Structural–Physical Effects at Thermal Degradation of PVC in Complex Polymer Objects

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ABSTRACT: The influence of structure formation on thermodegradation of poly(vinyl chloride) (PVC) in complex polymer objects is considered in the article. It was shown that structural-physical states of polymer mixtures depend on the method of obtaining a composite and affinity of the polymers. Composites of the same composition may be obtained, which possess rather different dehydrochlorination rates for PVC. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 85–89, 1999

Key words: structural-physical states; thermal degradation; poly(vinyl chloride); complex polymer objects

DISCUSSION

The chemical behavior of polymers is generally defined by their structural-physical heterogeneity, such as the solubility of a polymer system, its state (solution, solid, etc.), existence of associates of macromolecules, and supermolecular formations. For degradation of poly(vinyl chloride) (PVC) and its mixture with other polymers, it was shown that factors defining stability of macromolecules are the chemical structure of polymer chains, existence of low-molecular-weight additives, solvent,^{1,2} the structural-physical effect, and association in solutions in particular. Association of macromolecules in diluted solutions is accompanied by solvent substitution in the macromolecular coil volume, by monomer chains of neighboring macromolecules, with the corresponding growth of local density of chains in the coil. Such structural transition, when the system transitions from homogeneously distributed macromolecular coils to a system of associated polymer molecules, is accompanied by a jump-like

change of viscosity.³ For PVC solutions in cyclohexanone (CHN) and 1,2,3-trichloropropane (TCP), it was shown⁴ that the beginning of the association corresponds to PVC concentrations of 0.9 mas % in CHN and 0.6 mas % in TCP. This is accompanied by the corresponding change in the rate of PVC decomposition (Fig. 1, curves 1 and 2). If the rate of dehydrochlorination remains constant in the ranges in which PVC exists as isolated macromolecules, then after an increase of concentration up to values corresponding to the beginning of macromolecule association, the rate of PVC degradation begins to change, decreasing in CHN and increasing in TCP (Fig. 1, curves 3 and 4). The difference in the rates of PVC degradation in the present solvents is due to different values of the basicity index B for CHN and TCP.² However, due to concentration of the PVC solution, the rates of its decomposition in the absence of a solvent indicates a structure of PVC, with formation of a fluctuation network, consisting of dense aggregates, the molecular structure of which is similar to the PVC structure in to firm phase.

PVC macromolecules may be transferred into an associated and aggregated state, and, consequently, a change of the degradation rate may be

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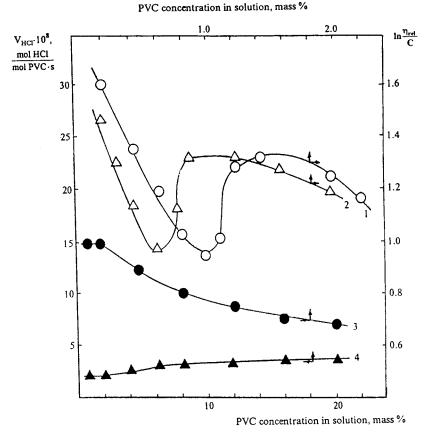


Figure 1 Dependency of the logarithm of reduced viscosity of solutions (1) and (2) and the rate of PVC thermal dehydrochlorination (3) and (4) on PVC concentration in CHN (1) and (3) and TCP (2) and (4) solutions at 423 K.

caused not only by a change of concentration of a polymer solution but also by addition of second polymer with low thermodynamic affinity to PVC. As an example, the following polymers relate to this class: poly(methyl methacrylate) (PMMA) and polystyrene (PS). The dependent polymer solution viscosity-polymer mixture concentration for solutions of polymer mixtures clearly shows (Figs. 2 and 3) that the presence of a second polymer (PMMA, PS) in the PVC-solvent system causes association of macromolecules in the range of solution concentrations, in which PVC is not yet associated. The increase of polymer-precipitator content causes a shift of the polymer solution concentration, at which the transition into the associated state happens at lower values.

Chemical influence of PMMA and PS on the degradation of PVC is well known.⁴ With PVC, they are depolymerized, forming the monomers, which inhibit PVC degradation in the absence of a solvent. It was shown for the PVC–PMMA system, the monomer action reverses in solution⁵; that is, the rate of PVC dehydrochlorination in-

creases, which should be also expected for the PVC-PS system, due to similarity of the systems. Let us note, that for the study of PVC degradation rate of mixtures in solution, the solutions of polymers were the concentration fortiori defining the presence of macromolecule associates (2 mas %). The extreme character of the change of the PVC dehydrochlorination rate in CHN, and the monotonous one in TCP (Fig. 4), is provided by the interaction of two factors, as follows: (1) As a consequence of the chemical influence of the second polymer, the rate of PVC degradation increases in both solvents (influence of monomers); and (2) as a consequence of the change of structural-physical characteristics, the increase of the association degree of macromolecules due to addition of the second polymer, the change of PVC degradation rate is different. In this case, it is provided by the different solvating ability of solvents in relation to the polymer.

Similar to the case of association of PVC macromolecules caused by simple concentration of the solution, addition of the second polymer (PMMA,

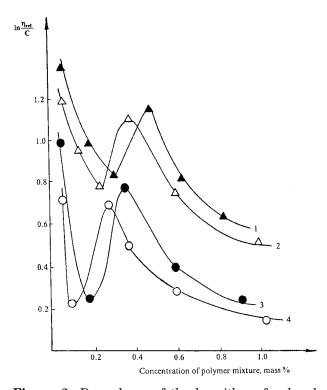


Figure 2 Dependency of the logarithm of reduced viscosity of solutions on the concentration of polymers in mixtures for the PVC–PMMA system: (1) and (3) 90 : 10 mass %; (2) and (4) 50 : 50 mas % in (1) and (2) CHN and (3) and (4) TCP at 423 K.

PS) with low thermodynamic affinity to PVC induces a decrease of PVC degradation in CHN and its increase in TCP. The rate of PVC dehydrochlorination changes severely (it decreases as a result of aggregation of macromolecules and it increases due to excretion of a monomer) if the experiment is conducted in CHN.

It is evident that solutions of polymer mixtures represent rather complicated systems at concentrations of several percent. These systems are composed of associates of molecules and display specific chemical behavior. Polymer objects made by mixtures of polymers in a melt are more complicated because properties and behavior of mixtures are defined, not only by mutual compatibility and physicochemical affinity of two polymers but also by the way the polymers are combined.

When samples are farmed under conditions of melt flow, the structure is fixed by rapid cooling, due to high viscosity of polymer melts. The structure remains with further heating of the samples, in the absence of dynamic tensions, at least during the experimental conditions. This allows a series of mixture composites with various microstructures to be obtained. Viscosity anomalies during polymer flow were observed for tested PVC–PMMA and PVC–PS polymer pairs. Three regions may be separated (Fig. 5) as follows:

- 1. A one-phase system, in which the association degree of each component grows and leads to an increase of viscosity;
- 2. a metastable state, in which a large amount of microemulsions is separated in the specific volume and the viscosity decreases;
- 3. a two-phase system, in which the number of particles decreases due to their structuring and the viscosity increases.

The minimum in the viscosity logarithm corresponds to the formation of the maximum number of microemulsion particles. Figure 5 shows that position of the minimum depends on the nature of polymers composing the mixture. Definite changes in the rate of PVC dehydrochlorination in the mixtures correspond to those in viscous characteristics of PVC–PMMA and PVC–PS systems. This reflects changes in their structural–physical state. The change of PVC dehydrochlorination rate depends on the second polymer content. The

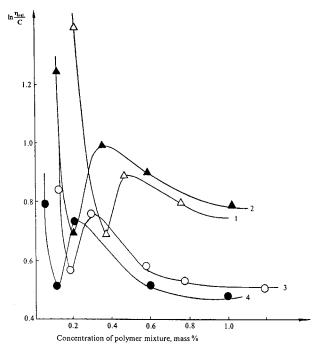


Figure 3 Dependency of the logarithm of reduced viscosity of solutions on the concentration of polymers in mixtures for the PVC–PS system: (1) and (3) 90 : 10 mass %; (2) and (4) 50 : 50 mas % in (1) and (2) CHN and (3) and (4) TCP at 423 K.

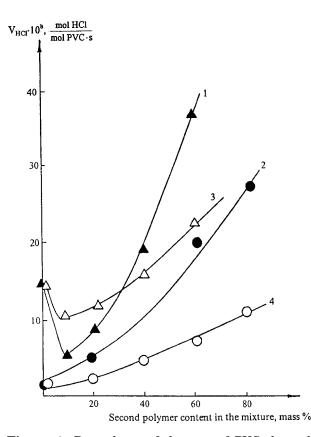


Figure 4 Dependency of the rate of PVC thermal dehydrochlorination in mixtures with (1) and (2) PMMA and (3) and (4) PS in (1) and (3) CHN and (2) and (4) TCP on the mixture composition at 423 K.

minimum of the degradation rate (Fig. 6, curves 1 and 2) corresponds to the minimum of $lg\eta$.

For mixtures of the same polymers obtained by mixing low-dispersed powders a different dependence of $V_{\rm HCl}$ on the mixture composition is observed. The rate of PVC dehydrochlorination decreases to a limit value and then increases with the second polymer content (Fig. 6, curves 3 and 4). Inhibition of PVC degradation correlates to the influence of PMMA and PS depolymerization products under the conditions of PVC degradation, in the absence of solvent. In this connection, the patterns observed are easily explained from the point of view of the change of the accessibility of polymer macromolecule chains for interaction with each other.

It is evident that at limited mutual solubility of selected polymer pairs, indicated by the flow curves, chemical interaction of PVC macromolecules with the products of depolymerization of the second polymers, methylmethacrylate and styrene, will be localized on the surface of the polymer contact that appears in the following regions (1) one-phase system and (2) formation of microemulsion. Efficiency of the influence, caused by the second polymer on PVC, grows in ranges (1) and (2). This leads to a more intensive decrease of the rate. At a higher content of the second polymer, when the structure of polymer mixture formed corresponds to range (3), the two-phase system, the condition of PVC macromolecule interaction with the products of PMMA and PS decomposition deteriorate due to deterioration of the polymer phase dispersion. As a consequence, the degree of PVC inhibition by the second polymer decreases, and the rate of PVC degradation increases.

Thus, the structural-physical state of polymer mixtures, dependent on the preparation method and affinity of polymers, generally defines the chemical behavior of polymers, the thermal stability of PVC, in particular. Forming polymer objects via changing structural-physical characteristics, one may obtain composites with the same composition but characterized by essentially different rate of PVC dehydrochlorination.

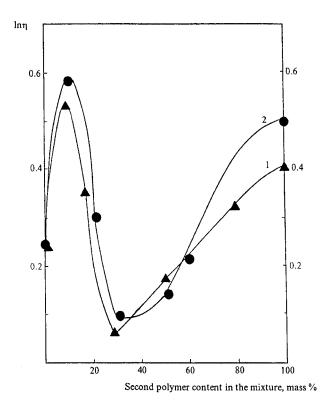


Figure 5 Dependency of the logarithm of melt viscosity on the composition of polymer mixture for (1) PVC–PMMA and (2) PVC–PS systems at 463 K; shift tension $\tau = 1.61$; PbSiO₄ content of three mass parts.

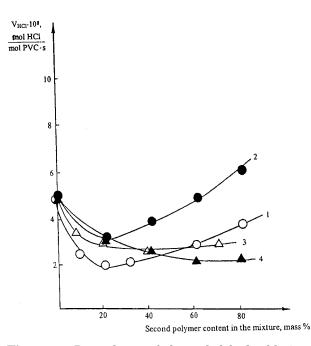


Figure 6 Dependency of thermal dehydrochlorination rate of PVC mixed with (1) PMMA and (2) PS for the mixtures obtained by combination in (1) and (2) melt and associated (3) and (4) coprecipitation in the presence of N_2 at 423 K.

EXPERIMENT

Mixtures of polymers were prepared by coprecipitation from solution and by combination in melt. Melts of polymer mixtures were prepared in viscosimeter MV-3M. To prevent degradation, a stabilizer was added (lead silicate). Melt flow through a capillary with pressure created by a weight allows measurement of viscosities of polymers and their mixtures. Solutions of polymer mixtures were prepared by mixing of equal-concentrated solution of pure polymers.

Solvents were purified by distillation. Study of viscosity of polymer solutions and their mixtures were performed according to standard technique with the help of Ubelode viscosimeter. Study of the rate of PVC dehydrochlorination was performed in a barbotage reactor according to the technique described in Minsker.⁶

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