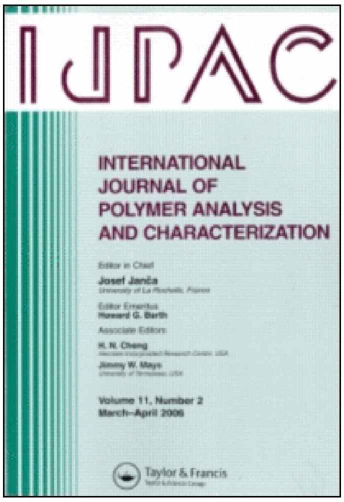

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Analysis and Characterization of Maleic Anhydride Copolymers. II. Some Aspects of Thermo-oxidative Decomposition*

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Six binary and ternary maleic anhydride copolymers with vinyl acetate, methyl methacrylate and styrene, useful as plastics, adhesives coatings, additives, etc., have been synthesized. Thermo-oxidative behavior under dynamic conditions of heating has been studied to test the possible changes during thermal treatments. The four or five thermo-oxidative steps of weight loss are characteristic for the studied copolymers. The characteristic temperatures, weight losses and overall kinetic parameters have been determined, and information about physical and/or chemical processes involved has been obtained.

Keywords: Maleic anhydride copolymers; Thermo-oxidative decomposition; Thermogravimetry

1. INTRODUCTION

The copolymers of maleic anhydride (MA) with different vinylic or acrylic co-monomers are interesting from both theoretical and practical points of view.[1] These copolymers and the polyelectrolytes derived from them by hydrolysis are used as plastics, printing inks, oil additives, detergent builders, dispersants/emulsifiers, scale and corrosion

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* For part I, see: G.C. Chitanu, I.L. Zaharia and A. Carpov, *Int. J. Polym. Anal. Charact.*, 4(1), XXX (1997).

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inhibitors, flocculants, biomaterials, drug delivery systems, etc.[2–4] Most of these polymers are subjected to thermal treatments during processing and utilization, which can lead to significant changes in their physico-chemical properties. Consequently, thermal analysis provides a useful tool for basic research, quality control and product development based on these copolymers.

Thermal analysis of MA copolymers was performed using pyrolysis-gas chromatography (PGC), thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). PGC allowed the evaluation of composition for a MA–styrene copolymer using a linear relationship between the styrene content in copolymer and in pyrolysis products, respectively.[5] The low styrene content in pyrolysis products for 1 : 1 MA–styrene copolymer was assigned predominantly to the alternating distribution of the co-monomers.[6,7] The TG analysis allowed acquisition of data on the thermal stability, the decomposition mechanism and the microstructure of copolymers.[8–10] The PGC and TG data analysis of the MA–styrene or MA–vinyl acetate copolymers showed a clearly different behavior of the statistical, alternating and block copolymers.[7,11] The results obtained by DSC for MA copolymers showed that the T_g depends on the co-monomer type and confirmed their alternating structure.[12,13] The incorporation of MA increased the thermal stability of a MA–methyl methacrylate copolymer compared to poly(methyl methacrylate).[12] While there are enough data concerning the thermal behavior of some binary MA copolymers, we have not identified in the literature any study concerning the ternary MA copolymers in comparison with binary ones. Such polymers and their derivatives are used as scale inhibitors in geothermal systems,[14] as additives in hide tanning,[15] etc. In this paper we have comparatively studied the thermo-oxidative behavior of several binary and ternary MA copolymers with styrene (S), and/or vinyl acetate (VA) and methyl methacrylate (MMA).

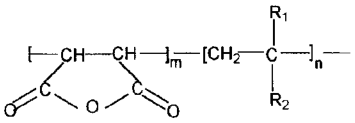
2. EXPERIMENTAL

2.1. Copolymer Synthesis

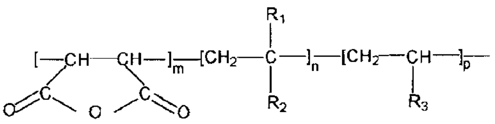
Analytical reagent-grade chemicals were used throughout. The monomers were commercial products that were carefully purified prior to use. Thus, MA was twice recrystallized from chloroform to remove the maleic acid developed by hydrolysis during storage. S, VA and MMA were freshly distilled under reduced pressure. Benzene and toluene were dried on Na for 48 h and then distilled. Chloroform and 2-butanone were dried with potassium carbonate for 24 h and then also distilled. Benzoyl peroxide, used as the free radical initiator, was recrystallized from dried methanol.

The copolymerization mechanism of MA is different from the classical one, because MA, which is an electron acceptor, can form charge transfer complexes (CTC) with the donor monomers. Depending on the co-monomer, the CTC participates, more or less, in chain propagation reactions, so that the MA copolymers have a predominantly alternating structure.[2,3]

Free radical copolymerizations were carried out in solution–suspension or in solution at 80°C to provide the conditions for a mechanism via CTC.[11] All the polymerizations were allowed to reach high conversions (80–90%). The copolymers were purified for 24 h with dried chloroform in a Soxhlet extractor or reprecipitated in diethyl ether from acetone to remove the unreacted monomers. Then they were dried at 40°C under reduced pressure for 3 days. The MA unit content of the copolymers was determined conductometrically as the acid number I_a in an acetone/water mixture (1 : 1) with aqueous 0.1 N NaOH, using a Radiometer AB Copenhagen CDM 2d conductivity



binary copolymer with $m = n$ or $m \neq n$
$R_1 = H$ or CH_3
$R_2 = C_6H_5$, $OCOCH_3$, $COOCH_3$.



ternary copolymer with $m \neq n \neq p$
R_1 and R_2 as above
$R_3 = C_6H_5$, $OCOCH_3$, $COOCH_3$, and $R_3 \neq R_2$

SCHEME 1 The structure of the maleic copolymers.

meter and a CDC 114 cell.[9] The composition of the ternary copolymers was roughly estimated from ^{1}H-NMR (nuclear magnetic resonance) spectra, using the chemical shifts at 3.8, 5.5 and 7.4 ppm, corresponding to MMA, VA and S, respectively. The spectra were recorded on a Brucker AC 300 MHz spectrometer. The proposed structure of the copolymers is given in Scheme 1.

The experimental conditions used for synthesis and some characteristics of the copolymers obtained are listed in Table I.

2.2. Characterization Methods

The TG (thermogravimetric) and DTG (differential thermogravimetric) curves were recorded on a Paulik–Paulik–Erdey-type Derivatograph, MOM Budapest, under the following operational conditions: heating rate (β) 12 K min^{-1} temperature range 293–873 K, sample weight 50 mg, using powdered samples, in platinum crucibles, 30 cm^3 min^{-1} air flow. Two TG curves were recorded for each copolymer, the actual β values being evaluated from the temperature–time curve and the calculated β values were further employed in evaluating the kinetic parameters. Three or four repeated readings (temperature and weight loss) were performed on the same TG curve, each of them having at least 15 points. Both integral (Coats–Redfern: CR,[19] Reich–Levi: RL[20]) single curve and differential (Swaminathan–Modhavan: SM[21]) methods of the kinetic parameter evaluation were used. The subscript of kinetic parameters indicates the evaluation method. For the last method the general expression of the conversion function was considered:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\mathrm{e}^{-E/RT}\underbrace{[\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p]}_{f(\alpha)} \qquad (1)$$

where $\alpha = w_t/w_\infty$ is the degree of conversion (ratio of the weight loss at time t and at the end of process), T is temperature in Kelvin, A is the pre-exponential coefficient, E is the activation energy, R is the gas constant, n is reaction order and m, p are other exponents, $f(\alpha)$ is the differential form of the conversion function. The exponents m, n, p may take different values with respect to the reaction mechanism or physical

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

Type of copolymer	*Synthesis and purification conditions of maleic anhydride copolymers*					I_a*	*Composition*** (mol)				$[\eta]^{30°C}_{acetone}$ (dl/g)	*Molecular weight**** (Daltons)
	Polymerization technique	*Solvent*	*Precipitation and filtration*	*Reprecipitation*	*Extraction with chloroform*		*MA*	*VA*	*S*	*MMA*		
MA–VA	solution–suspension	benzene	yes	no	yes	440	1	1	0	0	0.47	102,000
MA–MMA	solution	2-butanone	yes	yes	no	345	1	0	0	1.33	0.21	49,000
MA–S	solution–suspension	toluene	yes	no	yes	390	1	0	1	0	0.52	130,000
MA–VA–MMA	solution	2-butanone	yes	no	yes	370	1	0.53	0	0.43	0.09	—
MA–VA–S	solution–suspension	benzene	yes	no	yes	407	1	0.54	0.46	0	0.58	—
MA–S–MMA	solution	2-butanone	yes	no	yes	417	1	0	0.68	0.32	0.27	—

The following Mark–Houwink relations were used for average molecular weight evaluation: $[\eta]_{MA-VA} = 9.32 \times 10^{-5} M^{0.94}$;[16] $[\eta]_{MA-MMA} = 12.47 \times 10^{-4} M^{0.506}$;[17] $[\eta]_{MA-S} = 8.68 \times 10^{-5} M^{0.74}$;[18] solvent: acetone; $T = 30°C$. * Acid number, mg NaOH/g copolymer. ** Estimated from conductometric titration and/or ^{1}H-NMR spectra. *** From viscometric measurements, in acetone, at 30°C.

processes occurring during decomposition. From the mathematical point of view both positive and negative values of A, E or of the exponents can describe with enough accuracy the TG or DTG curves, but not all values have kinetic significance. Positive values of the kinetic parameters, A and E, must be used as a selection criterion for "the most probable kinetic parameters". Additional criterion applied in our studies was good reproducibility of kinetic parameters obtained from different readings of TG data. Using the obtained kinetic parameters the TG and DTG curves were simulated and for each experimental point on the DTG or TG curves, the average square error and also the correlation coefficient (r) were evaluated. Minimum values of the average square error and maximum values of the correlation coefficient were also among the selection criteria for kinetic parameters.

The parameters a and b of the isokinetic relation:

$$\ln A = a + bE \tag{2}$$

(where $b = 1/RT_{\mathrm{iso}}$, R is the gas constant, T_{iso} is the isokinetic temperature), describing the compensation effect, have been also determined.[22]

In order to verify if the chemical changes occur in the copolymer structures in various temperature ranges, the IR spectra were recorded using a Perkin-Elmer spectrometer 577 on KBr tablets.

3. RESULTS AND DISCUSSION

The derivatograms of the studied copolymers are presented in Figures 1 and 2 for binary and ternary copolymers, respectively. At least three thermogravimetric steps are distinguished for each copolymer; some copolymers even showed additional temperature ranges of thermogravimetric steps depending on the nature of co-monomer. In Tables II–V are listed the characteristic temperatures of decomposition steps, the corresponding weight losses, overall kinetic parameters, evaluated by Coats–Redfern (E_{CR}, $\ln A_{\mathrm{CR}}$), Swaminathan–Modhavan (E_{SM}, $\ln A_{\mathrm{SM}}$, n, m and p) and Reich–Levi (E_{RL}) methods.

The following temperature ranges of weight losses were studied: 20–120°C (step I – Table II), 120–220°C (step II – Table III), 220–310°C

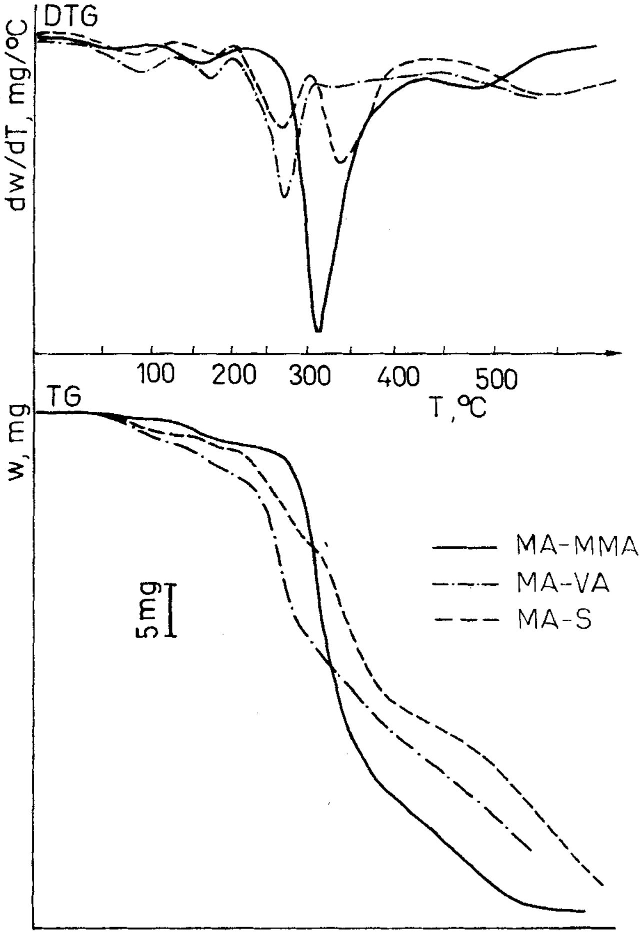


FIGURE 1 Derivatograms of the binary maleic anhydride copolymers.

or 430°C (step III – Table IV or step IV for some copolymers – Table V) and 430–580°C (step V – Table V).

All six polymers studied are mildly hygroscopic. The first thermogravimetric step is due to the physical phenomenon of water release from copolymer. The weight loss in this temperature range is between 1.0 and 4.75 wt.%. The overall activation energy E_{CR} varies from 54.5 to 82.73 kJ/mole while the E_{SM} varies from 43.10 to 82.32 kJ/mole.

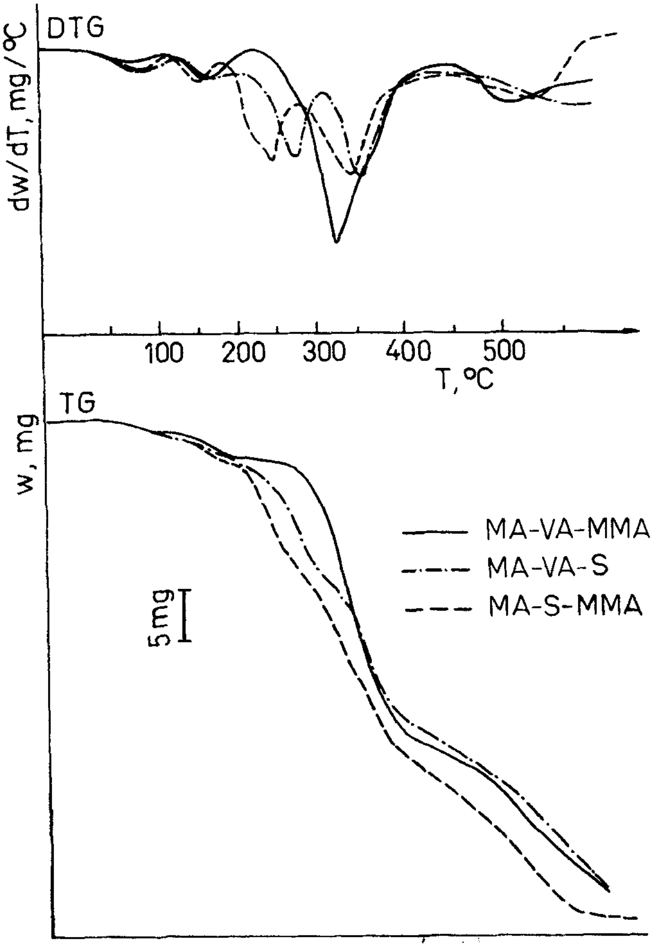


FIGURE 2 Derivatograms of the ternary maleic anhydride copolymers.

It seems that the water–copolymer physical bond is stronger for copolymer containing VA which is indeed more hydrophilic than S or MMA. The exponent *n* ("reaction order" is not suitable for such a physical process) takes values around unity. That should mean that all bonds with water are strong enough (for example hydrogen bonding type) so that water loss is close to a chemical reaction. ln *A* values vary between 13.5 and 29.7. The agreement between the overall kinetic parameters obtained by the both methods is satisfactory taking into

TABLE II Thermogravimetric data and overall kinetic parameters of the first step of binary and ternary copolymers of maleic anhydride

Copolymer	*Characteristic temperatures*			*Weight loss* (%)	E_{CR} (kJ/mole)	$\ln A_{CR}$	n	E_{SM} (kJ/mole)	$\ln A_{SM}$	n_{SM}	m	p
	T_i (°C)	T_m (°C)	T_f (°C)									
Binary copolymers												
MA–VA	35	86	132	4.75	82.12	27.94	2.0	75.62	25.59	1.89	0	−3.15
MA–MMA	25	69	91	1.00	82.73	29.54	1.9	56.62	18.42	0.23	−0.37	−1.02
MA–S	25	80	131	2.87	72.44	24.65	1.7	82.32	27.65	1.65	−0.4	0
Ternary copolymers												
MA–VA–MMA	26	74	110	1.50	87.83	31.12	2.3	84.00	29.66	2.23	0	0
MA–VA–S	26	78.5	125	2.88	78.76	26.86	1.8	76.95	26.15	1.80	0	0
MA–S–MMA	25	88	124	2.75	54.5	17.62	0.6	43.10	13.48	0.39	0	0

T_i, T_m, T_f are temperatures of onset of peak, corresponding to the maximum rate of weight loss and final temperature, respectively.

TABLE III Thermogravimetric data and overall kinetic parameters of the second step of binary and ternary copolymers of maleic anhydride

Copolymer	*Characteristic temperatures*			*Weight loss* (%)	E_{CR} (kJ/mole)	$\ln A_{CR}$	n_{CR}	E_{SM} (kJ/mole)	$\ln A_{SM}$	n_{SM}	E_{RL} (kJ/mole)
	T_i (°C)	T_m (°C)	T_f (°C)								
Binary copolymers											
MA–VA	134	175	210.5	5	118.15	32.09	1.8	115.39	31.29	1.78	144
MA–MMA	110	160	206	3.25	76.83	20.74	1.1	66.66	17.67	0.93	102
MA–S	141	182	199	2.62	77.49	20.10	0.7	57.72	14.52	0.52	110
Ternary copolymers											
MA–VA–MMA	115	168	224	3.86	87.01	23.51	1.2	80.44	21.67	1.19	107
MA–VA–S	125	170.5	194	3.86	49.26	12.19	0.4	52.39	13.05	0.40	80
MA–S–MMA	124	178	190	4.25	109.07	30.41	1.7	123.09	34.36	1.81	122.5

TABLE IV Thermogravimetric data and overall kinetic parameters of the third step of binary and ternary copolymers of maleic anhydride

Copolymer	*Characteristic temperatures*			*Weight loss* (%)	E_{CR} (kJ/mole)	$\ln A_{CR}$	n_{CR}	E_{SM} (kJ/mole)	$\ln A_{SM}$	n_{SM}	E_{RL} (kJ/mole)
	T_i (°C)	T_m (°C)	T_f (°C)								
Binary copolymers											
MA–VA	208	275	309	34.25	154.29	33.98	1.4	123.49	26.87	1.18	170
MA–MMA	235	316	430	72.5	172.69	34.64	2.7	160.05	21.88	2.5	205
MA–S	199	268	301	19.5	104.08	22.60	1.1	83.60	17.72	0.83	124
Ternary copolymers											
MA–VA–MMA	228	326	443	58	110.79	20.96	1.7	110.92	20.93	1.69	138
MA–VA–S	194	275	306	22.5	100.08	21.54	1.1	99.65	20.99	0.79	122
MA–5–MMA	190	248	280	22.75	177.53	42.23	2.4	160.73	37.5	1.83	193

TABLE V Thermogravimetric data and overall kinetic parameters of the fourth and fifth step of binary and ternary copolymers of maleic anhydride

Copolymer	*Characteristic temperatures*			*Weight loss* (%)	*Residual weight loss at* 600°C (%)	E_{CR} (kJ/mole)	$\ln A_{CR}$	n_{CR}	E_{SM} (kJ/mole)	$\ln A_{SM}$	n_{SM}	m	p
	T_i (°C)	T_m (°C)	T_f (°C)										
Binary copolymers													
MA–VA					56								
MA–MMA*	430	482	565	16.3	7	196.4	30.4	1.4	172.66	25.66	0.98	−0.27	−0.23
MA–S	302	341	438	34	41.01	251.29	49.20	3.6	251.65	48.57	3.28	−0.54	0
Ternary copolymers													
MS–VA–MMA*	456	510.5	572	23	13.63	190.86	28.05	1.4	200.77	29.56	1.43	0	0
MA–VA–S	306	353	440	31.75	39.0	232.68	44.70	2.9	280.0	42.47	2.76	0	0
MA–S–MMA	280	340.5	430	39.50	—	163.50	32.08	2.8	167.61	32.59	0.92	3.81	−4.09
MA–S–MMA*	430	530	581	26.8	4.0	143.2	20.87	1.2	140.3	19.3	0.26	0	−0.7

*Fifth step.

account the limitation of each of them. For this thermogravimetric step, a compensation effect between the kinetic parameters appear for both binary and ternary copolymers (Figure 3), described by the isokinetic relation:

$$\ln A = 0.3452E + 0.0234, \quad \text{with } r^2 = 0.9974. \tag{3}$$

The corresponding isokinetic temperature is about 75°C, which lies between T_m values of this step for all copolymers. With only a few exceptions which are in the experimental and evaluation error limits

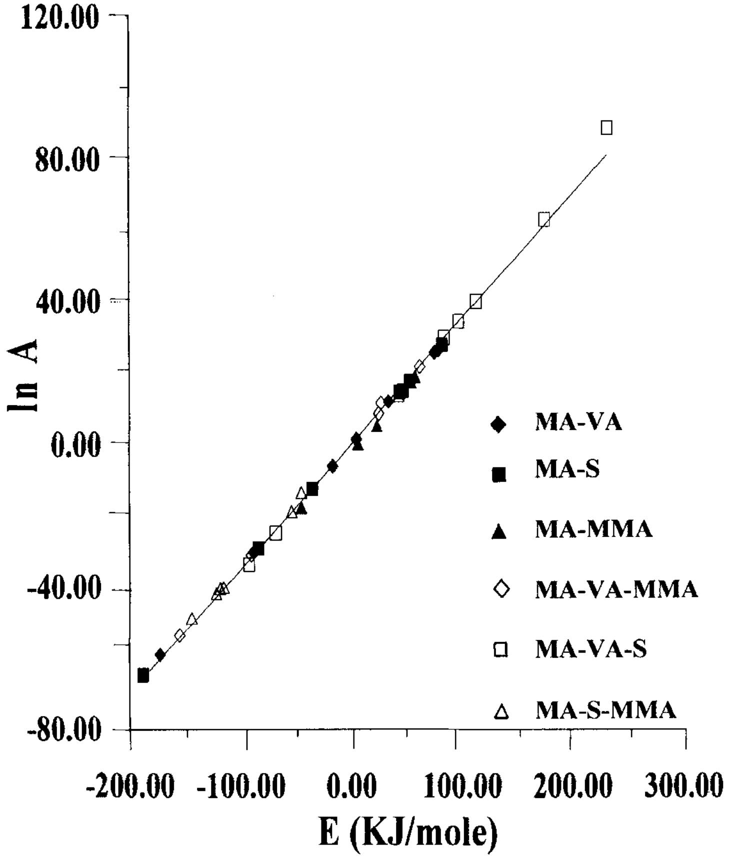


FIGURE 3 ln A versus E for the first thermogravimetric step of binary and ternary maleic anhydride copolymers.

the activation energy evaluated according to the Reich–Levi method is approximately constant for $0.1 < \alpha < 0.6$, the average E_{RL} values varying from 70 to 90 kJ/mole in accordance with overall values of kinetic parameters (Table II). Similar results for this step of binary maleic anhydride copolymers were found by other authors[13] who also attributed this DTG peak (of differential thermogravimetric curve) to the water desorption.

The second step could not be attributed to the loss of solvent or monomers because all temperatures are higher than the boiling points of the corresponding compounds. Both characteristic temperatures and weight losses are approximately constant for all copolymers, so it can be supposed that it is due to the common monomer; namely, maleic anhydride. It is possible that the residual co-monomer is lost by sublimation or that a dehydration reaction takes place as other authors have shown.[13] Low values for weight loss, overall activation energy and pre-exponential factor should indicate that the dehydration mainly occurs between a few hydrolyzed anhydride groups.

The existence of the same process for all copolymers is also a proof of the existence of a compensation effect (Figure 4) found as in the case of the corresponding first thermogravimetric step. The isokinetic relation and temperature are

$$\ln A = 0.2727E - 0.0082 \quad r^2 = 0.997 \tag{4}$$

and $T_{\mathrm{iso}} = 168°\mathrm{C}$, respectively.

The isokinetic temperature corresponds with an average T_{m} of DTG peak of all copolymers in this temperature range (see Table III). Our results and literature data[13] indicate that a first-order reaction is taking place for this stage. The influence of the neighboring co-monomers is evidenced both in the overall values of kinetic parameters (Table III) and E–α curves (Figure 5). For the binary copolymers, approximately constant values of E in the $0.1 < \alpha < 0.6$ interval were found (Figure 5(a)), while a variation of the activation energy with conversion degree is characteristic for the ternary copolymers (Figure 5(b)).

It seems that in binary copolymers the dehydration reaction is dependent on the co-monomer chemical nature: it is facilitated by styrene and MMA and it is hindered by VA. Also it could be concluded that the E_{SM} (from differential method) for ternary copolymers is much more reliable than E_{CR} (from integral method).

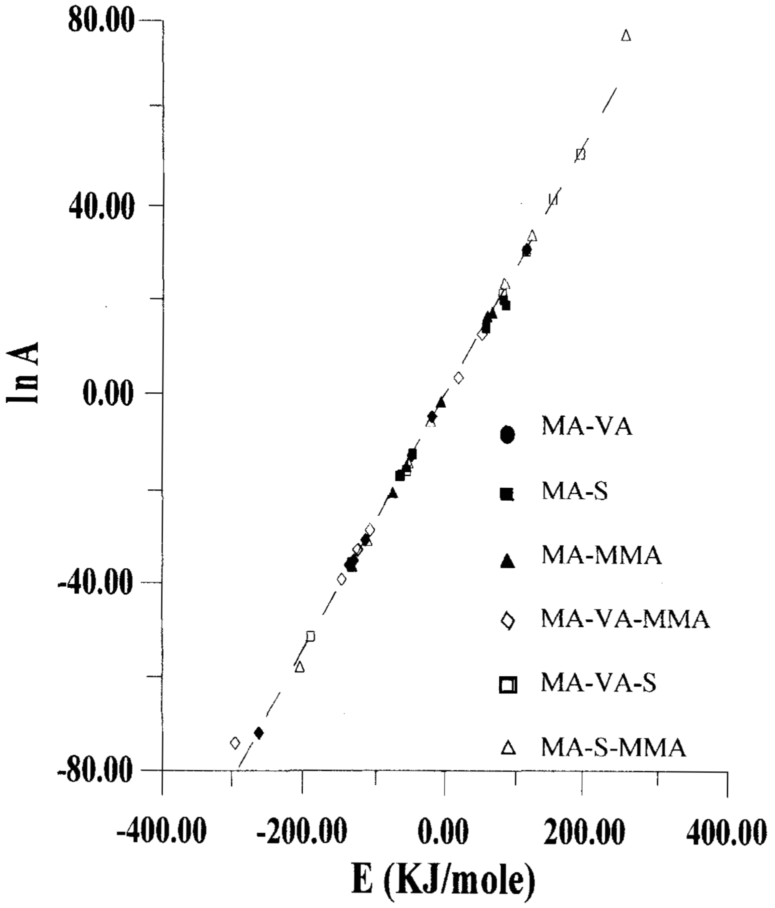


FIGURE 4 ln A versus E for the second thermogravimetric step of binary and ternary maleic anhydride copolymers.

The third step is the main one for decomposition of copolymers. It can mainly involve the side groups elimination, for the VA containing copolymers, or the random scission, for MMA containing copolymers, being particular for each copolymer both in respect to characteristic temperatures, weight losses and kinetic parameters. Binary copolymers containing VA or S show a narrow decomposition temperature range of about 100°C and a weight loss of 19.5–30 wt.%. Binary copolymers containing MMA decompose approximately totally during this step

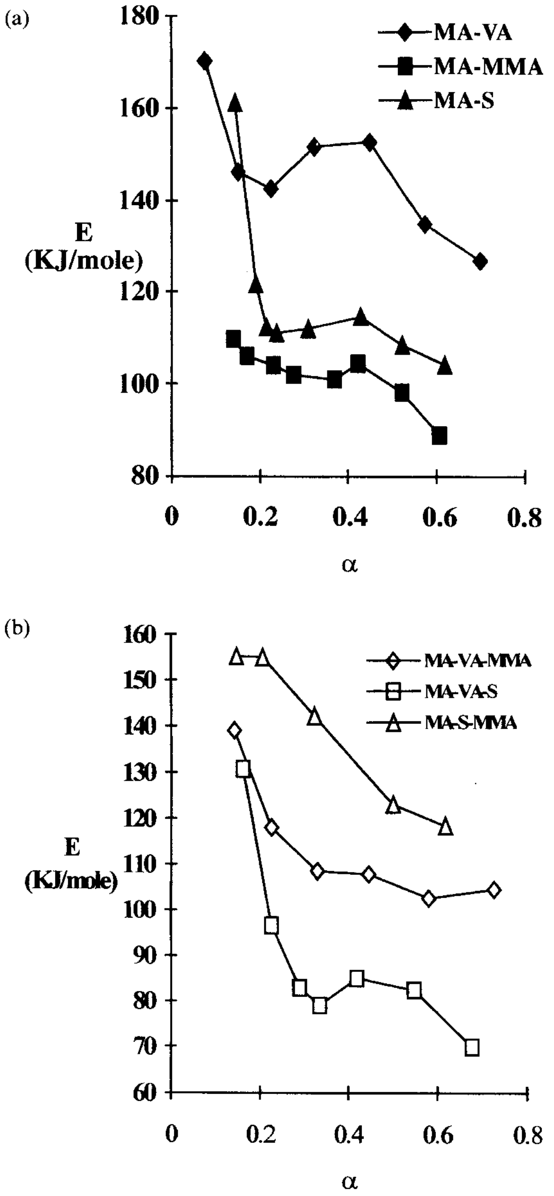


FIGURE 5 Variation of the activation energy evaluated by the Reich–Levi method with degree of conversion α, for the second thermogravimetric step of the binary (a) and ternary (b) maleic anhydride copolymers.

(72.5 wt.%) but the decomposition temperature range is wide, about 200°C. Ternary copolymers show also distinctive values for characteristic temperatures and weight losses depending on constituent co-monomers. Also, MMA containing copolymers decompose over a wider temperature range with higher weight losses than the corresponding values for other two copolymers. Comparing the weight losses of this step with theoretical values of acetic acid or MMA loss from the VA or MMA containing chains a satisfactory accordance was found. Kinetic parameters take specific values for each copolymer. The styrene containing copolymers show a lower thermo-oxidative stability and lower weight losses and overall kinetic parameter values than VA containing copolymers. Reaction order of this step is higher than 1.0. No compensation effect was found for this step, but activation energy remains approximately constant for a wide range of α ($0.05 < \alpha < 0.7$) (Figure 6). The higher values for $\alpha < 0.5$ could be due to the errors in area evaluation. The average value of E_{RL} agrees with overall E_{CR} and E_{SM} values.

The main decomposition step of the styrene containing maleic anhydride copolymers occurs between 280–438°C (Table V) with a weight loss of 30–40% and overall activation energy of 163.5–251.3 kJ/mole. It can be supposed as in this temperature range the main chain random scission started when the third step is accomplished.

Häußler *et al.*[23] showed that, at the beginning of degradation above 210°C carbon dioxide was found by Py-GC-MS analysis. The carbon dioxide is generated by formation of a spirodilactone structure,[23] the decarboxylation occurring between two neighboring anhydride groups. In helium, the maximum of the decarboxylation process was found to be about 330–340°C. In the second step, besides CO_2, the co-monomer styrene was also detected, a lactone structure being formed.[23] With further increase in temperature, complete decomposition with chain destruction takes place.

The characteristic temperatures for the third and fourth DTG peaks presented in the Tables IV and V are in satisfactory accordance with those cited by above-mentioned authors.[23–25]

The activation energy takes approximately constant values with respect to degree of conversion – the average value being in satisfactory agreement with overall activation energy. Therefore our results could be explained by the same reaction mechanisms. Moreover,

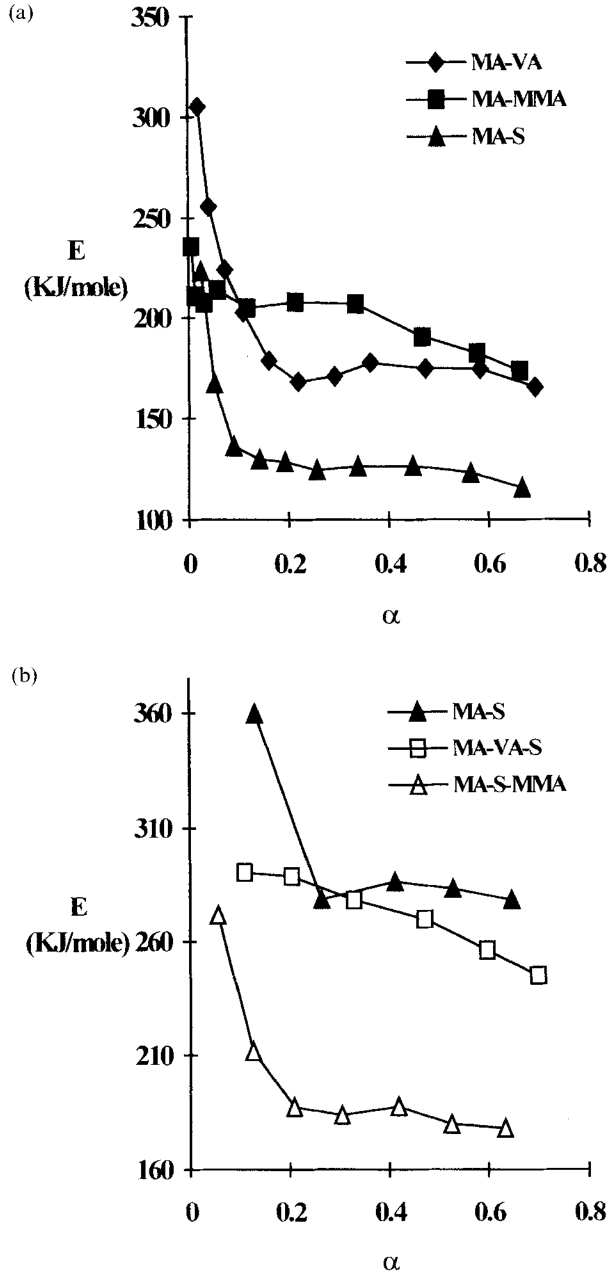


FIGURE 6 Variation of the activation energy evaluated by the Reich–Levi method with degree of conversion α, for the third thermogravimetric step of the binary (a) and ternary (b) maleic anhydride copolymers.

comparing the IR spectra of the copolymers with those of their decomposition solid products, significant structural changes can be observed (Figures 7 and 8). In the IR spectra of the decomposition products resulting from the copolymers containing vinyl acetate (Figure 7) the diminishing and then disappearance of the hydroxyl and carbonyl groups (1380 and 1040 cm^{-1} bands) and the formation of double bonds (1640 and 740 cm^{-1} bands) are evident. The changes are less evident in the IR spectra of the decomposition products of the copolymers for which the chain scission is the main reaction, as for the copolymers containing MMA or S (Figure 8). However, the shoulders corresponding to the lactone ring (1180 cm^{-1}) or double bonds (1640 cm^{-1}) are present. At the same time the bands corresponding to the carboxylic OH disappear (1380 cm^{-1} band).

At high temperatures (430–600°C), where other reactions of thermal cracking, cyclization and gasification of residue resulting from previous processes could occur, as expected overall activation energies have higher values (143–196 kJ/mole), generally following a complex kinetic law. This step is not complete for all copolymers up until

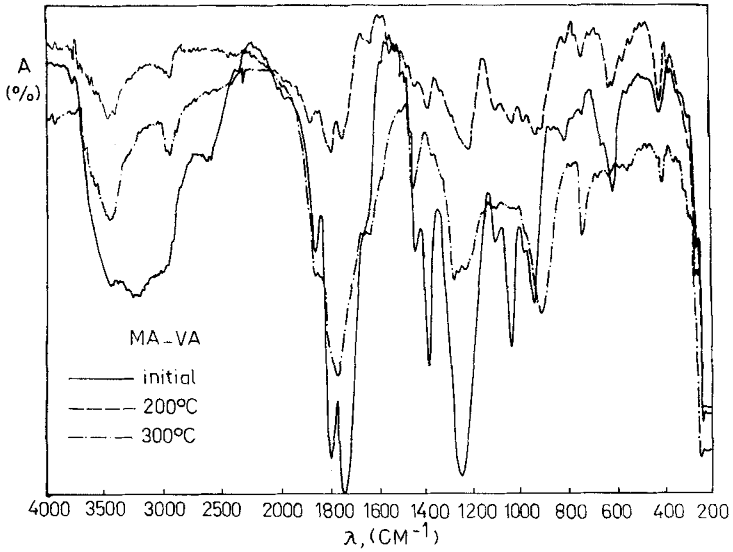


FIGURE 7 IR spectra of the maleic anhydride–vinyl acetate copolymer after heating to 200°C and 300°C.

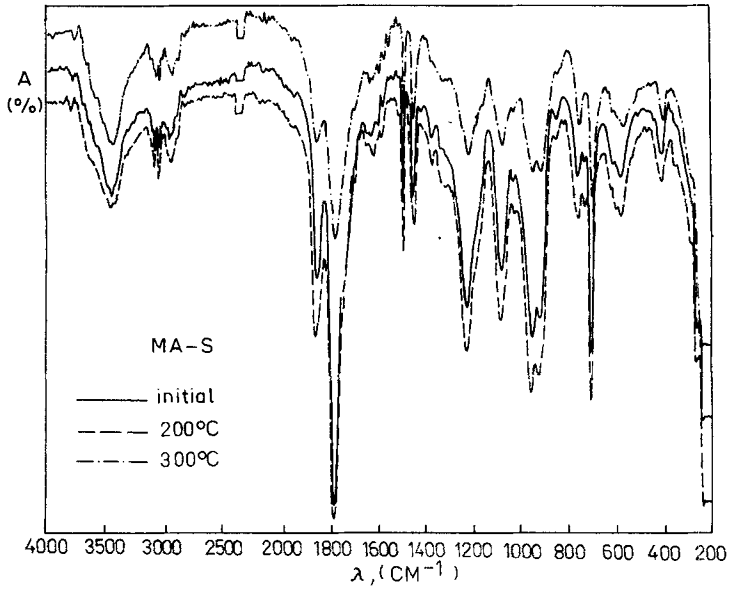
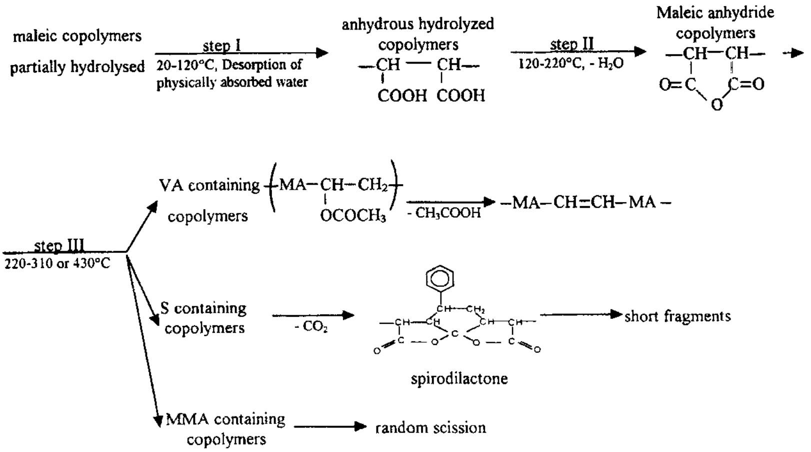


FIGURE 8 IR spectra of the maleic anhydride–styrene copolymer after heating to 200°C and 300°C.



SCHEME 2 The proposed mechanism of thermo-oxidative decomposition of the maleic copolymers.

600°C, so it was not possible to evaluate all characteristic values. The residual weight loss has appreciable values for VA containing copolymers (Table V). It is known that the acetic acid elimination leads to a polyene chain which makes crosslinking reactions possible, increasing the carbonaceous residue. The behavior during heating could be described as in Scheme 2.

4. CONCLUSION

The thermo-oxidative decomposition of three binary and three ternary copolymers of maleic anhydride with vinyl acetate, styrene or methyl methacrylate have been comparatively studied. Some similarities between thermo-oxidative behavior of the binary and ternary copolymers, probably due to their common co-monomer, MA, have been demonstrated. Thus, the second step of decomposition could be attributed to a characteristic reaction of hydrolyzed maleic anhydride units, such as dehydration. The first step of decomposition is also common for all copolymers. It is more prominent in the copolymers containing VA (the most hydrophilic co-monomer) and is ascribed to the loss of water adsorbed onto the copolymers. The quantity of absorbed water and hydrolyzed maleic anhydride units can be determined by thermogravimetric analysis.

The following steps of decomposition are different, depending on the nature of the co-monomer. For the copolymers containing VA the third step is principally, the elimination of acetic acid, as observed from the weight loss and the IR spectra. For the copolymers with styrene or methyl methacrylate these steps of decomposition consist rather in the random scission of the main chain. The characteristic temperatures, weight losses and kinetic parameters are specific for each binary or ternary copolymer, permitting their identification and eventually a discrimination between ternary copolymers and blends of binary copolymers with homopolymers.

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