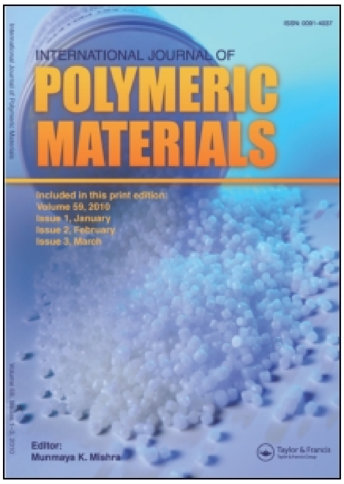

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Problems of Degradation and Stabilization of Polyvinyl Chloride in Blends with Other Polymers

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The degradation of PVC in binary blends with polymethyl methacrylate, polyuretane, ABC- and MBS-plastics, polyisobutylene, polyesters has been studied. It was shown different effect of polymeric additives on the elimination of HCl in the decomposition of PVC-, an accelerating, inhibiting and neutral effect.

KEYWORDS: Blends, PVC, thermodegradation, HCl elimination, polyenes, stabilization

A wide application of polymeric blends in manufacturing of practical materials of different kinds puts forward the problem of mutual influence of polymers in the processes of degradation and stabilization. The problem is particularly urgent for the blends, containing polymers of low thermal stability, particularly those containing polyvinyl chloride (PVC).

The study of degradation processes of PVC in binary blends with polymethyl methacrylate (PMMA), polyurethane (PU), ABS- and MBS-plastics, polyisobutylene (PIB), polyesters (PE) has shown different effects of polymeric additives on the elimination of HCl in the decomposition of PVC.[1–4] The character and the scope of the effect observed depend on the chemical nature of the polymeric additives, their amount in the composition and conditions of degradation (thermal, thermal-oxidative, static or dynamic).

THE DEGRADATION OF BINARY BLENDS OF PVC WITH THERMOPLASTIC POLYURETHANE

Polyurethane produces an accelerating effect on the PVC degradation.[1–3,5] The qualitative effect of polyurethane on the degradation of PVC is described through the concept of the catalytic property of nitrate-containing compositions, such as urethane groups and products of their interaction with HCl.

It is noteworthy that different kinetic dependences in the process of the HCl elimination are observed depending on the conditions of PVC–PU blends degradation. In the case when HCl evolved from PVC is instantly and quantitatively binded by an acceptor-stabilizer of HCl, for example barium stearate thus preventing the process of the hydrochlorination of the urethane groups with formation of the complexes of the type of quaternary ammonium salts which strongly accelerate the PVC degradation,[6]

$$—R—NH—C(O)—O—\rightleftarrows—R—\overset{HCl}{\dot{N}}H—C(O)—O—\rightarrow—[R—NH_2—C(O)]^{+}Cl^{-},$$

where the kinetic of PVC dehydrochlorination in the blend with PU is described by the linear dependence of $[HCl]=f(t)$ and $V_{HCl}=f(C_0)$ (Figure 1) in accordance with the equation

$$V_{HCl}=k_1a_0+k_3'a_0c_0,$$

where k_1 and k_3' are rate constants of PVC gross-dehydrochlorination without (s^{-1}) additives and the effective rate constant of PVC catalytic dehydrochlorination under the influence of urethane groups of PU (mol/mol PVC) s^{-1}; a_0 is the HCl content in the monomeric unit of the initial PVC (mol HCl/mol PVC); c_0 the urethane groups content in the polymeric blends, calculated using the data of the element analysis of the initial PU (mol/mol PVC).

The k_3' values are given in Table I.

In the absence of an acceptor-stabilizer of HCl, the possibility of interaction of the HCl, evolved with the urethane groups PU is realized with the formation of

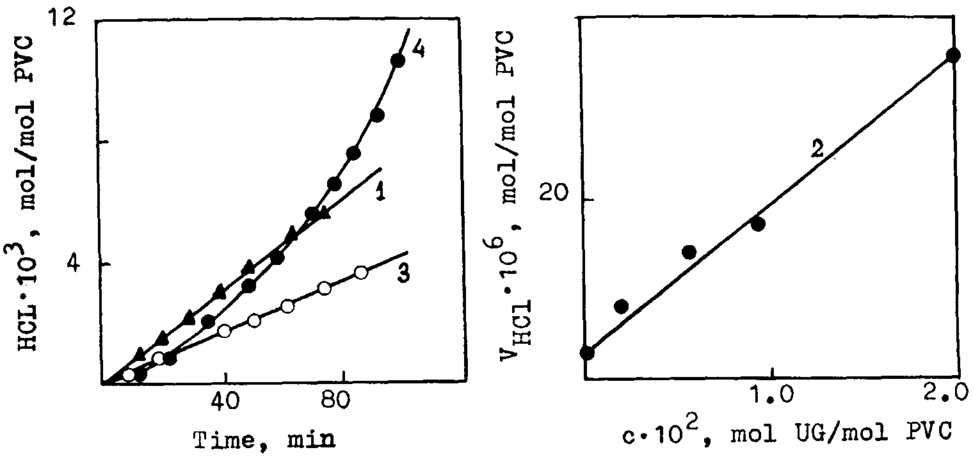


FIGURE 1 Degradation of PVC in the blend with thermoplastic polyurethane (448 K) in the presence of barium stearate, the acceptor of HCl, and dependence of the blend dehydrochlorination rate on the urethane groups concentration (2); the PVC dehydrochlorination without polyurethane (3). The PU content—15 mas.p; the content of barium stearate is 2 mas. p./100 mas. p. PVC.

TABLE I

Kinetic parameters of the catalytic dehydrochlorination in the blend with polyurethane ($V^0_{HCl} = 10^{-6}$ mol HCl/mol PVC · s, $Z_0 = 37.2 \cdot 10^{-5}$ mol/g PU)

T, K	$V^{steady}_{HCl} \cdot 10^6$, $\frac{\text{mol HCl}}{\text{mol PVC} \cdot \text{s}}$	$Z_d \cdot 10^6$, $\frac{\text{mol HCl}}{\text{g PU}}$	$(Z_0 - Z_d) \cdot 10^5$, $\frac{\text{mol}}{\text{g PU}}$	$V^*_{HCl} \cdot 10^6$, $\frac{\text{mol HCl}}{\text{mol PVC} \cdot \text{s}}$	$k''_3 \cdot 10^4$, s^{-1}	$k'_3 \cdot 10^2$, s^{-1}	$k_d \cdot 10^3$, s^{-1}	$k_2 \cdot 10^{-4}$, $\frac{\text{mol HCl}}{\text{s}}$
423	0.24 ± 0.03	0.7	37.13	0.16 ± 0.03	0.14 ± 0.02	0.40 ± 0.05	1.5 ± 0.03	0.8 ± 0.4
433	0.76 ± 0.04	3.5	36.85	0.32 ± 0.02	0.30 ± 0.05	0.84 ± 0.06	2.8 ± 0.05	2.6 ± 1.3
448	3.65 ± 0.06	8.0	36.40	1.17 ± 0.07	0.80 ± 0.05	2.45 ± 0.10	3.3 ± 0.07	3.3 ± 1.6
463	10.8 ± 1.1	14.6	35.74	3.08 ± 0.06	2.51 ± 0.15	4.17 ± 0.10	5.1 ± 0.12	6.9 ± 3.4

Note: V^*_{HCl} is the value of the HCl elimination rate, which are established after the penetration through the PU layer. Activation energy: $E_3 = 116 \pm 4$; $E''_3 = 107 \pm 8$ kJ/mol.

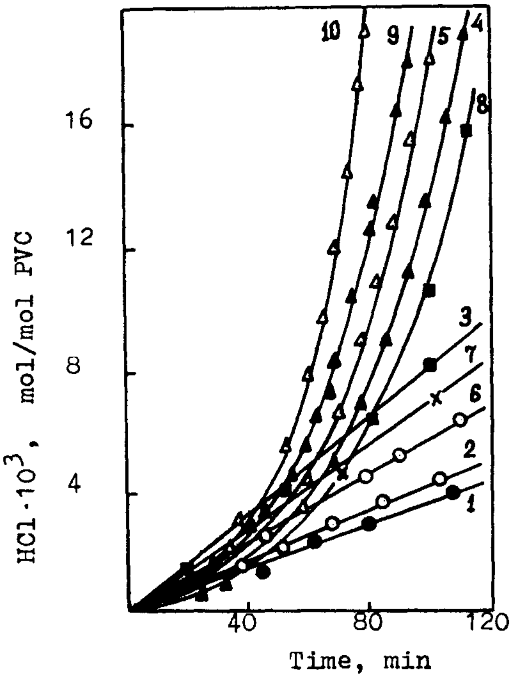


FIGURE 2 Kinetic curves of PVC thermal (1–5) and thermal-oxidative (6–10) degradation in the blend with thermoplastic PU (448 K) in the absence of an acceptor of HCl. ○—100 mas. p. PVC; ●—97.5 mas. p. PVC + 2.5 mas. p. PU; ×—95 mas. p. PVC + 5 mas. p. PU; □—85 mas. p. PVC + 15 mas. p. PU; ▲—75 mas. p. PVC + 25 mas. p. PU; △—50 mas. p. PVC + 50 mas. p. PU.

the hydrochloride complexes, which cause a strong acceleration of PVC dehydrochlorination and discolouration (Figure 2).

The fact of discolouration of the PVC degradated samples in the process of their treatment with a polar solvent (acetone) at room temperature proves the formation of these complexes Cl^- ions being identified in the solvent.

No discolouration occurs under the same conditions in a non-polar solvent (heptane). It should be taken into consideration that the process of dehydrochlorination of the urethane groups is reversible and the dynamic equilibrium is established between the hydrochlorination and dehydrochlorination reactions under the thermal degradation of polymeric blends.

The thermal stability of hydrochloride complexes of the urethane groups of PU (degradation rate constant k_d) has been determined using the kinetics of the HCl elimination from the pre-hydrochlorinated PU (Figure 3a), and is described by the equation

$$[\mathrm{HCl}] = z_{\mathrm{eq}}[1 - \exp(-k_d t)] \tag{2}$$

where z_{eq} is the equilibrium concentration of the hydrochlorinated urethane groups.

The kinetic parameters of the process of the formation of the HCl complexes

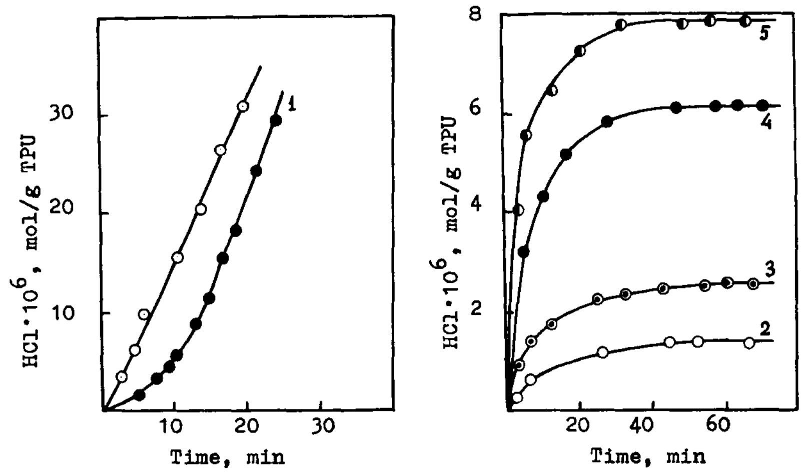


FIGURE 3 HCl absorption by polyurethane under the conditions of PVC-PU blends thermal degradation at 448 K (1) and the HCl elimination from the pre-hydrochlorinated PU (2–5) at 423 K (2), 433 (3), 448 (4) and 463 K (5); 6 is the HCl elimination in the PVC degradation without any additives. PU weighed amount is 0.05 g.

with the urethane groups have been determined in running the flow of HCl through a layer of PU under the equilibrium established (Figure 3).

PVC with a certain rate of dehydrochlorination V^0_{HCl} has been used as a source of HCl. The equilibrium is expressed by the ratio

$$k_2(z_0 - z_{\mathrm{eq}})[\mathrm{HCl}]_m = k_d z_{\mathrm{eq}} \qquad (3)$$

where z_0 is the total number of the urethane groups involved in the HCl binding; $[\mathrm{HCl}]_i$ is the instant concentration of HCl in the reaction volume, which determines V^0_{HCl}, k_2 is the rate constant of the HCl binding by the urethane groups. The values of the kinetic parameters of the reversible process of interaction of PU and HCl are given in Table I.

The ratio of the rate constants of the HCl binding with PU and the gross-process of the HCl elimination from PVC is $k_2/V^0_{\mathrm{HCl}} = 10^8$–$10^9$, which in accordance with Ref. 7 permits to attribute PU to the effective acceptors of HCl.

High values of k_2 account for the kinetic peculiarities of the dehydrochlorination process of the blends of PVC and PU, for example a considerable induction period preceding free evolution of HCl from PVC + PU composition and the autocatalytic character of the kinetic curves of HCl evolution (Figure 2). The steady value of V_{HCl} for PVC, which is established next to the initial non-linear period of dehydrochlorination of PVC–PU blends, is described by the equation

$$V_{\mathrm{HCl}} = k_1 a_0 + k_3' a_0 (z_0 - z_{\mathrm{eq}}) + k_3'' z_{\mathrm{eq}} a_0 \qquad (4)$$

where k_3'' is the effective rate constant of the PVC catalytic dehydrochlorination under the influence of hydrochloride complexes of the urethane groups.

Correspondingly, the initial task of stabilization of PVC–PU blends is in creating the conditions for a more rapid binding of HCl evolved from PVC by the effective acceptor-stabilizers of HCl, than in the case of the HCl interaction with PVC.

Under the thermal-oxidative conditions the thermoplastic polyurethane also somewhat increases the rate of degradation of PVC in the blend as compared with PVC without any polymeric additives (Figure 2).

THE DEGRADATION OF PVC BLENDS WITH POLYMETHYL METHACRYLATE

It is known,[8,9] that thermal stability of PVC–PMMA blends is increased while the rate of HCl evolution is somewhat decreased. If the PMMA content in the blend amounts to 30 wt% the effect of deceleration of PVC degradation is observed both in the case of thermal and thermal-oxidative degradation (Figure 4).

The decrease in the rate of PVC dehydrochlorination in the presence of PMMA results from the emergence of methylester of methacrylate acid which is the product of PMMA depolymerization in the reaction system.[10]

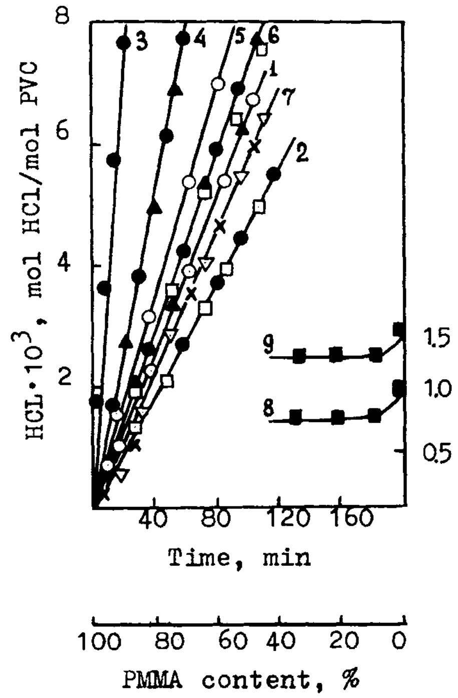


FIGURE 4 HCl elimination curves (1–7) and PVC dehydrochlorination rate in the blend with PMMA (8, 9). Degradation: 1–4, 7, 8—thermal; 5, 6, 9—thermal-oxidative. Temperature, K: 1, 2, 5–9–448; 3, 4–463; ○—100 mas. p. PVC; ●—90 mas. p. PVC + 10 mas. p. PMMA; ▲—80 mas. p. PVC + 20 mas. p. PMMA; □—70 mas. p. PVC + 30 mas. p. PMMA; ×—100 mas. p. PVC + 1.2 mas. p. methyl methacrylate; ▽—100 mas. p. PVC + 6 mas. p. methyl methacrylate; 8, 9—V_{HCl} at PMMA content 10, 20 and 30 mas. p. in the blend, respectively.

This has also been proved by a considerable decrease in V_{HCl} of PVC in the immediate presence of monomer–methylmethacrylate (Figure 4, curves 6, 7), the latter acting as a chemical stabilizer of PVC.

In the instances mentioned above the character of the effect of the additive under different degradation conditions remains unchanged. However, the influence of some polymeric additives on the process of PVC degradation is radically changed with the variation in the degradation conditions. In particular, this is true for PVC blends with ABS- and MBS-plastics, oligoisobutylene and butylrubber.

THE DEGRADATION OF PVC BLENDS WITH ABS- AND MBS-COPOLYMERS

Acrylonitrile butadien styrol (ABS) and methyl methacrylate butadien styrol (MBS) copolymers are widely used in modifications of impact strength of PVC-materials. A considerable amount of them (to 25% of mass total) is included in the polymeric compositions, but ABS alone and only in the case of the thermal degradation in inert atmosphere does not affect the PVC thermal stability. Irrespective of ABS content in the blend, the rate of PVC thermal dehydrochlorination does not change (Figure 5). The addition of ABS which is initially thermolized in vacuum (448 K, 10^{-2} Pa, during 1 hr) also does not affect the stability of the polymeric blend.

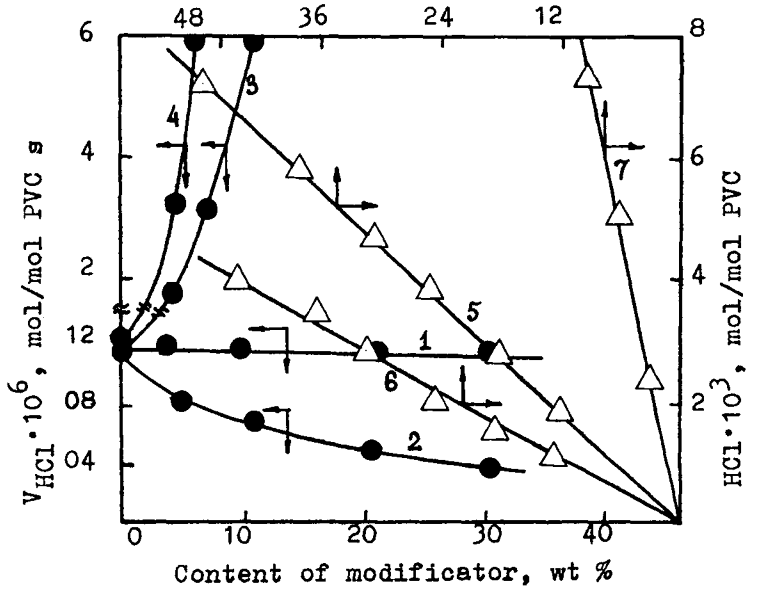
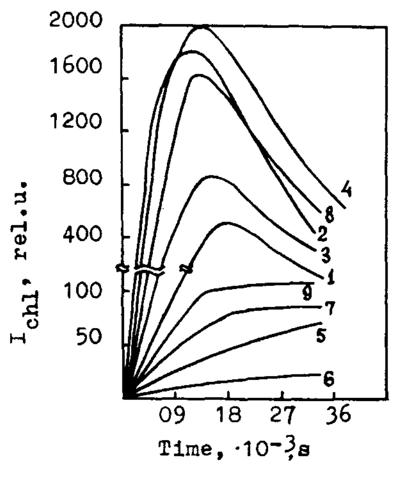


FIGURE 5 PVC dehydrochlorination in the blend with ABS- and MBS-copolymers. Degradation: 1, 2—thermal in the nitrogen current (448 K); 3, 7—thermal oxidative in the oxygen current (433 K), including 5, 6—in the presence of antioxidant-diphenylolpropane. The concentration of antioxidant, mas. p./100 mas. p. PVC: 5—0.1; 6—0.5. Copolymers: 1.3—ABS, 2, 4-7—MBS ("Incar-27"); 5, 6, 7—composition of blends—90 mas. p. PVC + 10 mas. p. MBS.

The MBS in contrast with ABS decreases V_{HCl} of PVC during the thermal degradation (Figure 5); the greater is its content in the blend with PVC, the greater is the degree. This must be the result of inhibition of PVC dehydrochlorination by methyl methacrylate, which is formed (like in the case of PMMA) after the degradation of MBS acrylate component at higher temperatures.

Under the thermal-oxidative degradation of polymeric blends of PVC, ABS and MBS (air, oxygen) the effect of the polymers changes greatly: ABS and MBS considerably accelerate the PVC degradation (Figure 5), V_{HCl} increasing with the growth of the polymeric additives content as well as the partial oxygen pressure in the reaction zone. At the temperatures above 453 K and copolymers content above 20 wt% the process of PVC thermal-oxidative degradation is considerably accelerated and accompanied by violent gas evolution. It can be clearly seen using the chemiluminescence method. For example, the thermal-oxidative degradation of PVC-ABS (MBS) blends at 413–433 K is accompanied by chemiluminescence, which is two-three orders more intensive than that of the pure PVC (Figure 6),



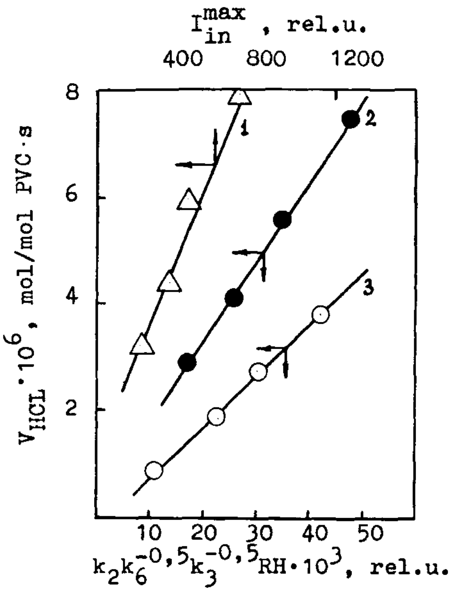


FIGURE 6 Chemiluminescence kinetics in the oxidation of blends of polymers (433 K, oxygen). Blends (components in mas. p.): 1–90 PVC + 10 ABS; 2–50 PVC + 50 ABS; 3–90 PVC + 10 MBS "Incar-27"; 4–50 PVC + 5 MBS "Incar-27"; 5–90 PVC + 10 MBS "Incar-27" + 0, 1 diphenylolpropane; 6–90 PVC + 10 MBS "Incar-27" + 0.5 diphenylolpropane; 7–50 PVC + 50 MBS BTA-3N (Japan); 8–50 PVC + 50 MBS BTA-3N after the extraction by heptane; 9–100 PVC.

FIGURE 7 Dependence of the relative change of the dehydrochlorination rate V_{HCl} in the thermal-oxidative degradation of PVC in blend with ABS- and MBS-copolymers on the relative change of maximum intensity of chemiluminescence I_{chl}^{max} (1) (433 K, oxygen) and on the oxidability of the copolymers (2, 3) (413–433 K, oxygen): 2–90 mas. p. PVC + 10 MAS. p. MBS; 3–90 mas. p. PVC + 10 mas. p. ABS.

chemiluminescence maximum intensity I_{chl}^{max} as well as V_{HCl} value being determined by the chemical nature of the second polymer and its content in the blend with PVC. It is important that the I_{chl}^{max} change (relative to the chemiluminescence of pure PVC) directly depends on the relative change of the HCl elimination rate from PVC, V_{HCl}, under the influence of ABS or MBS under the same conditions (Figure 7).

The revealed peculiarities of the thermal-oxidative degradation of PVC-ABS and MBS blends are due to the polymeric modificators degradation with formation of the products of oxidation, the main of which are hydroperoxides,[11] which promote the PVC degradation. High oxidation rate of individual polymers ABS and MBS has been proved by the chemiluminescence method. According to,[12] the chemiluminescence intensity I_{chl} at the ABS and MBS autooxidation is proportional to the concentration of the resulting hydroperoxides $I_t = C[ROOH]_t$, and the rate of oxidation is approximated by the equation:

$$-d[O_2]/dt = d[ROOH]\,dt = k_2k_6^{-1/2}k_3^{1/2}[ROOH][RH] \tag{5}$$

where k_2, k_6 are the reaction rate constant of propagation and termination of chains of oxidation; k_3 is the rate constant of the reaction of the degraded chain branching; [RH], [ROOH] are the concentrations of copolymer and hydroperoxides in the system.

The reaction proceeding under the kinetic conditions (P_{O_2} being high) the Eq. (5) may be transformed into:

$$\ln\left(\frac{I_t}{I^{max} - I_t}\right) = \ln\left(\frac{[ROOH]_0}{[RH]_0}\right) + k_2k_6^{-1/2}k_3^{1/2}[RH]_0t \tag{6}$$

where I_t and I^{max} are the values of current and maximum chemiluminescence intensity. The anamorpha of kinetic dependences $I = f(t)$ in $\ln(I_t/I^{max} - I_t) = f(t)$ coordinates. The values of $k_2k_6^{-1/2}k_3^{1/2}[RH]_0$ parameter, which characterize the rate of oxidation of ABS and MBS polymeric products have been calculated (Table II). The MBS oxidability is somewhat higher than that of ABS which results in greater accelerating effect of this copolymer at the PVC degradation. There is direct dependence between the parameters of oxidability of ABS and MBS $k_2k_6^{-1/2}k_3^{1/2}[RH]_0$ and the relative change in the rate of gross-dehydrochlorination of polymeric blends V_{HCl} under the thermal-oxidative degradation (Figure 7).

TABLE II

Oxidative stability of ABS- and MBS-copolymers based on the data of chemiluminescence (in the medium of oxygen)

	$k_2k_6^{-1/2}k_3^{1/2}[RH]_0 \cdot 10^3$, rel. u.	
T, K	ABS-copolymer	MBS-copolymer
413	0.8	1.5
419	2.0	2.6
425	2.9	3.3
433	4.2	4.8

The process of ABS and MBS oxidation with oxygen being the main reason of PVC degradation acceleration in the corresponding polymeric blends indicates the possibility of effective stabilization of PVC blends with ABS (MBS) antioxidants. Addition of certain stabilizers of phenol, for example diphenylolpropane results in the strong decrease in the rate of the PVC-ABS and MBS thermal-oxidative degradation. This fact is also proved by the data on the thermal-oxidative degradation of PVC in the blends with pre-stabilized MBS of commercial grade BTA-3N (Japan), which does not practically accelerate the PVC degradation. However, the extraction treatment of MBS BTA-3N by heptane results in the MBS acceleration of PVC decomposition practically at the same extent as that of the non-stabilized MBS (Figure 6).

DEGRADATION OF PVC BLENDS WITH POLYISOBUTYLENE AND BUTYLRUBBER

In the thermal degradation PVC-PIB-BR in the inert atmosphere polymeric additives do not affect the PVC thermal stability. However, the dynamic effect of oligoisobutylene with $MM = 800 \div 900$ and butylrubber in the amount of 0.5–10 mas. p. PVC considerably stabilizes the PVC degradation. The decrease in the polymer melt viscosity, the increase in the flowability of composition, the decrease of heat evolved as a result of friction and under the influence of shift efforts eliminate temperature fluctuations in the polymer melt mass and accordingly decelerate mechanochemical degradation of polymers.

In case when the content of polymeric additives, which are well compatible with PVC, is high, one more factor, affecting the PVC degradation and conditioned by solvation effects, should be taken into consideration similarly to the PVC degradation in solutions.[13,14] Indeed, it is to this effect that the inhibition of PVC degradation in the inert atmosphere in the presence of polyesters, for example on the basis of products of reesterification of dibutyl adipinate by diethylene glycol or propylene glycol-1,2 owes to.

Thus, the example of the degradation of the binary blends of polymers, including PVC, permits to determine a number of factors, defining the character and rate of PVC dehydrochlorination in polymeric blends. The main factors are: 1, chemical nature of polymeric additive, i.e. the presence in the macromolecules of functional groups capable of accelerating the HCl elimination from PVC; 2, thermal and thermal-oxidative stability of polymeric additive, causing the formation of low-molecular and polymeric products of degradation, which either accelerate or decelerate the PVC degradation; 3, solvation effects.

Employing the polymeric blends, one should take into consideration the influence of polymeric additives on the PVC degradation under processing and exploitation aging and, accordingly when choosing effective ways of stabilizing the polymeric blends using PVC.

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