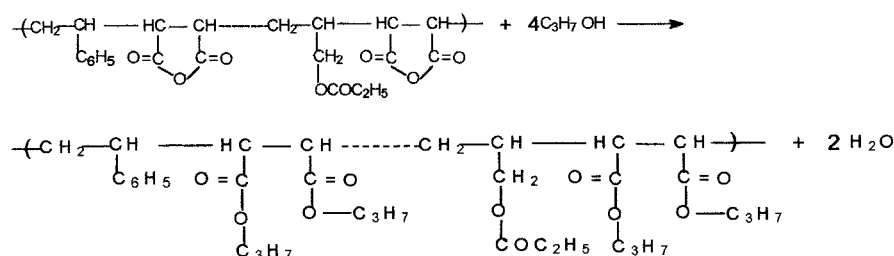


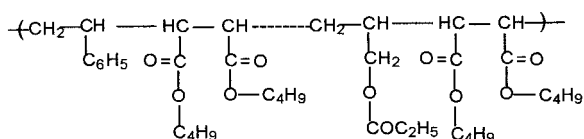
Figure 1 FTIR spectra: (1) MA-St-AP, (2) PrMA-St-AP, (3) BuMA-St-AP, (4) PnMA-St-AP, and (5) BzMA-St-AP.



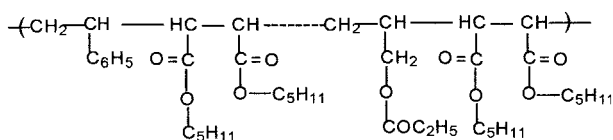
Scheme 1 Mechanism of the ester derivative PrMA-St-AP.

The stress-strain curves of each polymer were recorded to determine the thermomechanical characteristics of the MA terpolymer and the *n*-alkyl maleate terpolymers. The stress and strain values of each polymer were read from the original curves, as plotted on a computer. These are shown in Figure 2. With these curves, the elastic modulus (*E*) values, in terms of the maximum stress and strain values without deformation, were obtained. On inspection of the stress-strain curves, the terpolymer ester derivatives were found to be more elastic than the terpolymer. In other words, the terpolymer had a harder structure than the ester derivatives.

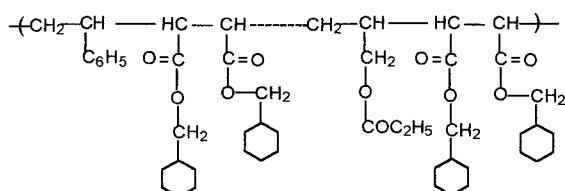
The glass-transition temperature (T_g) of each terpolymer and the ester derivatives was determined by the *E* method; that is, the *E* values at certain temperatures were recorded, and log *E*-temperature curves were drawn. These curves are shown in Figure 3. The mean temperature at which the *E* value falls suddenly on these curves gives the T_g value.¹⁷ These values are given in Table II.



Scheme 2 Composition of the ester derivative BuMA-St-AP.



Scheme 3 Composition of the ester derivative PnMA-St-AP.



Scheme 4 Composition of the ester derivative BzMA-St-AP.

The stress-strain curves of each terpolymer and the ester derivative were recorded at increasing load and temperature conditions. From these curves, strain-temperature curves of the terpolymer and the ester derivatives were drawn via computer. These curves are shown in Figure 4. The thermal coefficient of expansion (α), a value commonly used for the comparison of the thermomechanical properties of polymers, was found from the linear parts of the curves. These values are given in Table II.

DISCUSSION

On initial inspection of the colors and physical forms of the obtained polymers, we found that the anhydride polymer was in the form of white powders whereas the *n*-alkyl maleate terpolymers were in the form of hard resins of different colors. The solubilities of the terpolymer and the ester derivatives in some of the most common solvents are given in Table I. As shown in the table, there was no difference between the solubility of the terpolymer and that of the ester derivatives. It may be thought that the ester derivatives should be more soluble because the number of subgroups existing in the ester increase because of the transformation into *n*-alkyl maleate of the MA structure.

The number of esters formed during polymerization depends on the reaction conditions.¹⁸ In this study,

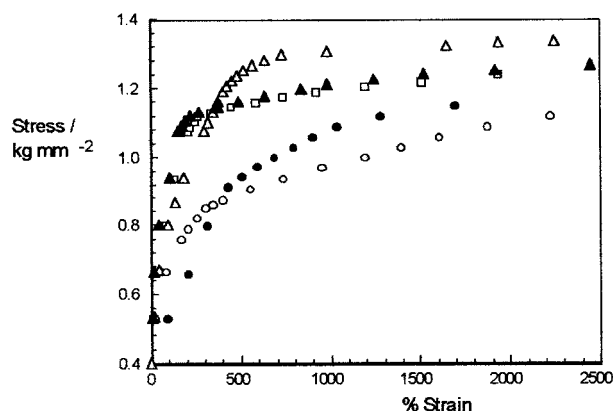


Figure 2 Stress-strain curves: (▲) MA-St-AP, (△) PrMA-St-AP, (○) BuMA-St-AP, (■) PnMA-St-AP, and (□) BzMA-St-AP.

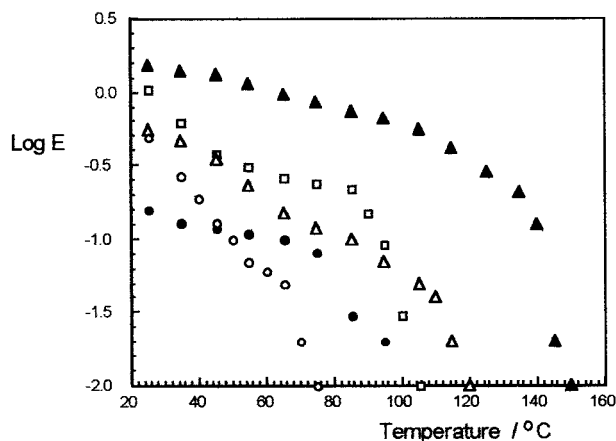


Figure 3 Temperature- E curves: (▲) MA-St-AP, (△) PrMA-St-AP, (○) BuMA-St-AP, (■) PnMA-St-AP, and (□) BzMA-St-AP.

great differences were not observed because the obtained derivatives were produced under the same conditions. However, we could clearly see that there was an increase in the ester numbers of the n -alkyl maleate terpolymer with respect to the maleate anhydride terpolymer. The reason for this was that there was an increase in the number of ester subgroups connected to the main chain as a result of the esterification taking place during the opening of the MA ring.

The $[\eta]$ values of the terpolymer and ester derivatives were calculated from viscosity measurements. When the results were considered (see Table I), the $[\eta]$ value of the original terpolymer was greater than those of the n -alkyl maleate terpolymers. A possible mechanism for this increase was the entrance of the alkyl groups with linear chain structures as a result of the opening of anhydride rings during esterification. This resulted in an increase in the free volume ratio.

Because there were no major differences between the number of ester groups of the MA polymer and the alkyl maleate esters, there were no obvious differences observed in the FTIR spectra. The specific anhydride functional group peaks in the MA terpolymer were found to diminish in the n -alkyl maleate terpolymers. This was proof of the esterification of the anhydride chains.

When comparing the thermomechanical analysis re-

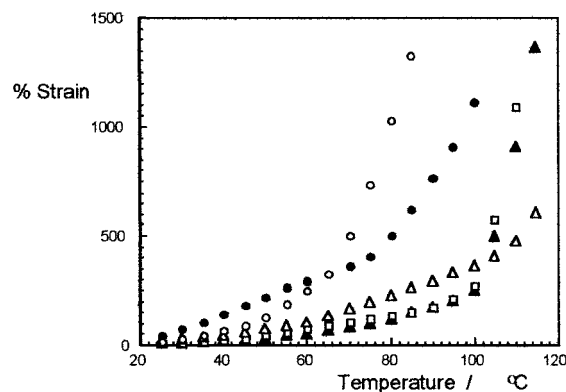


Figure 4 Temperature-strain curves: (▲) MA-St-AP, (△) PrMA-St-AP, (○) BuMA-St-AP, (■) PnMA-St-AP, and (□) BzMA-St-AP.

sults of the polymers, we could see that the n -alkyl maleate terpolymers were more elastic than the original terpolymer. For example, the T_g of the n -alkyl maleate terpolymers decreased with increasing carbon numbers in the alcohols. α values, however, increased. Other thermomechanical properties were also observed to change in the same way. As a result, we conclude that the thermomechanical properties of the MA can be improved by the esterification of the MA units.

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TABLE II
 T_g and α Values of MA-St-AP and n -Alkyl Maleate

Polymers	T_g (°C)	α (°C ⁻¹)
MA-St-AP	126	1.26
PrMA-St-AP	88	1.50
BuMA-St-AP	76	2.06
PnMA-St-AP	74	6.70
BzMA-St-AP	-	3.78