

Characterization and synthesis of maleic anhydride-styrene-vinyl acetate terpolymer ester derivatives

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Maleic anhydride is one of the best studied electron-acceptor monomers [1]. It cannot be homopolymerized under normal conditions [2] but is often used for grafting and especially for alternating copolymerisation with electron-donor monomers [3]. During the last 25 years, the radical copolymerization of various functional monomers of the acceptor–donor type and synthesis of new functional polymers with given structure and important properties have attracted considerable interest [4, 5]. It is well known that complex-radical terpolymerization of donor–acceptor monomer systems is an effective method for the synthesis of functional macromolecules with given composition, structure and properties [6, 7].

Maleic anhydride copolymers are used for many purposes according to a detailed summary of their applications by Trivedi *et al.* [8]. Depending on the requirement, many of the maleic anhydride copolymers can be modified by reaction at the maleic anhydride ring [9–11]. Maleic anhydride, styrene and vinyl acetate are able to form charge transfer complexes [12]. Due to this complex formation the alternating copolymerization of the monomers can be initiated by a free radical mechanism. The reaction products are alternating copolymers providing high polarity and mechanical and thermal stability [13].

It is known that maleic anhydride, firstly, forms copolymer with monomers which are rich in terms of electrons by charge transfer complex formation reaction, according to Scheme 1 below [14–17]. We prepared maleic anhydride-styrene-vinyl acetate terpolymer with donor–acceptor system. Later, we synthesized the ester derivatives of the terpolymer by employing the reactive characteristics of maleic anhydride with ring opening [18–24] as shown below. The aim was to obtain polymers, which have better characteristics with linear chained ester derivatives, by opening the ring-structured maleic anhydride units that give rigid characteristics to polymer. The ester numbers of these terpolymer and its ester derivatives were calculated, their solvents were determined and viscosimetric, thermo-mechanic and thermal characterizations were carried out.

VA and St (Merck) were distilled before use. They have the following characteristics: VA, bp 72 °C; styrene, 138 bp °C. MA (Sigma) were recrystallized from benzene by sublimation under vacuum. AIBN was purified by recrystallizing twice from chloroform solution. Propyl alcohol, butyl alcohol, pentyl alcohol and benzyl alcohol (Merck) were distilled before use.

In this study, first, the terpolymer was produced by using monomers MA, S and VA taking the mole proportions of 2:1:1 in methyl ethyle ketone in the presence of AIBN as initiator at 70 °C. After this, the ester derivatives of MA-S-VA terpolymer were obtained by using propyl, butyl, pentyl and benzyl alcohols. The ester derivatives were produced by keeping a terpolymer alcohol ratio of 1:4 in separate tubes without an initiator at 150 °C constant temperature for 4 hrs.

The solubilities of terpolymer and its esters in tetrahydrofuran (THF), toluen (T), cyclohexanone (CH), acetone (A) and water chosen as widely as being used solvents, are provided in Table I.

The unit viscosity factor and ester number of each polymer was determined by viscosimetric method. For viscosimetric characterization, solutions of all samples in THF, with a molarity of 0.1 g dL⁻¹, were prepared. The time flow of the solutions and solvents was recorded by Ubbelohde type viscosimeter placed in a thermostatic water bath at 30 °C. Specific viscosity (η_{sp}) and relative viscosity (η_r) were calculated (Equations 1–2). By using these values, with Solomon-Ciuta equation (Equation 3) intrinsic viscosity [η] was calculated.

$$\eta_r = t/t_0 \quad (1)$$

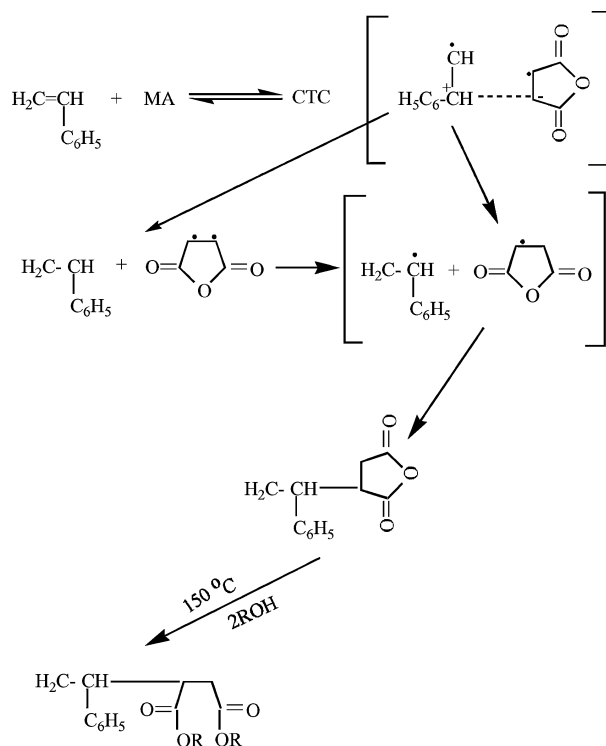
where t_0 is flow time of solvent, t is flow time of solution.

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

$$[\eta] = \frac{1.414}{C}(\eta_{sp} - \ln\eta_r)^{1/2} \quad (3)$$

where [η] is intrinsic viscosity, C is the molarity of the solution.

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Scheme 1 Formation of ester derivative and terpolymer.

In order to determine the ester numbers, 1.0 gram of sample polymers were put into erlenmeyer flasks of 150 cm³. 25 cm³ ethyl alcohol, 50 cm³ benzen and solution of 2 M 25 cm³ KOH in ethyl alcohol were added. The obtained solution was boiled under reflux condenser for 1 hr. After refrigerating the solution, 1 M HCl was titrated by using Equation 4 the ester numbers were calculated.

$$n_{es} = M_{w(KOH)}(M_1V_1 - M_2V_2)/m_p \quad (4)$$

where, n_{es} is ester number in polymer, M_w is molar mass of KOH, M_1 is molarity of KOH, V_1 is volume (cm³) of KOH, M_2 is molarity of HCl, V_2 is volume (cm³) of HCl, m_p is mass (g) of polymer sample [25].

For the FTIR spectra, Perkin-Elmer 1600 FTIR was used. A Shimadzu TMA-50 was used for thermomechanical characterization of the polymers in film form.

The maleic anhydride terpolymer was a white powder, whereas, *n*-alkyl maleate terpolymers were formed as a rigid resin of brown or yellow colour. As seen in Table I, there is no difference in the solubilities of terpolymers containing ester groups and their ester

TABLE I Solubilities, colors, $[\eta]$ values, number of esters of MA-St-VA and *n*-Alkyl maleate in different solvents

Polymer	THF	A	CH	DMF	T	Water	Color	$[\eta]$	Numbers of esters
MA-St-VA	+	+	+	+	-	-	White	0.79	705
PrMA-St-VA	+	+	+	+	-	-	Yellow	0.23	812
BuMA-St-VA	+	+	+	+	-	-	Brown	0.30	717
PnMA-St-VA	+	+	+	+	-	-	Brown	0.77	790
BzMA-St-VA	+	+	+	+	-	-	Brown	0.43	784

derivatives in the same solvents. Since transformation of maleic anhydride to *n*-alkyl maleate increases the number of ester side groups on the main chain, it can be thought that this can help the ester derivatives to dissolve easier.

Ester numbers are known to be dependant upon the reaction conditions [26] during the polyesterification processes. Since all of the obtained *n*-alkyl maleate ester derivatives are acquired under the same conditions, no big difference in ester numbers was observed. But, an increase in the number of *n*-alkyl maleate terpolymer ester numbers, with respect to maleic anhydride terpolymer can be easily seen. Therefore, this is concluded to be derived from the increase in the number of ester side groups connected with the main chain in relation to the opening of the maleic anhydride ring due mainly to esterification.

The $[\eta]$ value of MA-St-VA terpolymer has the largest value with respect to other polymers. In maleate derivatives, the linear-chained structures induced by the opening of the maleic anhydride ring facilitates the flow of polymers in the solutions, and thus decreases the $[\eta]$ values.

The difference between the chemical structure of the MA terpolymer and the alkyl maleate terpolymers was the anhydride unit. The differences in the FTIR spectra between the terpolymer and ester derivatives are shown in Fig. 1. The maleic anhydride peaks, seen at 1785-1790-1855-1020 cm⁻¹ in the terpolymer, were not observed in the ester derivatives [27, 28]. This is important evidence showing the changing of anhydride rings into ester derivatives.

Stress-strain curves of the polymers were recorded to determine the thermomechanical characteristics of the MA terpolymer and the *n*-alkyl maleate terpolymers. These are shown in Fig. 2. Some thermomechanical parameters such as the elasticity modulus (E), maximum stress and strain without deformation obtained from Fig. 2 are given in Table II. The stress-strain curves apparently reveal that the terpolymer ester derivatives are more elastic than the terpolymer because they possessing lower E values (Fig. 2).

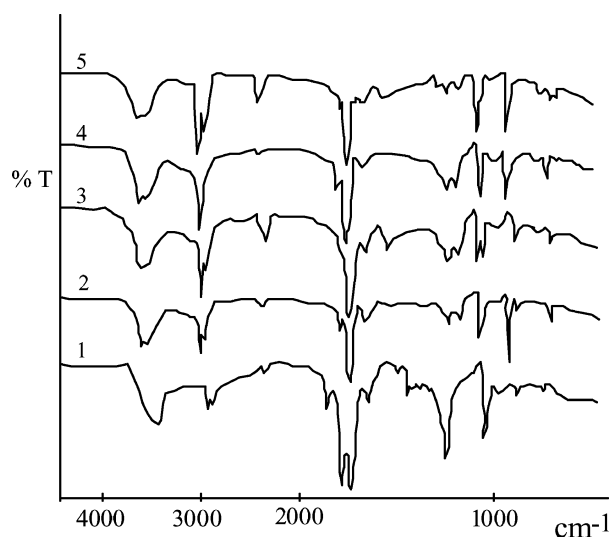


Figure 1 FTIR spectra. (1) MA-St-VA, (2) PrMA-St-VA, (3) BuMA-St-VA, (4) PnMA-St-VA, and (5) BzMA-St-VA.

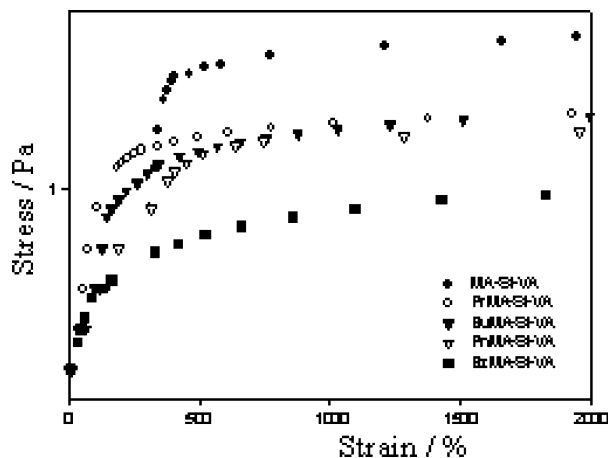


Figure 2 Stress-strain curves.

The glass transition temperature (T_g) values of the terpolymers and ester derivatives were determined by Log E -temperature curves. These curves are shown in Fig. 3. The mean temperature described by the sudden drop in the T-E curves in Fig. 3 determines the T_g values [29]. These values are also given in Table II.

The stress-strain curves of the terpolymers and the ester derivatives were recorded at increasing temperatures. From these curves, strain-temperature curves of the terpolymer and ester derivatives were drawn. These are shown Fig. 4. The coefficient of thermal expansion (α) that is commonly used for comparing thermomechanical properties of polymers was found from the linear parts of the curves. These values are given in Table II.

It is possible to broaden the usage areas of polymers by changing T_g values of polymers by chem-

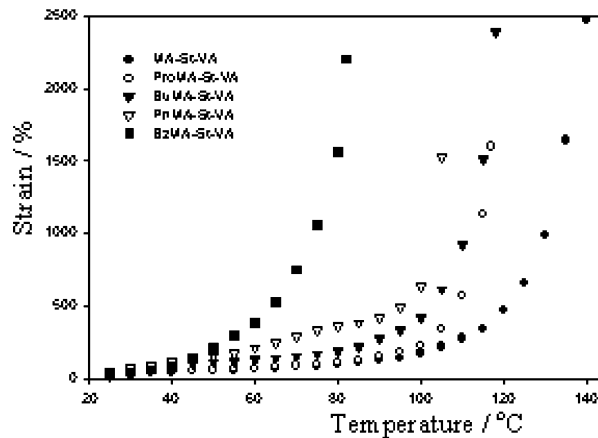


Figure 4 Temperature-strain curves.

ical and physical means. An important factor affecting the T_g value is chain elasticity. The chain elasticity of polymers decreases as the number of polar and bulky side groups increases [30], whereas it increases as the lengths of $-(O)-$, $-(COO)-$, $-(OCOO)-$ groups and $(CH_2)-$ units increases [31, 32]. The huge and steric barriered molecular structure of side groups, which affects the activity of polymer chain, decreases the free volume necessary for mobility. In this situation T_g value increases. The replacement of polar and ring-structured groups with linear-chained groups in the main chain can increase the elasticity of polymer.

The explanation with respect to the approaches mentioned above is correct for the considerations of the thermomechanical characteristics of MA-St-VA terpolymer and its maleate derivatives. The thermomechanical curves given in Figs 2 to 4 and the data reported in Table II shows that the MA-St-VA terpolymer has a harder structure than the ester derivatives, and the more the number of carbons in the alcohols used in esterification, the more elastic structure the material has, because the ester derivatives include linear-chained OCOR groups rather than ring-structured MA groups.

Consequently, the terpolymerization of styrene, vinyl acetate and maleic anhydride was carried out in the methyl ethyl ketone at 70 °C for 2 hrs. After this, maleic anhydride units in the terpolymer MA-St-VA were modified by using *n*-propyl, *n*-butyl, *n*-pentyl and benzyl alcohols in the cyclohexanone at 150 °C for 4 hrs. Particularly, the results of thermomechanical analyses showed that the ester derivatives are more elastic than the terpolymer.

TABLE II T_g , α and E values of MA-St-VA and *n*-alkyl maleate

Polymers	T_g (°C)	α (°C ⁻¹)	$(E) \times 10^{+3}$ (Pa)	Stress ^a (Pa)	% Strain ^a
MA-St-VA	126	1.26	7.01	1.390	455
PrMA-St-VA	88	1.50	6.06	1.186	563
BuMA-St-VA	76	2.06	3.07	1.160	452
PnMA-St-VA	74	6.70	2.20	1.120	697
BzMA-St-VA	-	3.78	2.90	0.886	710

^aMaximum stress and strain values without deformation.

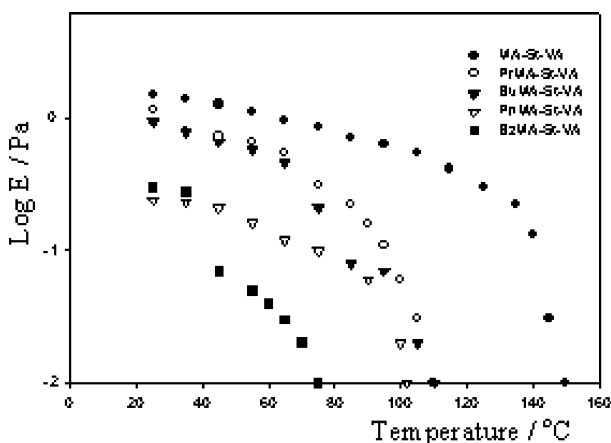


Figure 3 Temperature-E curves.

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