Thermal Characterization of *n*-Alkyl Maleate-Styrene-Allyl Propionate Terpolymers

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ABSTRACT: Thermal characterization of maleic anhydride-styrene-allyl propionate (MA-St-AP) terpolymer and its ester derivatives named as *n*-alkyl maleate and shown as *n*Pr MA-St-AP, *n*Bu MA-St-AP, *n*Pn MA-St-AP, and *n*Bz MA-St-AP was carried out. The thermal characterization was performed using thermal analysis techniques such as TGA, DTA, DSC, and TMA. Different results were observed between the original terpolymer and its ester derivatives. Thermal stabilities of the terpolymer and its ester derivatives were compared by using various measurements plotted as TGA, DTA, DSC, and TMA curves. The increase in the alcohols' carbon numbers added to the original terpolymer results in ester derivatives with different thermal stability behavior. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 600–604, 2007

Key words: thermal degradation; charge transfer complexes; maleic anhydride; TGA; DTA; DSC; TMA

INTRODUCTION

It is well known that an alternating copolymer can be easily obtained by the copolymerization of an electron-rich monomer and an electron-deficient monomer through the formation of charge transfer complexes. One of the extensively studied systems is maleic anhydride (MA) and styrene. Polymerization can be initiated by radical initiators such as AIBN, but the polymerization process is uncontrollable.[1] In recent years, MA has become an important monomer of copolymers and terpolymers.[2–6] Polymer degradation and stabilization as well as polymer recycling have been extensively studied in the past decades. The thermal stability of polymers and copolymers has been extensively studied employing the method of thermogravimetric analysis (TGA) by several authors[7–13] in the past because of its application in various polymer industries.

There are many studies on thermal degradation of styrene/MA copolymers and no studies on thermal degradation of ester derivatives of styrene-MA. In this study, Maleic anhydride-styrene-allyl propionate (MA-St-AP) terpolymer ester derivatives were prepared over anhydride units using alcohols with varying number of carbons. Depending on the alcohol carbon numbers, the ester derivatives exhibit different thermal properties when compared with those of terpolymer.

The polymers thermal behavior was studied by TGA, differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermomechanical analysis (TMA). TMA tests were performed only in the penetration mode. The polymers' glass transition and degradation temperatures were obtained by TGA, DSC, DTA, and TMA curves.

It is known that MA first forms copolymer with monomers, which are rich in terms of electrons, by charge transfer complex formation reaction.[14–24] MA-St-AP terpolymer was prepared with the donor acceptor system. Then, the ester derivatives were synthesized by using the different kinds of alcohols. At the end of such a reaction, MA units, which have the ring structure, are opened and alkyl groups are bound into the terpolymer. Consequently, the thermal properties of MA-St-AP terpolymer will be changed.

EXPERIMENTAL

Materials

The monomers and the other materials used in the synthesis of MA-St-AP terpolymer and its ester derivatives (*n*-alkyl maleate terpolymers) were given in our previous work.[4] In this study, their chemical structures are given in Scheme 1.

Characterization of terpolymer and ester derivatives

TGA, DSC, and DTA experiments were carried out using a Shimadzu TG-50, DSC-50, and DTA–50. The experiments use 0.010 g polymer sample, at a heating
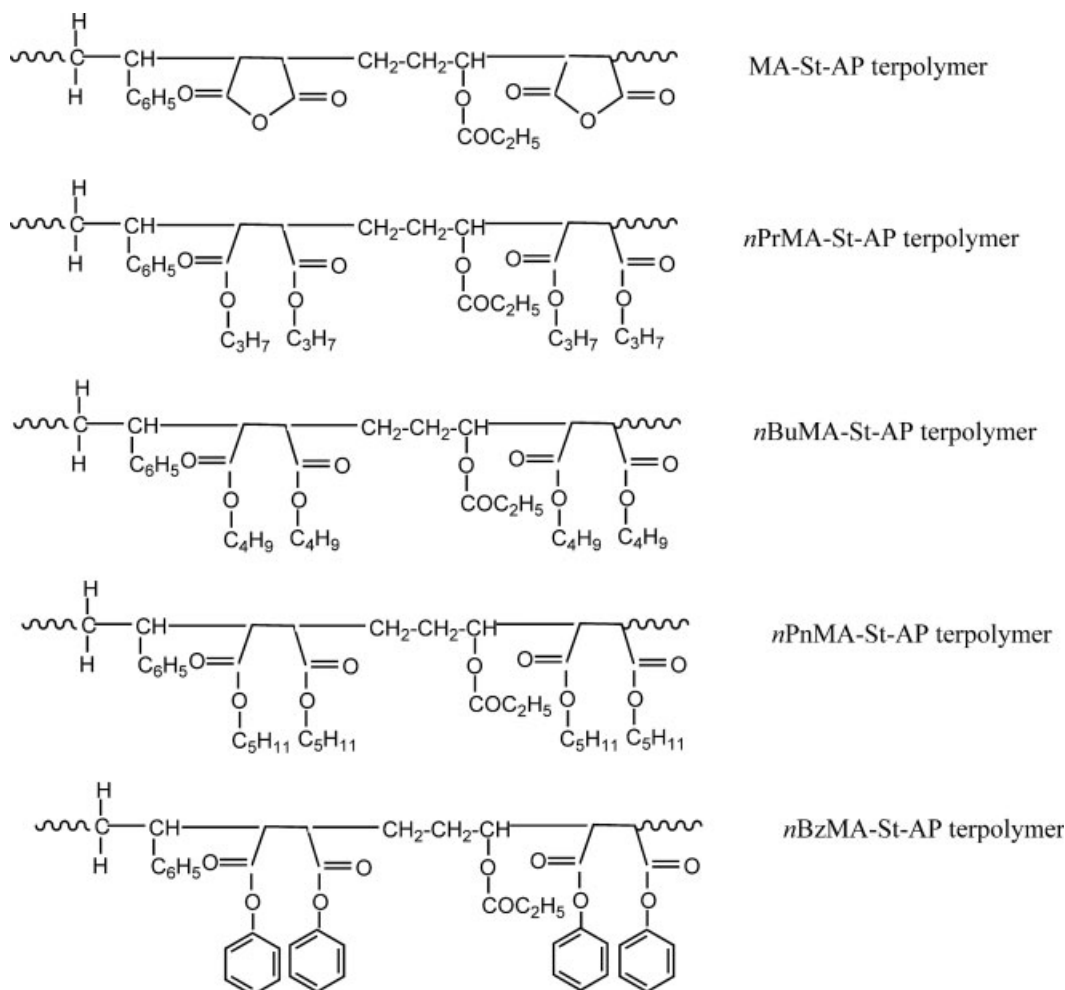
Scheme 1 Chemical structures of the terpolymer and its ester derivatives.

rate of 10°C min^{-1} from 25 to 600°C, under a flowing (25 mL min^{-1}) nitrogen atmosphere.

Penetration curves of the polymer films were recorded on a Shimadzu TMA-50 at a heating rate of 10°C min^{-1} and under 1 g fixed loading from room temperature to 150°C in a flowing (25 mL min^{-1}) nitrogen atmosphere. For the determination of the penetration–temperature curves of the polymer samples, 0.5 g of polymer samples in tetrahydrofuran (THF) were cast into a dry and clean Pyrex Petri dish
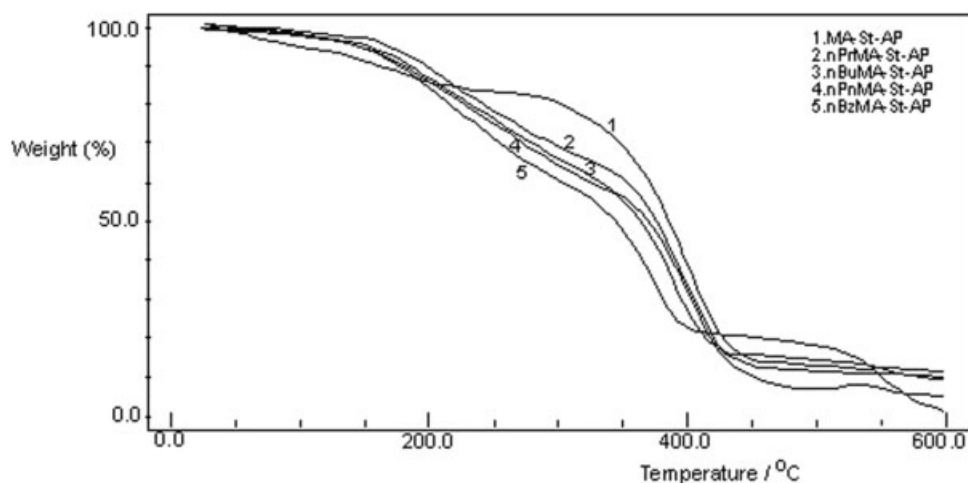
Figure 1 TGA curves of the terpolymer and its ester derivatives.

TABLE I
Values of T_i, T_h, T_m, T_f, C_m, and E_a of MA-St-AP Terpolymer and Its Ester Derivatives

Polymer	T_i (°C)	T_h (°C)	T_m (°C)	T_f (°C)	C_m (%)	E_a (kJ mol^{-1})
MA-St-AP	331	386	398	431	40.3	123.28
nPrMA-St-AP	357	365	390	419	35.4	121.64
nBuMA-St-AP	362	377	400	430	34.3	126.03
nPnMA-St-AP	368	371	407	440	29.2	129.62
nBzMA-St-AP	341	346	376	395	33.5	150.80

of 50 mm diameter. The films were obtained by evaporation of the solvent at room temperature and were dried under vacuum at 50°C. All the films prepared in this way were 0.1 mm in thickness.

RESULTS AND DISCUSSION

The difference between the chemical structure of the original terpolymer and the ester derivatives is the anhydride unit (Scheme 1). The explanations belong to these spectra, and FTIR spectra of all the polymers have been given in a previous work.[4]

TGA curves of MA-St-AP terpolymer and n-alkyl maleate are shown in Figure 1. There was a two-step thermal degradation in all the polymers used. The first thermal degradation step was seen in a temperature range of 100–150°C, resulting in at least 5% weight loss. This was not a basic degradation, because it mainly involved small molecules on the surface of the polymer such as water. The reason for the weight loss in MA-St-AP terpolymer within this temperature range was due to absorption of more humidity by the MA terpolymer. The first degradation step of the ester derivatives lasted at 300–350°C, leading to ∼ 50% weight loss. On the other hand, in the main thermal

degradation of MA-St-AP terpolymer the weight loss started at about 300°C.

The characteristic degradation temperatures obtained from the thermograms (Fig. 1) are summarized in Table I. The activation energy (E_a) at degradation was determined by Freeman-Carroll method. These were initial reaction temperature (T_i), half-time temperature (T_h), maximum rate temperature (T_m), final reaction temperature (T_f), and amount of remained substance at maximum rate (C_m).

Thermal stability and behavior of the polymers were related directly to their chemical structures. Thermal stabilities of the ester derivatives were observed to be better than those of the original terpolymer at the beginning of the thermal degradation reaction (Scheme 1). T_i values of thermal stabilities of the original terpolymer were found to be lower than those of the ester derivatives, because linear alkyl groups were being replaced instead of the ring-structured MA units in MA-St-AP terpolymer. Thus, thermal stabilities of the terpolymer changed significantly by different alcohol carbon numbers used in ester derivatives preparation. Thus, it can easily be said that the results of TGA analysis were in accord with our expectations and with the chemical structure of the terpolymer and its ester derivatives.

The DSC and DTA curves (Figs. 2 and 3) were supported by TGA curves. In the DTA curves (Fig. 3), small endothermic peaks were observed at around 150°C and at such a temperature the adsorbed water was removed. The endothermic and exothermic peaks with higher intensity were observed at about 350–400°C. Thus it could be suggested that endothermic and exothermic events occur simultaneously at this temperature range. Superposing in temperature the TGA curves, we can easily correlate the weight loss against DTA curves. Weight loss is a direct result of
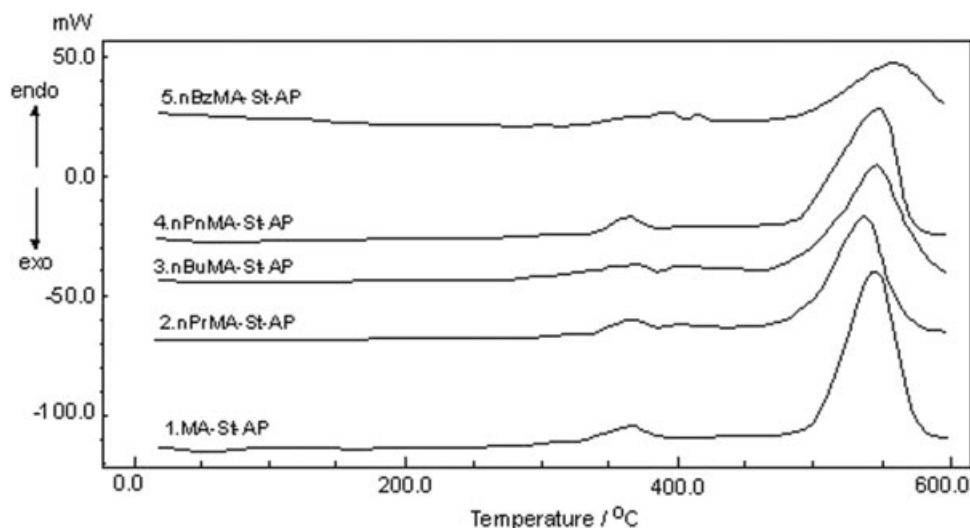
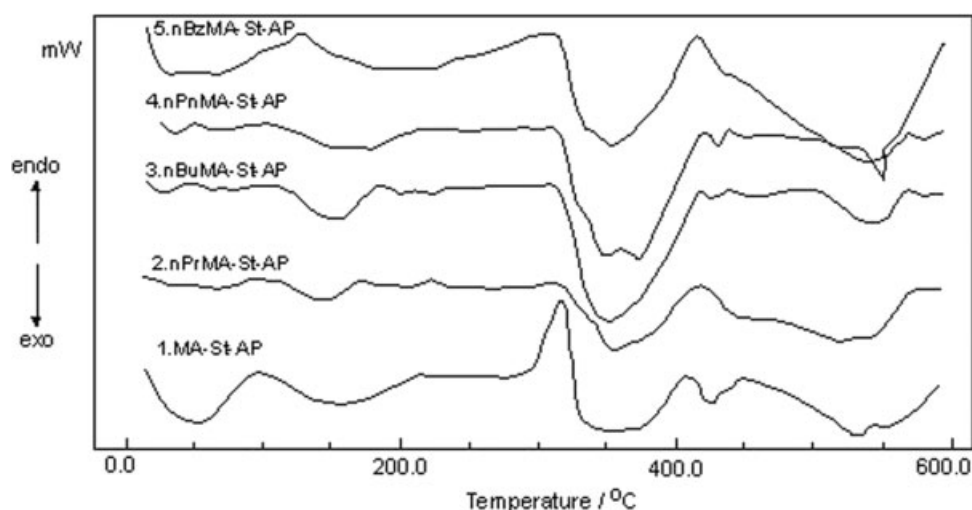**Figure 2**　DSC curves of the terpolymer and its ester derivatives.

Figure 3 DTA curves of the terpolymer and its ester derivatives.

breaking down of the main chain, branches and ring opening reactions, and so it is an endothermic event. The exothermic peaks were due to the crosslinking or ring formations by the combination of the radicals emerging during the thermal degradation process. What was interesting here was that the very high endothermic peaks registered at about 550°C in DSC curves were not observed in DTA curves. The reason for this behavior may be due to the change in the heat capacity of carbonized residues with phase change and such chemical events were detected much more sensitively in DSC curves.

According to the values in Tables I and II, and the TGA-DSC curves, MA-St-AP terpolymer was generally more stable than the ester derivatives. The values of the ΔH were automatically obtained by the DTA and DSC instruments.

Penetration experiments were performed to determine the glass transition temperature (T_g) of MA-St-AP and n-alkyl maleate terpolymers (Fig. 4, Table II). T_g can be obtained from TMA curves in the penetration mode. As could be seen, the T_g value of MA-St-AP terpolymer was the highest. However, T_g values of the ester derivatives decreased with the increase in

the number of carbons of alcohols used in esterification. The T_g value of nBzMA-St-AP maleate terpolymer was different from that of other maleate terpolymers. The reason for this could be that the ring-structured phenyl group in benzyl alcohol made the structure much more rigid. These results supported those of the TGA, DSC, and DTA.

CONCLUSIONS

As seen from the DTA, TGA, and TMA curves, the results suggest that the MA-St-AP terpolymer was generally more stable than its ester derivatives, depending on the number of carbon atoms each alcohol possessed; however, the ester derivatives were more elastic than the original terpolymer.

TABLE II
Parameters Obtained from the DTA, DSC, and TMA Curves

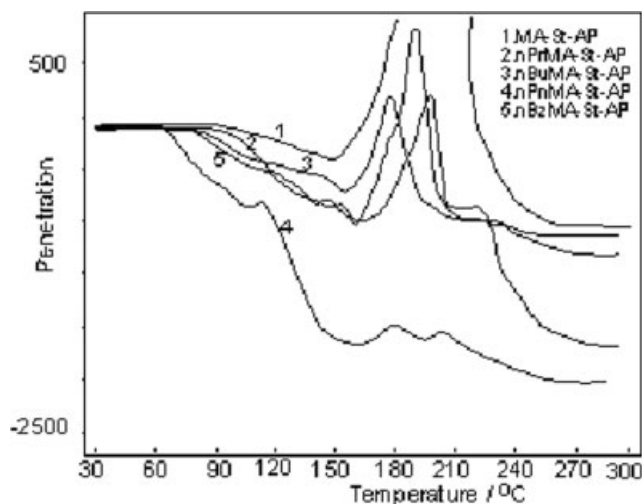| Polymer	Main peak of DSC		Main peak of DTA		TMA
	T (°C)	ΔH (J g^{-1})	T (°C)	ΔH (J g^{-1})	T_g (°C)
MA-St-AP	325	280	366	294	117
nPrMA-St-AP	360	202	368	196	89
nBuMA-St-AP	355	175	370	184	75
nPnMA-St-AP	320	168	365	170	55
nBzMA-St-AP	360	180	380	190	66

Figure 4 Penetration–temperature curves of the terpolymer and its ester derivatives.

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