

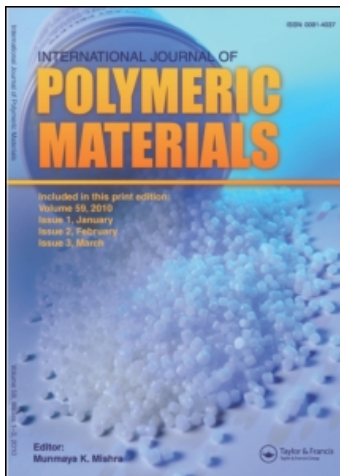
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E. I. Kulish<sup>ab</sup>; S. V. Kolesov<sup>ab</sup>; K. S. Minsker<sup>ab</sup>; G. E. Zaikov<sup>ab</sup>

<sup>a</sup> Bashkirian State University, Ufa <sup>b</sup> Institute of Chemical Physics, Moscow

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## The Degradation of PVC Blends with Poly- $\alpha$ -olefins

E. I. KULISH, S. V. KOLESOV, K. S. MINSKER and G. E. ZAIKOV

*Bashkirian State University, Ufa 450076, Frunze 32; Institute of Chemical Physics, Moscow 117334, Kosygin*

The thermal stability of PVC blends with poly- $\alpha$ -olefins is reviewed.

**KEY WORDS** Thermal degradation, PVC, poly- $\alpha$ -olefins, blends

The materials produced on the basis of PVC blends with poly- $\alpha$ -olefins are characterized by higher durability, stability to shock loading, weldability with high frequency currents, stability of shape and other important properties.<sup>1–3</sup> Due to this solutions plasticates as well as rigid multicomponent systems based on PVC blends with poly- $\alpha$ -olefins have found a wide application in the manufacture of construction, packing and other materials for the motor car industry, shipbuilding, construction, medicine, radioelectronics and other industries. However, the problems of thermal stability have not been practically studied, that being of great importance for the materials containing PVC.

Poly- $\alpha$ -olefins are of the class of polymers, that do not contain functional groups, are PVC-incompatible, and are stable at temperatures under which PVC undergoes thermal degradation. Therefore, we may suppose that poly- $\alpha$ -olefins should not affect the thermal stability of PVC blends. True, in PVC blends with poly- $\alpha$ -olefins (polyethylene (PE), polypropylene (PP), polyisobutylene (PIB)), obtained in the form of precipitated powders or films poured off from a common solvent, as well as plasticized compositions, poly- $\alpha$ -olefins do not affect the PVC thermal stability at all (Table I). However, under certain conditions the presence of poly- $\alpha$ -olefin affects the PVC dehydrochlorination rate, in particular during degradation in solutions.

The thermal stability of PVC itself in solutions is known to be greatly dependent on the nature of the solvent being used, that being determined by two main types of interactions between the solute and the solvent,<sup>4</sup> i.e., non-specific and specific solvation. Non-specific PVC interaction in solutions is described by an equation, taking into account the solution polarity  $P$  (permittivity), segmental mobility of the macromolecules  $\Delta\tau/\tau$  and the Flory-Huggins interaction parameter  $\chi$ ;

$$V_{\text{HCl}} = V_{\text{HCl}}^0 + a*\chi + b*P + c*\Delta\tau/\tau,$$

where  $V^0_{\text{HCl}}$  is the dehydrochlorination rate of PVC in the gaseous phase; and  $a$ ,

TABLE I

The degradation rate of the PVC blend with poly- $\alpha$ -olefins										
$V_{\text{HCl}} \cdot 10^8, [ \text{mole HCl} / ( \text{mole PVC} \cdot \text{s} ) ]$										
poly- $\alpha$ -olefin content in the blend, % mass.	mass subsided pulvers			films poured off the common solvent			plasticized composition			
	PE	PP	PIB	PE	PP	PIB	PE	PP	PIB	
0	5,53	5,53	5,53	5,51	5,51	5,51	5,48	5,48	5,48	
10	5,41	5,51	5,48	5,48	5,52	5,47	5,48	5,50	5,47	
50	5,60	5,48	5,40	5,41	5,58	5,51	5,52	5,51	5,40	
90	5,52	5,53	5,58	5,63	5,48	5,52	5,51	5,52	5,52	

$b, c$  are the constants of sensitivity of the  $V_{\text{HCl}}$  value to variations in the corresponding parameter of the PVC interaction with the solvent.

The specific PVC interaction may be estimated from the basicity parameter  $B$  (or the donor number  $Dn$ ). In Reference 5 it was found that the liquid phase degradation rate of PVC may be lower ( $B < 50 \text{ cm}^{-1}$ ) or higher ( $B > 50 \text{ cm}^{-1}$ ) than the value of the initial PVC degradation rate depending on the numerical value of the basicity parameter. When poly- $\alpha$ -olefins are added to the system new "PVC-solvent" phenomena are observed. In dilute (2 mass.%) solutions in 1,2,3-trichloropropane and 1,2,4-trichlorobenzene ( $B < 50 \text{ cm}^{-1}$ ) where poly- $\alpha$ -olefins addition exceeds 10% of the mass of the polymer blend, the result is a considerable increase in the PVC dehydrochlorination rate (Figure 1, curves 1-5). The simplest explanation that could account for the effect of the second polymer under these conditions proves to be oxidation of the poly- $\alpha$ -olefins during the process of preparing the solution at high temperature. The accelerating effect of the oxidation of the solvent, plasticizers<sup>6</sup> as well as of the products of oxidation of the second polymer in the PVC blend<sup>7</sup> is a well-known phenomenon. However, chemiluminescence studies of the solutions prepared at high temperature in an inert gas flow testifies to the fact that the polymers are not oxidized under these conditions.

On the contrary, during the degradation of a PVC blend with poly- $\alpha$ -olefins in cyclohexanol with PVC dehydrochlorination rate in the blend decreases as the poly-

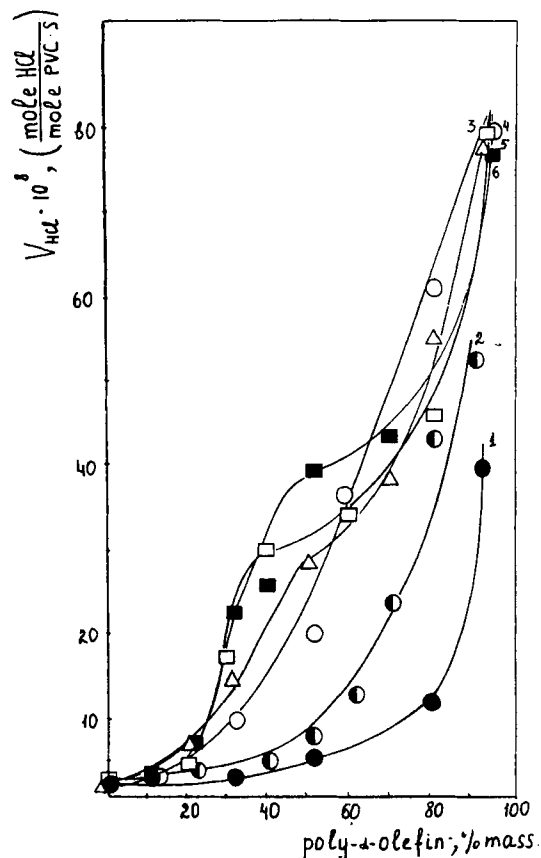


FIGURE 1 The dependence of the degradation rate of a PVC blend with poly- $\alpha$ -olefins on the poly- $\alpha$ -olefin content in the blend ( $N_2$ , 423 K, 2% polymer solution in the solvent with  $B < 50 \text{ cm}^{-1}$ ): 1—the PVC-PE blend in 1,2,4-trichlorobenzene; 2—the PVC-PP blend in 1,2,4-trichlorobenzene; 3—the PVC-PE blend in 1,2,3-trichloropropane; 4—the PVC-PP blend in 1,2,3-trichloropropane; 5—the PVC-PIB blend in 1,2,3-trichloropropane; 6—the blend of PVC with polyethylene wax in 1,2,3-trichloropropane.

$\alpha$ -olefin content in the blend increases over the whole range of poly- $\alpha$ -olefin concentration (Figure 2, curves 1–3). A similar dependence of the degradation rate of PVC in solutions on the blend composition is also observed when low-molecular weight polyethylene wax is applied as the second component of the blend. It is the same as for the case of PVC blends with poly- $\alpha$ -olefins. As the wax content increases in the blend it leads to a PVC degradation rate increase for solvents with basicity  $B < 50 \text{ cm}^{-1}$  (1,2,3-trichloropropane—Figure 1, curve 6) and a PVC dehydrochlorination rate decrease when a solvent with high basicity is used (cyclohexanol—Figure 2, curve 4).

A visual polythermal study of the solutions indicates that for the conditions selected they yield only a liquid phase. For variations of the conditions, for instance, a reduction of the temperature to 383 K or an increase of the solution concentration up to 10% mass, there results a phasal separation of the polymer blend that im-

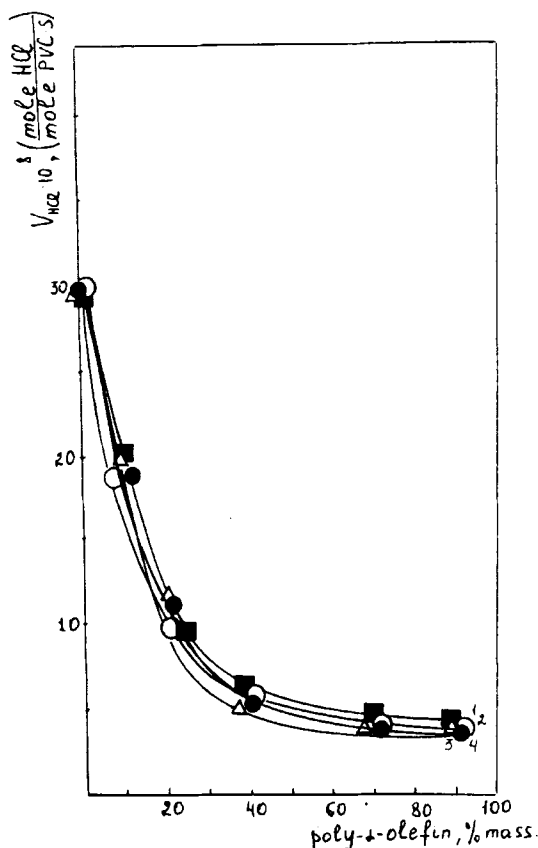


FIGURE 2 The dependence of the degradation rate of a PVC blend with poly- $\alpha$ -olefins on the poly- $\alpha$ -olefin content in the blend ( $N_2$ , 423 K, 2% polymer solution in the solvent with  $B > 50 \text{ cm}^{-1}$ ): 1—the PVC-PE blend in cyclohexanol; 2—the PVC-PP blend in cyclohexanol; 3—the PVC-PIB blend in cyclohexanol; 4—the blend of PVC with polyethylene wax in cyclohexanol.

mediately causes a change in the character of the dependence of the dehydrochlorination rate PVC blend with poly- $\alpha$ -olefins on the poly- $\alpha$ -olefin content in the blend. In particular, polyethylene under the conditions of thermodynamic incompatibility with PVC, stops effecting the thermal stability of PVC in the solvents studied as well as PVC powders, produced during mass subsidence from a collective solution, and films poured from the collective solvent.

If the hydrocarbon dodecane is taken as a low-molecular weight analogue of poly- $\alpha$ -olefins, within the same concentration range one can observe the same PVC dehydrochlorination rate dependence on the blend composition. The effect of the paraffin hydrocarbon decane, in particular, was discussed in Reference 8 for the degradation of the PVC in a mixture of thermodynamically "good" and "poor" solvents, with hydrocarbon playing the part of the "poor" solvent, i.e., the precipitant. It was shown that the consecutive addition of an increasing quantity of the precipitant to the PVC solution is accompanied by a continuous variation in the  $V_{HCl}$  value, the PVC dehydrochlorination rate decreasing with the addition of

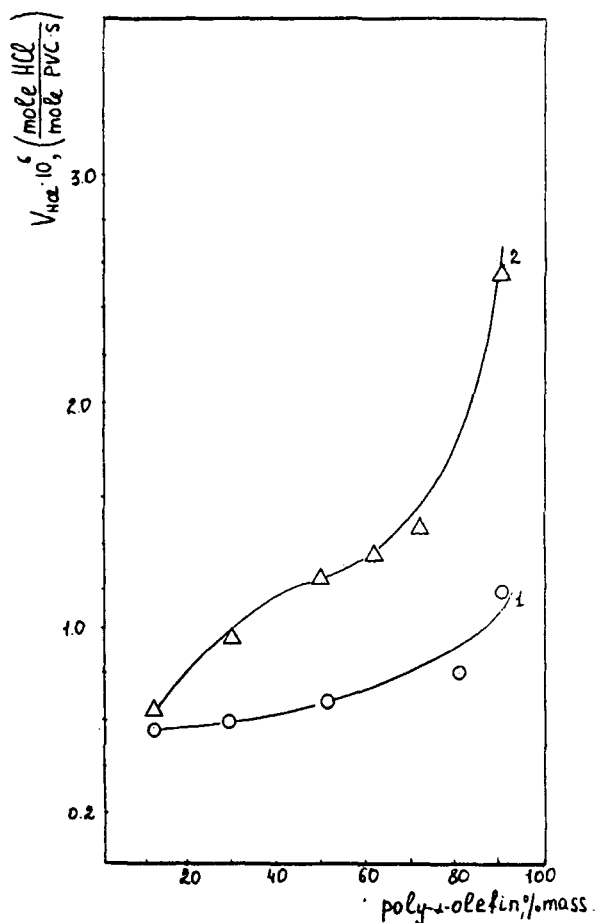


FIGURE 3 The dependence of the degradation rate of a PVC blend with PE on the PE content in the blend ( $N_2$ , 448 K): 1—the PVC-PE blend prepared by the method of elastically deformed dispersion; 2—rolled films of PVC-PE.

the precipitant to a solvent with the basicity  $B > 50 \text{ cm}^{-1}$  (cyclohexanon) and increasing for the degradation in a solvent with basicity  $B < 50 \text{ cm}^{-1}$  (*o*-dichlorobenzene). Since the polymer and the solvent interaction determining the rate of the liquid-phase PVC degradation does not depend on the solvent basicity only, but on a number of physicochemical parameters of the solution ( $\chi$ ,  $P$ ,  $\Delta\tau/\tau$ ), the observed variation on the PVC degradation rate *versus* the dissolving mixture's compositions may be determined by a non-specific interaction as well. Heally, in Reference 8 demonstrates that the PVC dehydrochlorination rate in a mixture of thermodynamically "good" and "poor" solvents (decane) is essentially dependent on the value of the phase permittivity, the Flory-Huggins interaction parameter and is also determined by the conformational changes of the macrochains under the effect of the precipitant. As the observed dependencies of the PVC dehydrochlorination rate on the hydrocarbon of the paraffin are similar to those taking place in the degradation of the PVC blends with poly- $\alpha$ -olefins, all this allows us

to consider the effect of poly- $\alpha$ -olefins and low-molecular weight hydrocarbons (the so-called "poor" solvents) from one point of view, i.e., as the effect of the medium in which PVC degradation occurs.

Under certain conditions the effect of the poly- $\alpha$ -olefins becomes evident in the absence of the solvent as well. For instance, during the formation of a new high-dispersing polymer phase from the collective melt of two polymers when the method of elastically deformed polymer dispersion is used. In this case the polymer blend is subjected to combining the conditions of plastic flow under high pressure and shifting deformation effects. For specimens prepared by this method and containing 10–90 mass. % of polyethylene the observed relationships are similar to those taking place during PVC degradation in diluted solutions of 1,2,3-trichloropropane and 1,2,4-trichlorobenzene. We can also observe a considerable increase in the PVC dehydrochlorination rate with the increase in polyethylene content in the blend. This is true for the case of blends obtained both in the form of powders and in the form of films rolled from these blends (Figure 3, curves 1, 2). The chemiluminescence of the PVC-PE blends starts at the same temperature as in case of the pure polyethylene which had not undergone elastic deformed dispersion. The dependence of the chemiluminescence intensity on temperature also coincides. All this gives reason to consider the given case as not accompanied by the formation of oxidation products the degradation of which could have accelerated the PVC thermal degradation. It should be noted that thermomechanical curves of the PVC-PE blends with a low content of PE (90% of PVC—10% of PE) give a distinct picture of the pour point and the point of vitrification of PVC ( $T_v = 360$  K,  $T_p = 451$  K) and the melting point of the crystalline phase of PE ( $T_m = 381$  K), that is characteristic of the blends of thermodynamically incompatible polymers. However, thermodynamic curves of the blends with PVC content  $\leq 50\%$  do not show the transition corresponding to PVC vitrification. It is only the melting point of polyethylene that is seen in the curves. The presence of PVC in the blend is not revealed in these thermomechanical curves, possibly due to the system's high dispersity.

Thus, despite the chemical inertness of poly- $\alpha$ -olefins under conditions of PVC degradation, their presence in the blend may affect PVC thermal stability in cases when the polymers are properly combined either in a high-dispersing polymer phase or in a diluted collective solution. The poly- $\alpha$ -olefins effect is possibly of a non-chemical nature and it should be considered as a specific case of the medium effect on PVC thermal degradation.

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