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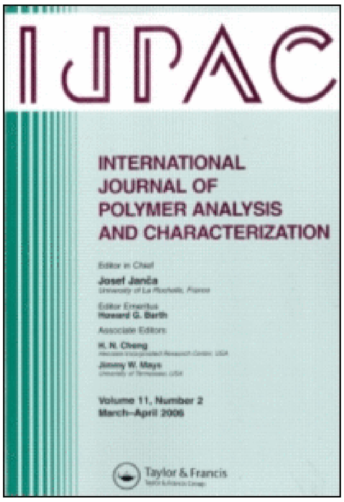

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Analysis and Characterization of Maleic Copolymers – III. Differential Scanning Calorimetry Study

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Endothermic physical processes and transition temperatures below 220°C of several binary and ternary copolymers of maleic anhydride with vinyl acetate, methyl methacrylate and/or styrene were studied by differential scanning calorimetry and infrared spectroscopy. To improve resolution of differential scanning calorimetry peaks and allow correct assignment of the chemical and physical processes in the studied temperature range, multiple heating–cooling or isothermal treatments were performed. The recyclization of hydrolyzed maleic acid units to maleic anhydride units, occurring around 160–190°C, was confirmed by infrared spectra.

Keywords: Maleic anhydride copolymers; Glass transition temperature; Differential scanning calorimetry

INTRODUCTION

It is well known that differential scanning calorimetry (DSC) allows the determination of first and second order transition temperatures of polymers. The glass transition temperature, T_g, of copolymers, a quasi-second order transition, is sensitive to the nature, amount, distribution of the co-monomers and the stereochemistry of copolymers.[1–3]

Thermogravimetric, DSC and pyrolysis-gas chromatography (Py-GC) investigations on the alternating or/and random copolymers

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of maleic anhydride (MA)–styrene (S) copolymers,[4–7] MA–acrylamide,[8] MA–vinyl acetate (VA),[6,9] MA–methyl methacrylate (MMA) have been reported.[10] It was stated that incorporation of MA increases the thermal stability of MA–MMA copolymer compared to poly(methyl methacrylate) homopolymer.[10] It was also established that T_g values of the alternating maleic anhydride copolymers are independent of monomer feed ratios,[6] but vary with co-monomer nature.

Dhal *et al.*[6] reported the T_g values for alternating MA copolymers with VA, S, ethyl vinyl ether and n-butyl vinyl ether, which ranged from 56°C to 127°C, the highest values corresponding to MA–S copolymer. Their values are probably affected by the presence of –COOH groups (resulting from partially hydrolyzed MA), so that they did not obtain, in fact, the actual T_g values for these copolymers. Häussler[5] determined the T_g values of alternating MA–S copolymers through a stepwise temperature program in order to eliminate the influence of hydrolyzed maleic anhydride groups, and obtained, also for MA–S copolymer, a T_g value of 210°C, higher than that given in Ref. [6]. This latter technique seems to be more accurate because partially hydrolyzed groups could be totally dehydrated.

The purpose of this paper is to elucidate some aspects of the glass transitions of six binary and ternary maleic anhydride copolymers with vinyl acetate, styrene and/or methyl methacrylate by coupling DSC results with infrared (IR) spectroscopy. Because the DSC analysis was performed in nitrogen, a comparison with previously reported thermogravimetric results, recorded in air[11] on the same copolymers, was made for the first (F) and second (S) thermogravimetric steps, which also appear in the first runs of the DSC measurements of several copolymers.

EXPERIMENTAL

Some characteristics of the studied copolymers are presented in Table I (for details on copolymer synthesis see Ref. [11, Table I]). Binary copolymers of maleic anhydride with vinyl acetate or styrene are alternating, being obtained under charge transfer complex (CTC) conditions.[11] In the literature we did not find information about the sequence distribution in MA ternary copolymers. According to the terpolymerization

TABLE I Some characteristics of the binary and ternary maleic anhydride copolymers with vinyl acetate, styrene or methyl methacrylate

Type of copolymer	I_a*	*Composition*† (moles)				$[\eta]_{\text{acetone}}^{30^\circ\text{C}}$ (dl/g)	*Molecular weight*‡ (Daltons)
		MA	*VA*	*S*	*MMA*		
MA-VA	440	1	1	0	0	0.47	102,000
MA-MMA	345	1	0	0	1.33	0.21	49,000
MA-S	390	1	0	1	0	0.52	130,000
MA-VA-MMA	370	1	0.53	0	0.43	0.09	—
MA-VA-S	407	1	0.54	0.46	0	0.58	—
MA-S-MMA	417	1	0	0.68	0.32	0.27	—

* Acid number, mg NaOH/g copolymer. † Estimated from conductometric titration and/or ^{1}H-NMR spectra. ‡ From viscometric measurements, in acetone, at 30°C.

mechanism, which can involve charge-transfer complexes between MA and the two other co-monomers, our terpolymers were generated by a donor 1-donor 2-MA system (MA-VA-S ternary copolymer) or a donor-MA-neutral monomer system (MMA containing terpolymers).[12] In the first case, a terpolymer containing 50 mole% MA will be obtained, in which the distribution of the co-monomers could be assumed to be regular. For the other two terpolymers both CTC and free monomer are involved, thus a composition different from 50 mole% AM and an irregular distribution of the monomers can be expected. In the IR spectra (see Figure 4) one can observe the bands or shoulders at 1060 and 1140 cm^{-1} for MMA containing copolymers or terpolymers that are ascribed to longer MMA sequences.[13]

The investigation methods used were DSC and IR spectroscopy. These results were compared with thermogravimetric data previously presented.[11] DSC curves were recorded by means of a Mettler DSC 12E instrument under the following conditions: heating rate 20°C/min, nitrogen flow 50 ml/min, mass of sample 2–5 mg; investigated temperature range being from 20°C to 220°C. Before each measurement the samples were dried in high vacuum in the presence of phosphorus pentoxide for a minimum of 48 h at 25°C. An isothermal heating run at a temperature about 10–15°C below that of the maximum of the second thermogravimetric peak (Ref. [11, Figure 1 or Table III]) was performed to assure complete water elimination, which could influence the glass transition region. The peak area was calibrated with indium (heat of fusion of indium is 28.43 J/g with a melting point of 156.6°C) to evaluate process heat, (ΔH).[14] In the kinetic parameters evaluation, conversion degree (α) is $\alpha = \Delta H_t/\Delta H_\infty = A_t/A_\infty$ where ΔH_t and ΔH_∞ are process heat at time "t" and for the whole process, respectively; A_t and A_∞ are the corresponding areas. The peak areas were determined by the weighing of a calibrated paper. The procedures for the evaluation of kinetic parameters by integral Coats–Redfern (CR)[15] and Reich–Levi (RL)[16] and differential Swaminathan Modhavan (SM)[17] methods are given in Ref. [11].

In order to verify if there are chemical modifications of the copolymer structures over various temperature ranges, the IR spectra were recorded after the each run so it was possible to correctly assign the T_g. IR spectra were recorded using a Perkin-Elmer spectrometer 577 on KBr pellets.

RESULTS AND DISCUSSION

Comparing our thermogravimetric results[11] with results from the previous thermal studies,[3–7] it was concluded that the first (F) and second (S) steps of weight loss (both occurring below 220°C) correspond, respectively, to the physically bound water loss and to the cyclization of carboxylic groups formed during storage by partial hydrolysis of maleic anhydride units (Figure 1).

For DSC curves (recorded in N_2) – Figure 2, temperature domains of these peaks ranged from 30°C to 130°C and 125–220°C for the first and the second processes, respectively. The first endothermic peak, due to loss of physically bound water, occurs in the same temperature range as in thermogravimetric analysis. In the inert atmosphere the elimination of chemically bound water from recyclization of maleic acid units to maleic anhydride takes place over a higher temperature range than in an oxidative atmosphere. Both processes are endothermic. The overall heat of physical process of water loss varies between 15 and 59 J/(g sample) while the overall heat for the formation of anhydride ring ranges from 40 to 100 J/(g sample). The higher values were obtained for vinyl-acetate-containing binary or ternary copolymers which are more hydrophilic.

The overall kinetic parameters evaluated from DSC data for these two processes (Table II) are in good agreement with those obtained from thermogravimetric data (see Ref. [11, Tables II and III]). The first

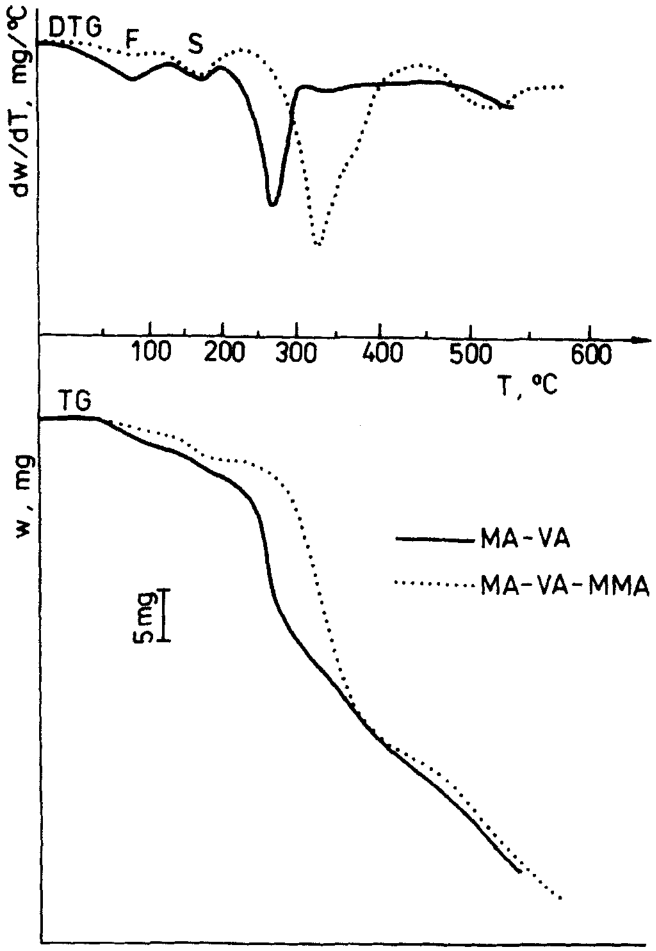

FIGURE 1 TG curves of MA-AV and MA-VA-MMA copolymers.

endothermic process has an overall activation energy of ~80–90 kJ/mole while the second process exhibits higher values than in the first process indicating its different nature, a chemical reaction taking place. This is assigned to formation of anhydride ring. Reaction order is close to 1 for most processes. The concordance between the results obtained by the three mentioned methods are good, considering the limit of experimental and evaluation errors.

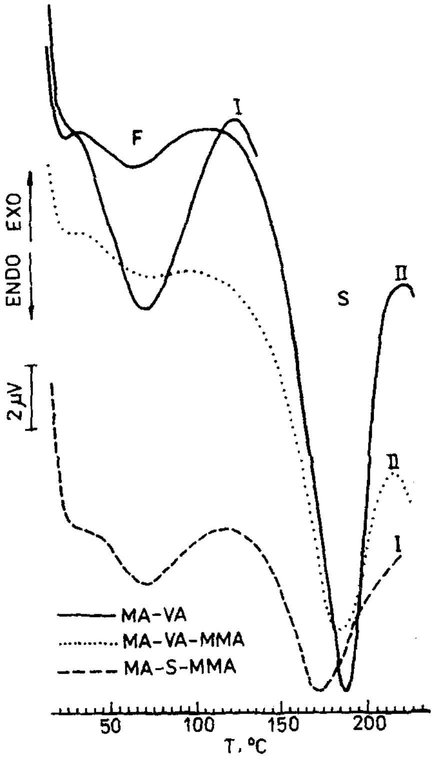

FIGURE 2 DSC curves of the MA–VA, MA–VA–MMA and MA–S–MMA copolymers: I, first and II, second heating runs.

By performing several heating runs in the DSC, for five of six maleic copolymers, these peaks were eliminated. After prolonged drying in high vacuum, several copolymers do not exhibit these peaks whereas for copolymers containing vinyl acetate, which are more hydrophilic, it has not been possible to eliminate these steps. The IR spectra do not indicate any change in the chemical structure for the styrene- or methyl methacrylate-containing copolymers during heating below 220°C. For the vinyl acetate-containing copolymers, after successive heating up to 220°C the bands corresponding to physically bound water and carboxylic groups disappear (see below). This indicates that DSC curves recorded after elimination of these two endothermic peaks are the actual DSC curves for maleic anhydride copolymers without partially hydrolyzed anhydride rings.

TABLE II DSC data and overall kinetic parameters of the two endothermic processes of some binary and ternary copolymers of maleic anhydride

Copolymer	*Characteristic temperatures* (°C)			E_{CR} (kJ/mole)	E^*_{CR} (kJ/mole)	n_{CR}	E_{RL} (kJ/mole)	E_{SM} (kJ/mole)	ln A_{SM}	n_{SM}
	T_i	T_m	T_f							
First endothermic process, F										
MA–VA	28.5	785	127.5	89.66	82.12	2.1	90	68.79	23.82	1.69
MA–S–MMA	35	70	120	80.14	54.5	1.4	91	71.67	25.25	1.42
Second endothermic process, S										
MA–VA	125	189	223	134.88	118.15	1.2	142	111.83	29.59	1.12
MA–VA–MMA	134	185	216	129.96	87.01	1.1	120	111.75	29.96	1.20

T_i, T_m, T_f are temperatures of onset of peak, corresponding to the maximum rate of weight loss and final temperature, respectively; E_{CR}, E_{RL}, E_{SM} are the overall activation energy evaluated by Coats–Redfern, Reich–Levi and Swaminathan–Modhavan methods, A_{SM} is pre-exponential factor, n_{CR} and n_{SM} are the reaction order evaluated by the corresponding methods; E^*_{CR} – the global activation energy evaluated from thermogravimetric data by Coats–Redfern method.

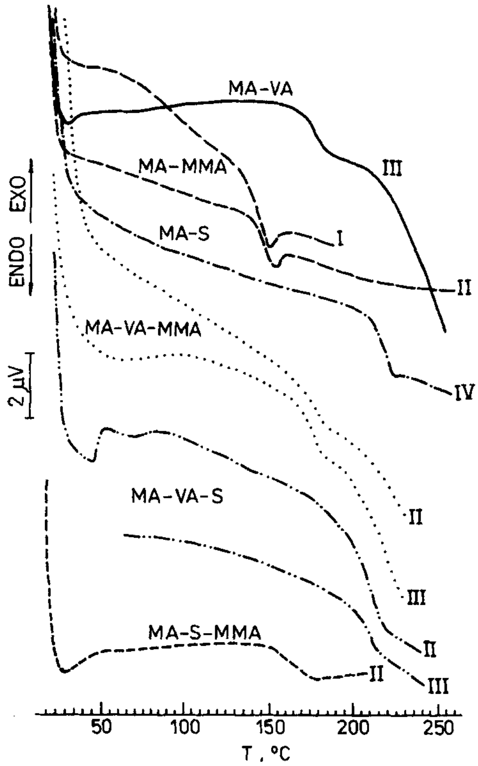

FIGURE 3 DSC curves of the binary and ternary copolymers after dehydration: I, first; II, second; III, third; and IV, fourth heating runs.

The studied copolymers exhibit two types of endothermic transitions. The first type is a water-induced one occurring around 50–55°C for ternary copolymers (Figures 2 and 3). The second kind (Figure 3) is probably a glass transition temperature, whose value depends on the structure of copolymer (Table III).

Other authors (Dhal *et al.*[6]) found a glass transition of 75°C for MA–VA copolymers. Our data show a $T_g = 175°C$ for this type of copolymer. The fact that the curves were recorded at a different heating rate (5°C/min besides 20°C/min) cannot explain such large difference. It could be due to the hydrolyzed MA groups, which probably was not taken into account by Dhal and which dramatically lowers the glass transition. It is also possible that a water induced transition is present.

TABLE III DSC data for binary and ternary copolymers of maleic anhydride

Copolymer	*Run*	*Endothermic transition* (°C)
Binary copolymers		
MA–VA	III	175
MA–MMA	I	85
	I	148
	II	151
MA–S	III	218
	IV	218
Ternary copolymers		
MA–VA–MMA	I	46
	II	54
	II	175
	III	175
MA–VA–S	II	50
	II	205
	III	210
MA–S–MMA	II	165

The T_g value (218°C, the highest obtained value) for alternating MA–S copolymers is in good agreement with that obtained by Häussler of 210°C.[5] The MMA-containing copolymers exhibit lower T_g values ($T_g = 151°C$), probably due to the long sequences of this co-monomer (diads and triads). The second order transitions of ternary copolymers (T_g varies from 165°C to 210°C) lies between those of the binary copolymers containing the same co-monomers. The small increase of T_g values in consecutive heating runs (i.e. in the first run T_g value of MA–MMA was of 148°C and in the second one being 151°C; for MA–VA–S, the T_g value obtained in the second run was 205°C and in the third – 210°C) could be due to a plasticizing effect of water traces or carboxylic acid groups, which are eliminated by previous heating.

The IR spectral data give us information about the chemical modifications in maleic copolymers structure after successive heatings. The samples heated below 200–220°C do not show changes other than those related to the water release and cyclization of carboxylic groups from partially hydrolyzed maleic anhydride units.

In all spectra (Figure 4) there are bands at 1860–1780 cm^{-1}, 1230 cm^{-1} extended up to 920 cm^{-1} of the –C=O and –CO–O–CO– groups.[18] They are shifted to longer wavelengths and are less distinctive

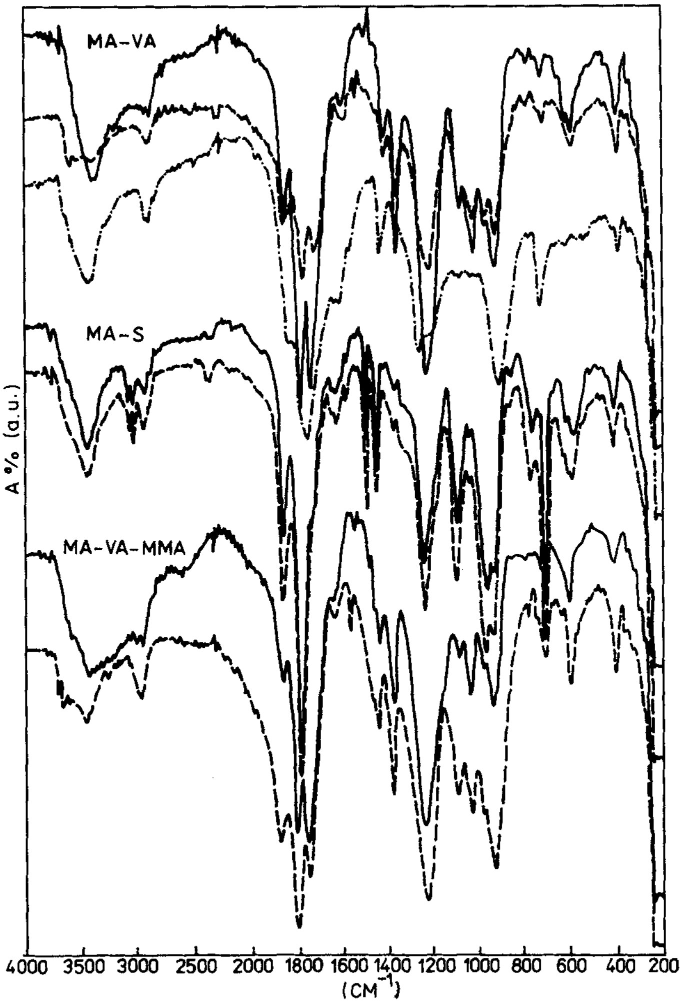

FIGURE 4 IR spectra of the binary and ternary MA-containing copolymers before (———), after (-----------) heating under DSC conditions and after (— — — —) heating at 300°C.

in the IR spectra of heated polymers. The shift of the 1780 cm^{-1} band to smaller wavelengths, 1760–1750 cm^{-1} in the spectra of unheated copolymer is due to the partially hydrolyzed anhydride rings.[18] This indicates that during heating the cyclization of carboxylic acid groups occurred.

After heating, a pronounced modification of IR spectra in the 3450–2350 cm^{-1} range due to the water release, clearly corresponding to $-CH_3$ and $-CH_2$ groups shifted by the proximity of anhydride group, is evident. The disappearance in the IR spectra of the heated copolymers of the peak from the 1380 cm^{-1} wavelength corresponding to –OH from COOH groups, indicates the recyclization of maleic acid to maleic anhydride. Only by heating at temperatures above 220°C, namely at 270–300°C, do the IR spectra show the appearance of the bands or shoulders in the 700–840, 1295–1310 and 1410–1420 cm^{-1} regions corresponding to double bonds (Figure 4).

CONCLUSIONS

We conclude that only by, at least two or three successive heating DSC runs are the actual T_g values of maleic anhydride copolymers obtained. The final heating temperature must be below 220°C. After the first run, recyclization of maleic acid to maleic anhydride occurs. T_g values of MMA-containing copolymers are lower than those of styrene-containing copolymers. The temperature of the second order transitions of ternary copolymers are between those of the binary copolymers containing the same co-monomers.

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