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EFFECTS OF COPOLYMERS MODIFYING PVC AND OF MIXING ABILITY OF COMPONENTS IN THERMAL DEHYDROCHLORINATION AND DECOMPOSITION OF BLENDS

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The thermal dehydrochlorination and decomposition in air and in nitrogen of films made of PVC and blends of PVC and VC/VAC, MBS, MMA/MA or ABS were studied. Both processes take place at higher temperature in air than in nitrogen. In air, ABS and MMA/MA cause an apparent increase in the decomposition temperature of PVC, whereas in nitrogen these copolymers accelerate its decomposition.

The influence of modifying copolymers on the thermal dehydrochlorination and decomposition of PVC depends not only on the type, but also on the quantity of copolymer.

Small amounts of modifying copolymers in samples affect their thermal stability in the opposite way to larger contents of the copolymers. This shows that the structure of films with an incompatible mixture of PVC and copolymers plays the major role in the degradation processes.

Numerous studies have proved that the thermal stability of PVC depends on its type, molecular weight, chain structure and ending, the atmosphere, industrial impurities, and additives such as plasticizers, lubricants and fillers [1–13].

A considerable effect is exerted on the thermal stability of PVC in polymer blends by the other polymer [14–20]. The reason for this is the interaction of small, mobile molecules or radicals formed during the degradation of one of the polymers with macromolecules or macroradicals of the other polymer, and vice versa. These interactions can catalyze or block degradation processes. The effectiveness of the interactions depends on the compatibility of the two polymers, and therefore the structure of the film if samples are prepared in such a form. In the case of polymers which are not compatible, the films are heterogeneous. In the continuous phase formed by one polymer, the second phase consists of the other polymer in the form of domains. The quantity of the domains and their degree of dispersion determines the progress of the degradation processes.

The aim of our work was to compare the influences of small amounts of copolymers modifying PVC on its thermal dehydrochlorination and decomposition in air and nitrogen.

Experimental

The samples of PVC (S-60 Tarwinyl with $\bar{M}_v = 43300$ g/mol) and its blends with 1–10 wt.% of modifying copolymers were prepared in the form of films about 0.025 thick. They were obtained by solvent evaporation from a 2% cyclohexanone solution of polymer poured onto glass plates and dried in air at 22°. After 3 days they were removed from the plates and dried in air for another week. The films were then extracted with methanol in a Soxhlet apparatus for 40 h to remove the residual cyclohexanone; this was controlled by IR analysis. The samples were next dried under reduced pressure to constant weight.

The films containing VC/VAC (a copolymer of vinyl chloride and 10% vinyl acetate (Winacets 60/10)) were transparent. This suggests that these polymers are compatible. They very slight turbidity of PVC films containing ABS (a terpolymer of acrylnitrile, butadiene and styrene in the ratio 23:29:48), MBS (a terpolymer of methyl methacrylate, butadiene and styrene in the ratio 44:14:42) and especially MMA/MA (a copolymer of methyl methacrylate and 31% methyl acrylate) indicates that these polymeric components are not compatible. These terpolymers were fraction soluble in cyclohexanone obtained from commercial product (Blendex 101), (Kane Ace B-28) and Paraloid. The polymers were purified by extraction with hot water and hot methanol.

Thermal analyses were carried out in a Paulik–Paulik–Erdey derivatograph type OD 102 in air and in nitrogen atmospheres, and at a heating rate of 5 degree/min, with heating programme 500°, and the sensitivities TG 100 mg, DTG 1/5 and DTA 1/5.

A two-stage process of thermal decomposition of PVC, recorded as two different peaks in the DTG and DTA curves allows determination of the following parameters:

T_1^0 – temperature of starting point of reaction 1 (dehydrochlorination of PVC);
T_1^{max} – temperature of maximum rate of process 1;
T_2^0 – temperature of start of reaction 2 (decomposition of PVC);
T_2^{max} – temperature of maximum rate of process 2.

Results and discussion

The values of the thermal parameters characteristic of PVC in the presence of various modifying copolymers are presented in Figs 1–4.

The processes of dehydrochlorination and decomposition of PVC take place at higher temperature in air (curve II) than in nitrogen (curve I). This is probably caused by the reaction of oxygen with radicals formed during the breaking of chemical bonds.

The effect of oxygen on the course of the degradation processes of PVC depends on the copolymer contained in the samples. It can be seen to be insignificant in samples containing VC/VAC (Figs 1a and 3a), but considerable in samples containing

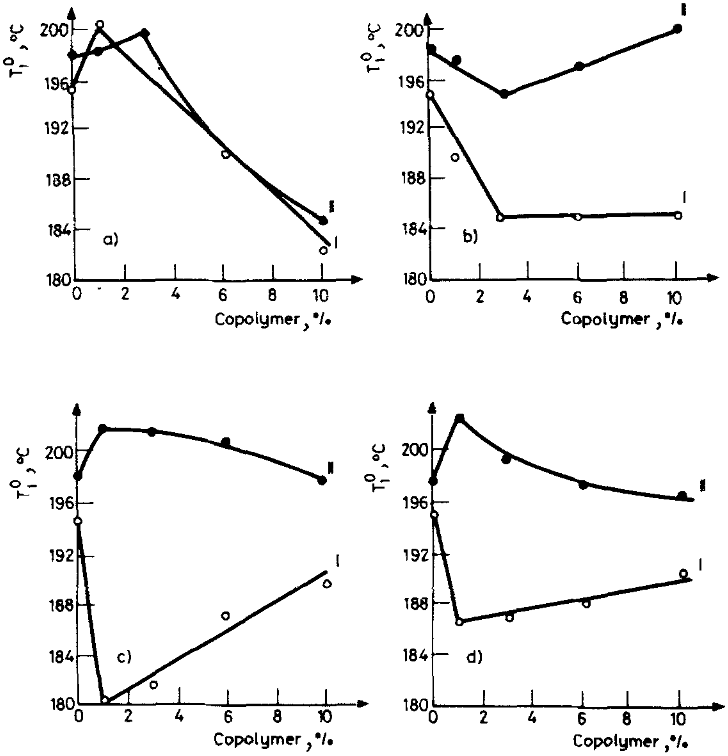

Fig. 1 T_1^0 of PVC films containing different amounts of modifying copolymers: (a) VC/VAC, (b) MMA/MA, (c) ABS, (d) MBS degraded in nitrogen (curves I) and in air (curves (II)

MMA/MA (Fig. 3b). This testifies to very different contributions of the decomposition products of the copolymers in the reactions with oxygen.

An increase of the copolymer content from 1 to 10% in the samples degradated in nitrogen gradually decreases T_2^0 and T_2^{max} (Figs 3 and 4, curves I) and the related E_2 (Table 1); E_1 is lowered (Table 1), while T_1^0 and T_1^{max} (Figs 1 and 2, curves I) are increased. Only the samples containing VC/VAC behave differently. As the content of this copolymer increases, the values of T_1^0 and T_1^{max} decrease, both in nitrogen and in air (Figs 1 and 2, curves I and II). This is caused by the catalytic effect of acetic acid liberated from VC/VAC on the dehydrochlorination process. In the presence of air, MBS and ABS too cause the decrease of T_1^0 and T_1^{max} (Figs 1c and 1d, 2c and 2d, curves II).

For all samples, the activation energy of dehydrochlorination in air varies irregularly with the copolymer concentration of the sample. Its value is smaller than the E_1 determined for this process in nitrogen (Table 1).

The value of E_1 is affected by different factors, such as the diffusion or evaporation of volatile components, as well as by simultaneous chemical reactions. Under different

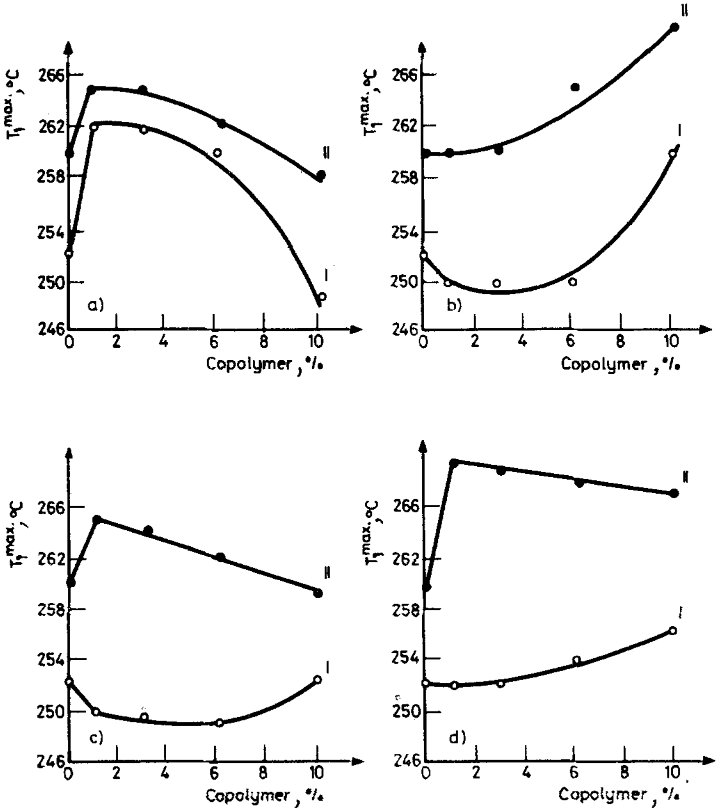

Fig. 2 T_1^{max} of PVC films containing different amounts of modifying copolymers: (a) VC/VAC, (b) MMA/MA, (c) ABS, (d) MBS degraded in nitrogen (curves I) and in air (curves II)

conditions, e.g. in air and nitrogen atmosphere, these factors, have different apparent influences on E_1.

In samples degraded in air, ABS and MMA/MA cause apparent increases in the decomposition temperature of PVC (Fig. 3b and 3c), but in nitrogen these copolymers accelerate its decomposition.

The courses of curves I and II (Figs 1–4) indicate that a small amount of modifying copolymer in the sample affects its thermal stability in the opposite way to larger content of the copolymers. These curves exhibit maxima and minima. This is evidence that the studied parameters influence the different reactions in opposite directions.

Acetic acid evolved from VC/VAC and ammonia evolved from ABS catalyze the dehydrochlorination of PVC. On the other hand, reactive nascent radical chlorine species produced by scission of C–Cl bonds in PVC can diffuse to the copolymer phase and react with tertiary hydrogen atoms. Such a reaction delays the dehydrochlorination of PVC and necessitates reinitiation; the reaction is the more possible, the shorter the route travelled by the diffusing Cl from one phase to the other. This

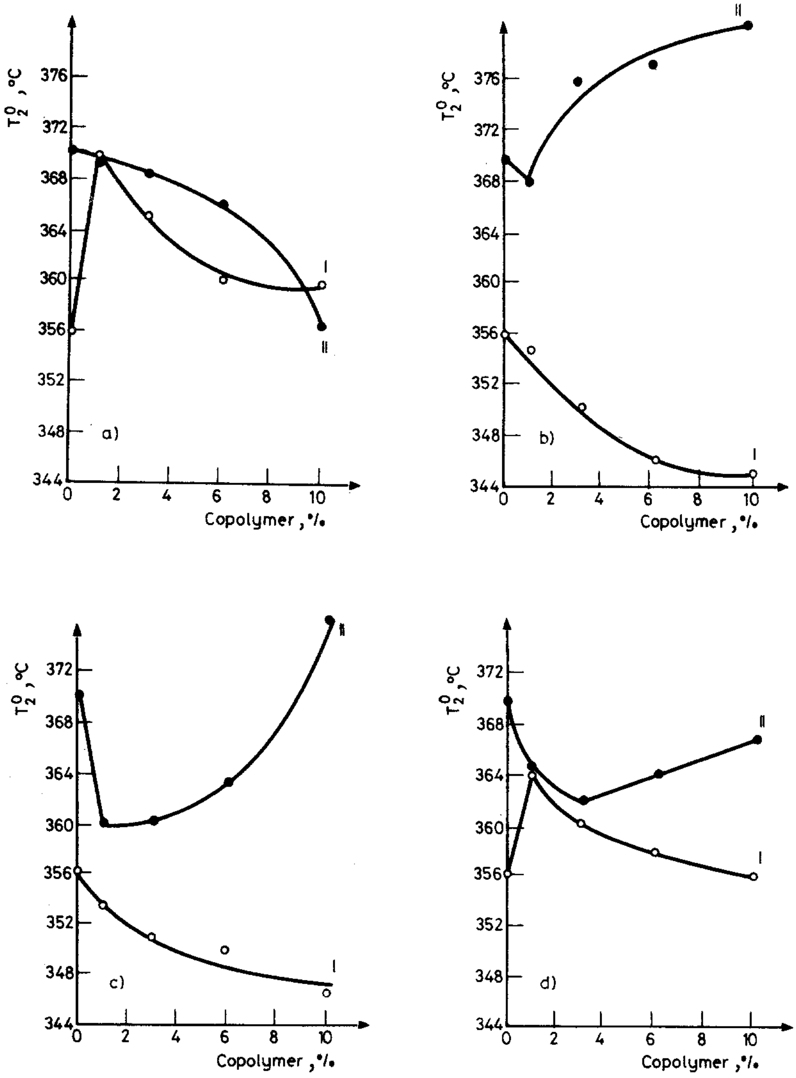

Fig. 3 T_2^0 of PVC films containing different amounts of modifying copolymers: (a) VC/VAC, (b) MMA/MA, (c) ABS, (d) MBS degraded in nitrogen (curves I) and in air (curves II)

depends on the dispersion of the copolymer in the continuous PVC phase. The degree of dispersion depends on the mixing ability of the polymers. Such ability decreases with the increase in concentration of the other polymer. Different effects on the thermal stability of PVC are possible, therefore, depending on the concentration of copolymer, and the results show the great influence of the film structure on the course of degradation processes in nitrogen as well as in air.

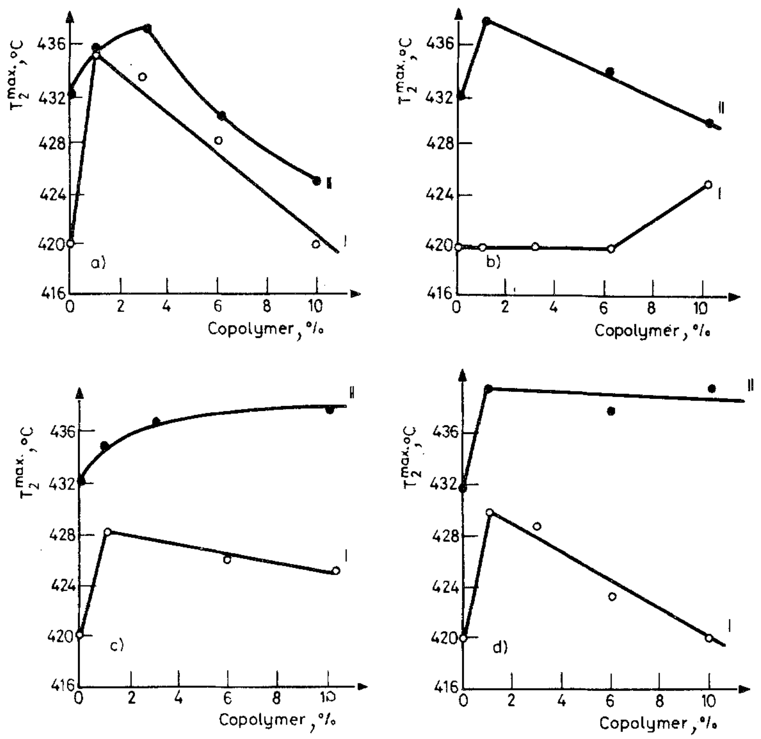

Fig. 4 T_2^{max} of PVC films containing different amounts of modifying copolymers: (a) VC/VAC, (b) MMA/MA, (c) ABS, (d) MBS degraded in nitrogen (curves I) and in air (curves II)

Table 1 Activation energies [23] of dehydrochlorination E_1 (in nitrogen) and E_1' (in air) and of decomposition E_2 of PVC films containing modifying copolymers

Amount of copolymer in PVC film, wt %	Activation energy			Reaction order		
	E_1, kJ/mol	E_1', kJ/mol	E_2, kJ/mol	n_1	n_1'	n_2
1% VC/VAC	211.4	160.0	259.6	1.4	2	2
3% VC/VAC	198.6	197.8	249.6	1.4	2	2
6% VC/VAC	188.6	150.2	238.0	1.4	2	2
10% VC/VAC	182.0	174.1	237.9	1.4	2	2
1% MMA/MA	227.3	168.4	221.8	1.4	2	2
3% MMA/MA	181.3	155.6	231.3	1.4	2	2
6% MMA/MA	181.3	149.8	199.7	1.5	2	2
10% MMA/MA	169.0	176.0	185.6	1.5	2	2
1% ABS	220/6	200.2	240.2	1.5	2	2
3% ABS	227.3	189.8	215.7	1.5	2	2
6% ABS	225.0	202.7	201.2	1.5	2	2
10% ABS	234.0	246.8	205.2	1.5	2	2
1% MBS	234.0	178.2	239.0	1.4	2	2
3% MBS	230.0	198.1	240.0	1.4	2	2
6% MBS	181.6	170.8	216.0	1.4	2	2
10% MBS	163.2	168.0	194.7	1.4	2	2

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Zusammenfassung — Die thermische Dehydrochlorierung und die Zersetzung von aus PVC und Gemischen von PVC mit VC/VAC, MBS, MMA/MA oder ABS hergestellten Filmen wurden in Luft- und Stickstoffatmosphäre untersucht. Beide Prozesse verlaufen in Luft bei höheren Temperaturen als in Stickstoff. In Luft verursachen ABS und MMA/MA eine scheinbare Erhöhung der Zersetzungstemperatur von PVC, in Stickstoff jedoch beschleunigen diese Kopolymeren die PVC-Zersetzung. Die Beeinflussung der thermischen Dehydrochlorierung und der Zersetzung von PVC durch modifizierende Kopolymere hängt nicht nur von der Natur, sondern auch von der Menge des Kopolymeren ab. Kleine Mengen von modifizierenden Kopolymeren beeinflussen die thermische Stabilität gerade in entgegengesetzter Weise wie größere. Es scheint, daß die Struktur der Filme mit inkompatiblen Mischungen von PVC und Kopolymeren in den Degradationsprozessen die Hauptrolle spielt.

Резюме — Изучены термические процессы дегидрохлорирования и разложения пленок из ПВХ и смесей ПВХ и ВХ/ВАЦ, МБС, ММА/МА или АБС в атмосфере воздуха и азота. Оба процесса в атмосфере воздуха протекают при более высокой температуре, чем в атмосфере азота. В атмосфере воздуха АБС и ММА/МА вызывают явное увеличение температуры разложения ПВХ, тогда как в атмосфере азота эти сополимеры ускоряют его разложение. Действие видоизмененных сополимеров на процесс термического дегидрохлорирования и разложения поливинилхлорида, зависит не только от типа сополимера, но также и от его количества. Наличие небольших количеств модифицированных сополимеров в образцах оказывает противоположное действие на их термоустойчивость по сравнению с образцами с большим содержанием сополимера. Показано, что именно структура пленок с несовмещающейся смесью ПВХ и сополимеров играет главную роль в процессах разрушения.