Journal of Thermal Analysis, Vol. 24 (1982) 83–94

THERMAL AND THERMOXIDATIVE DECOMPOSITION OF TERNARY GRAFTED COPOLYMERS OF ABS TYPE

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(Received December 2, 1981)

The thermal (under high vacuum, 10^{-5} mm Hg) and thermoxidative decompositions of ternary grafted copolymers of ABS type were studied, the dependence of the characteristic thermal data on the overall composition being followed over narrow ranges of variation of comonomer content.

It was found that the nature of the solid products obtained on thermal decomposition is dependent on the copolymer structure.

The thermal and thermoxidative decompositions of ternary acrylonitrile (AN) – butadiene (B) – styrene (S) systems (ABS) have been relatively little investigated, though these macromolecular compounds have broad applications [1]. This fact can be accounted for primarily by their large variety, as they are constituted of binary or ternary copolymers of various types as well as of their mixtures with corresponding homopolymers.

There have been numerous studies concerning the thermal behaviour of S/AN, B/AN and S/B binary copolymers [2–6], their mixtures and vulcanized products [7, 8]. In the present paper, the influence of the overall composition on the thermal and thermoxidative behaviour of ABS ternary grafted copolymers has been investigated.

Experimental

Materials

The investigated samples consisted of ABS ternary copolymers obtained industrially by grafting AN and S on polybutadiene latex [9]. Their characteristics are given in Table 1.

The composition was established by NMR spectral measurements and by the Kjeldahl method. The amounts of S and AN comonomers are larger than those in copolymers investigated elsewhere [2].

Methods of investigation

The termoxidative behaviour was followed on a MOM derivatograph of Paulik–Paulik–Erdey type, using powders of copolymers purified by precipitation from methylene chloride solutions. For decomposition the following conditions

Table 1

Characteristics of the ABS copolymers

No.	Composition					$[\eta]$ dl/g	Symbol
	Kjeldahl		NMR spectra				
	AN, wt.%	AN, mol%	S, mol%	AN, mol%	B, mol%		
1	21.99	41.50	54.49	41.16	4.35	1.24	S-54
2	21.21	40.02	52.08	44.09	3.83	1.34	S-52
3	21.90	41.32	52.00	43.99	4.0	1.20	S-52
4	22.75	42.93	50.69	44.14	5.12	1.17	S-50
5	19.66	37.11	49.59	47.88	2.53	1.21	S-50
6	22.14	41.78	44.32	51.77	3.92	1.31	AN-52
7	16.164	31.39	69.21	26.39	5.40	1.21	S-69

were used: heating rate 10 degree/min, sample weight 20 mg, granulation 0.1–0.5 mm.

The thermal decomposition was carried out in the high-vacuum equipment described previously, together with the operational conditions [10, 11]. The heating rate used was the same as in the thermoxidative decomposition.

Methods of characterization of thermal decomposition products

The "cold" fraction is fully soluble in dimethylformamide (DMF), so that its quantitative determination from the solutions resulting after its dissolution is quite possible. The solid residue remaining in the reaction vessel after decomposition was determined by weighing. In the knowledge of the amount of these products, the volatile fraction containing both the components condensed in traps cooled with liquid nitrogen (–196°) and those non-condensable under working conditions can be determined by difference. The non-condensable compounds of the volatile fraction may be: CO, H_2, HCN, etc. [12]. The composition of the gaseous fraction condensable at liquid nitrogen temperature was determined chromatographically by means of a PYE chromatograph (Series 104, model 34), provided with a detector of thermal conductivity, bridge current 50 mA, carrier gas argon, with a flow rate of 30 ml/min, temperature 180°. For separation of the components, a column (1.5 m × 0.4 mm i.d.) filled with Porapak Q and a similar one with Apiezon L (15%) on Chromosorb P (30/40 mesh) were used for gaseous and for liquid fractions, respectively.

The component identification was carried out on the basis of the retention times of the pure components; for quantitative determination of the main substances in the liquid fraction, standard curves were plotted (Fig. 1).

For characterization of the cold fraction, IR, UV and NMR spectral measurements were used, as well as vapour pressure osmometry and elemental analysis.

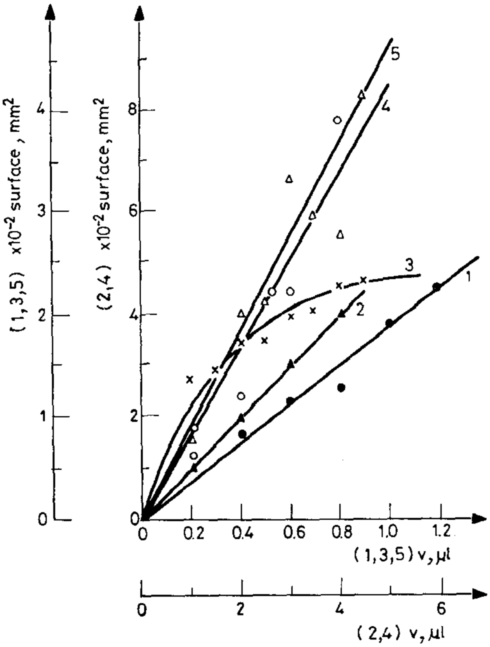

Fig. 1. Standard curves for: benzene (△), toluene (○), styrene (▲), acrylonitrile (×), acetonitrile (●)

The IR spectra were recorded on a Perkin–Elmer 577 spectrometer, from KBr pellets. The UV spectra were recorded on a UNICAM SP-800 spectrometer, using a solution of constant concentration (0.24 g/l) in DMF.

The NMR spectra of the solutions in DMSO-d_6 were obtained on a JEOL C-6OHL spectrometer at a frequency of 60 MHz at 150°, good solubilities and resolutions thus being obtained.

The Knauer vapour pressure osmometer was calibrated with solutions of trimethylbenzene in DMF at 110°, the concentration varying between 0.2 and 2 g/dl.

Elemental analysis was carried out for both the "cold" fraction and the solid residue. The carbon, hydrogen and nitrogen contents were determined by means of the modified Pregl method and the Kjeldahl method.

Results and discussion

The TG, DTG, DTA and thermomanometric curves for copolymers with various overall compositions are plotted in Figs 2 and 3, the characteristic values determined from these curves being listed in Tables 2 and 3.

The temperatures characteristic of thermoxidative degradation and the weight losses can be observed to increase with increasing styrene content within certain

Table 2

Temperatures characteristic of the DTG and DTA curves, weight losses and overall activation energies for the thermoxidative decomposition of the ABS copolymers

Sample	T_i, °C DTG	T_m, °C DTG	ΔW, %	T_m, °C (DTA I)	T_m, °C (DTA II)	E_{CR}, kJ/mol	E_{FC}, kJ/mol
S-54	242	401	53	376	446	108.78	81.42
S-52	263	383	55.5	346	445	128.89	137.03
S-52	277	378	55.3	358	437	125.05	113.13
S-50	284	402	54.92	383	450	154.64	130.96
S-50	284	404	56.25	382	454	169.68	123.46
AN-52	299	410	57.3	386	456	178.24	445.79
S-69	294	411	59.5	378	454	181.05	182.40

T_i, T_m — temperatures corresponding to the beginning of the decomposition and to the maximum degradation rate, respectively.

ΔW — weight losses; I and II, first and second stage of degradation;

E_{CR} and E_{FC} — overall activation energies evaluated by Coats-Redfern and Freeman-Carroll methods

Table 3

Temperatures characteristic of the thermal decomposition of the ABS copolymers in vacuum

Sample	Vacuummeter I						Vacuummeter II		
	Stage I			Stage II					
	T_i, °C	T_m, °C	T_f, °C	T_i, °C	T_m, °C	T_f, °C	T_i, °C	T_m, °C	T_f, °C
S-54	42.0	120	216	235	390	513	305	433	460
S-52	39.7	120	213	245	391	504	329	440	477
S-50	37.4	126	211	250	395	505	310	425	478
AN-52	35.0	98	177	275	435	494	386	447	484
S-69	20.0	136	236	260	395	513	—	—	—

limits. In the thermomanometric curves (thermal decomposition) the same variations occur during the second stage of pressure variation, but the differences are smaller and the temperatures characteristic of decomposition lower. The first stage is due both to the removal of some compounds of low molecular weight retained within the polymer and to certain structural changes [13]. This fact was also established by investigating a sample kept for two hours at 150°, which turned yellow.

To estimate the differences between the investigated samples, the apparent overall energies of activation were evaluated, as well as the variation of the energy of activation with the degree (α) of thermoxidative degradation. In this context

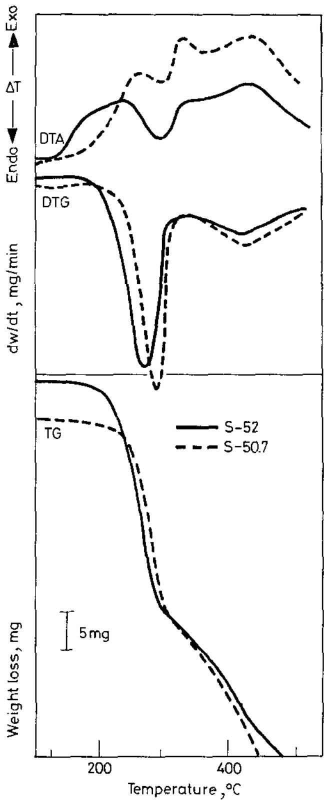

Fig. 2. TG, DTG and DTA curves for two ABS copolymers

the Freeman–Carroll [14], Coats–Redfern [15] and Reich–Levi [16] methods, respectively were used.

As can be seen in Fig. 4, all obtained values increase with increasing styrene content, the differences being kept throughout the entire decomposition reaction (first stage).

It can clearly be seen that although the differences in composition are relatively small, they have a large influence on the thermal behaviour, and a comparison between samples is possible only over narrow ranges of composition and for copolymers resulting from the same type of polymerization. For differences in composition larger than 10% in styrene comonomer the sense of variation is changed, as can be seen by comparing the obtained data with those corresponding to copolymers with high styrene content (sample 7, Tables 1–3).

To obtain certain information regarding the influence of chemical structure on the thermal behaviour, the products of thermal decomposition in vacuum were characterized. The amounts of these products are given in Table 4.

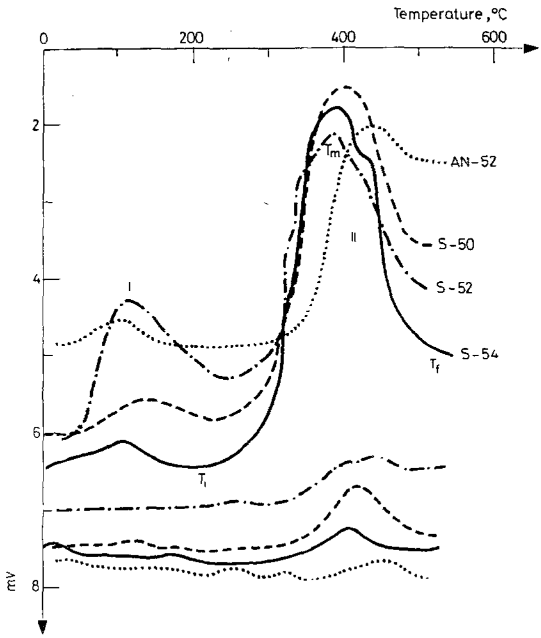

Fig. 3. Thermomanometric curves for various ABS copolymers

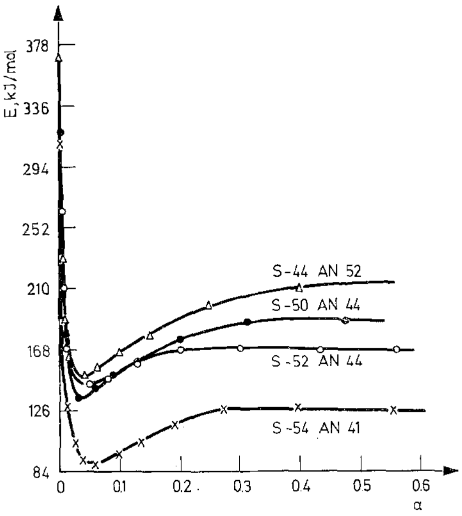

Fig. 4. Variation of activation energies corresponding to the first stage of thermoxidative degradation of ABS copolymers

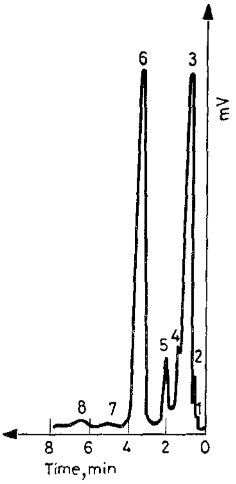

Fig. 5. Chromatogram of liquid fraction resulting from the thermal decomposition of ABS copolymers; (1) $C_1 - C_4$ hydrocarbons; (2) acetonitrile; (3) acrylonitrile; (4) benzene; (5) toluene; (6) styrene; (7) benzonitrile; (8) α-methylstyrene

Table 4

Amounts of products resulting from thermal decomposition of the ABS copolymers

Sample	Cold fraction, %	Residue, %	Volatile fraction, %
S-69	33.06	0.83	66.11
S-54	34.18	4.52	61.13
S-52	39.81	4.76	55.42
S-50	43.61	4.02	52.37
AN-52	41.03	17.91	41.06

As can be seen in Table 4, the amounts of "cold" fraction and of residue increase with decreasing styrene content, the amount of volatile fraction diminishing.

The volatile fraction consists of gaseous and liquid products. Among the gaseous products, hydrogen, methane, ethane, ethene, propane, propene and butadiene have been identified. In the chromatogram, small amounts of liquid products of high volatility, such as acrylonitrile and benzene, could be detected. The chromatogram of the liquid fraction is given in Fig. 5.

The composition is seen to be the same as in the case of binary copolymer decomposition, the products being formed by elimination and chain scission reaction. The liquid fraction has the following average composition: 0.5% acetonitrile, 5.5% acrylonitrile, 1.75% benzene, 0.38% toluene, 87.5% styrene, 0.5% benzonitrile and 3.87% other compounds. The differences between the nature

Table 5

Characteristics of the "cold" fraction

Sample	$\bar{M}_n$	INS, %	IA, %	Remarks	Composition				Empirical formulae
					C, %	H, %	N, %	Residue	
S-69	728.16	6.936	45.08	Contain compounds of low molecular	86.36	8.13	7.58	traces	$C_{13}H_{15}N$
S-54	590.10	5.88	41.11	weight	84.29	7.60	7.86	traces	$C_{13}H_{14}N$
S-52	652.23	6.46	41.84	weight	85.35	8.28	7.3	traces	$C_{14}H_{15}N$
S-50	322.5	4.25	38.99	Do not contain compounds of low molecular weight	85.54	7.80	7.32	traces	$C_{14}H_{16}N$
AN-52	457.0	5.47	36.98	Do not contain compounds of low molecular weight	73.61	7.15	8.47	8.84	C_4H_4N

INS, IA — unsaturation and aromaticity indices

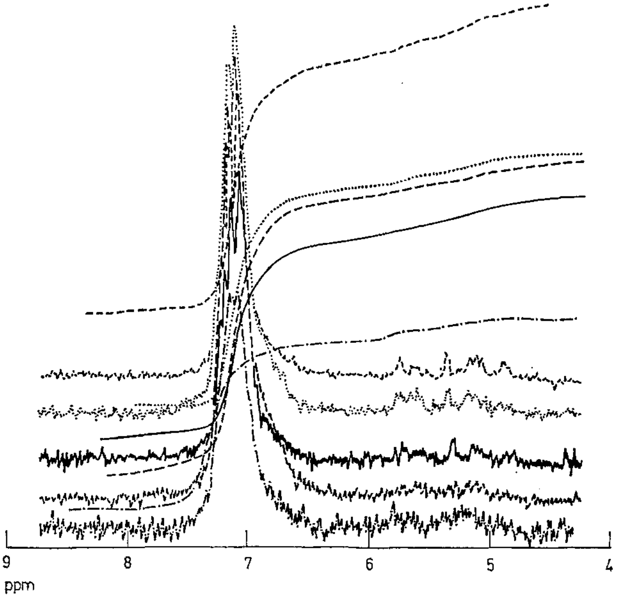

Fig. 6. NMR spectra of the "cold" fraction resulting from the thermal decomposition of various ABS copolymers. – – – – S-69; – • • – S-54; ——— S-52; — — — S-50; – • – – • – AN-52

and amounts of gaseous and liquid products resulting from the decompositions of the investigated copolymers were not distinguishable, but can be noticed in the characteristics of the "cold" fraction, as may be seen in Table 5.

The molecular weights are found to decrease with decreasing styrene content. According to NMR data (Fig. 6), the "cold" fraction consists of a mixture of products having in the main an aromatic character, but the styrene signals are not to be found. The signal at 6.8 – 7.5 ppm is larger and hence the molecular weights are relatively high. At the same time, more maxima are to be found, determined by the various types of bonds of the phenyl radical. In the case of fractions resulting from copolymers with high styrene contents this signal is more complicated, due to the presence of certain compounds of low molecular weight.

The compounds containing pyrimidinic rings occurring commonly in the products of decomposition of copolymers with high acrylonitrile content are not to be found (they should occur at 8.59 ppm).

For the sake of comparison, from the NMR spectra unsaturation and aromaticity indices were calculated as the ratio of the integrals corresponding to the protons belonging to the respective bonds and the total integral. The values are given in columns 3 and 4 of Table 5. The unsaturation index is observed to remain approximately constant, while the aromaticity index decreases with styrene content.

The percentage composition changes from one product to another, as well as the combustibility. The empirical formulae showed the modification of the reaction products as a function of the composition of the copolymers submitted to thermal decomposition. This fact has also been found for binary styrene/acrylonitrile copolymers by other authors [17].

In the IR and UV spectra, the differences between the "cold" fractions resulting from the studied copolymers are not distinguishable. The spectral data indicate the presence of certain aromatic compounds and the existence of free nitrile groups, but a $-C{=}N$-type conjugation is not found (the bands in the 1565 cm^{-1} and 360 nm regions are absent). The IR and UV spectra are given in Figs 7 and 8.

The results indicate the appearance of some fragments of variable length constituted of at least two comonomers, as has previously been shown by gas chromatographic pyrolysis [18].

In ABS copolymers with high styrene content the chain scission is highly non-uniform, a large series of products being obtained.

The carbonaceous residue resulting from thermal decomposition of the copolymers has the following average elemental composition: 75.3% C; 6.6% H; 5.9% N; and 12.1% incombustible fraction; hence, the nitrogen remains in the structure of all reaction products.

In conclusion, it may be stated that during the thermal decomposition of ABS copolymers the majority of liquid and gaseous products are the same as in the pyrolysis of polyacrylonitrile and of polystyrene. The "cold" fraction and the residue proved to be characteristic, depending on the copolymer overall composi-

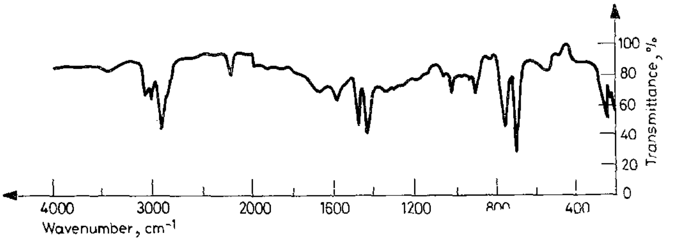

Fig. 7. Typical IR spectrum of the "cold" fraction resulting from the thermal decomposition of ABS copolymers

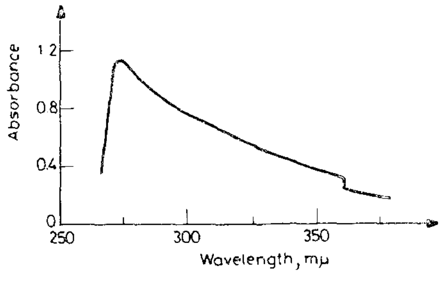

Fig. 8. Typical UV spectrum of the "cold" fraction resulting from the thermal decomposition of ABS copolymers

tion and structure. These characteristics are largely similar to those of binary S/AN copolymers, as regards both the chemical nature and the length of the formed fragments [24]. Hence, the graftings occurring during the reaction of the styrene-acrylonitrile mixture with the polybutadiene chain are constituted of chains of binary copolymers.

The degree of alternation of these comonomers in graftings (evaluated by means of copolymerization constants [19, 20]) is 0.443, and therefore the formation of longer sequences of the same comonomer is unlikely. This fact is also confirmed by the nature of the products of thermal decomposition, as evidenced by analysis of the "cold" fraction and residue.

Since the ternary grafted copolymers ABS are formed of incompatible components [18, 21, 22], the graftings and the main chain decompose independently, though the possibility arises of scissions at the ramification points, with the formation of components containing fragments of polybutadiene chain.

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ZUSAMMENFASSUNG — Die thermischen (unter Hochvakuum, 10^{-5} mm Hg) und thermooxidativen Zersetzungen ternärer Kopolymere der Typen ABS wurden untersucht, wobei die Abhängigkeit der charakteristischen thermischen Daten von der allgemeinen Zusammensetzung über enge Bereiche der Änderung des Komonomergehaltes verfolgt wurde. Es zeigte sich, daß die Beschaffenheit der bei der thermischen Zersetzung erhaltenen festen Produkte von der Kopolymerstruktur abhängig ist.

Резюме — Изучено термическое (под вакуумом 10^{-5} мм Hg) и термоокислительное разложение тройных привитых сополимеров типа АВС. Установлено, что термические данные зависят от общего состава полимеров в узких областях изменения содержания сомономера. Найдено, что природа твердых продуктов, полученных при термическом разложении, зависит от структуры сополимера.