

COMPATIBILITY OF BINARY SYSTEMS OF POLY(METHYL METHACRYLATE), POLY(VINYL CHLORIDE) AND POLY(VINYL ACETATE)

II. Time and temperature-dependences

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The influence of the thermal treatment on the stability in time of the dispersion degree of films containing binary polymer mixtures, poly(vinyl chloride)/poly(methyl methacrylate), poly(vinyl chloride)/poly(vinyl acetate) and poly(vinyl acetate)/poly(methyl methacrylate), was studied by thermogravimetry and optical microscopy with phase contrast. The dispersion degree depends particularly on the composition of the polymer mixture and can be improved by thermal treatment at temperatures above the glass temperatures of both homopolymers.

It seems that this thermal treatment yields exclusively metastable structures with a general tendency to phase separation in a short time after thermal treatment, the heterogeneity mixtures (as film) being more pronounced.

Noshay and Grath [1] have discussed the minimum conditions necessary to obtain compatibility in polymer/polymer mixtures: the identity of the solubility parameters and the occurrence of intermolecular interactions between the mixture components.

Polymer mixture incompatibility (phase separation) is a generally observed phenomenon, but due to the high viscosity of the systems, the phase separation processes are slow [2, 3].

The variation in time of some properties of copolymer mixtures was recently reported [4]. Some publications generalize the phase separation phenomenon with temperature increase for miscible polymer mixtures [5–10]. The higher stability of compatible systems after thermal treatment is presented as a particular case, the phase separation phenomenon being dependent on temperature, time, mixture, composition etc.

Taking into account the previous data, we have studied the time and temperature effects on the degree of dispersion of binary homopolymer mixtures containing poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc), using thermogravimetry. The results have been compared with microscopic observations on the polymer mixture films.

Experimental

The homopolymers used were characterized in a previous paper [11] which described the preparation of the mixtures and the experimental methods of investigations. It is stressed that IR spectroscopy did not reveal conclusive modifications. For the PVC/PVAc system the microscopic observations were analyzed from a semi-quantitative point of view, with evaluation of the dispersion degree of the system, calculated as the ratio of the dispersion phase surface to the total surface (S_d/S_t).

In order to study the time and temperature effects, films containing the components in the ratios 10/90, 30/70, 50/50, 60/40 and 80/20 were treated for an hour at 60°, 70° or 135° immediately after preparation (and drying). Thermally treated and untreated samples were kept at room temperature during the whole period of the investigation. The glass temperatures (T_g) of the components are $T_{g,PVC} = 82^\circ$, $T_{g,PMMA} = 176^\circ$ [12] and $T_{g,PVAc} = 28-31^\circ$ [13]; thermal treatment was carried out at higher temperatures than the T_g of the components only in the case of the PVC/PVAc system.

Results and discussion

Figures 1–3 present the variations in time of the apparent activation energies for the first step of thermoxidative degradation in air for the binary untreated homopolymer mixtures of PVC, PMMA and PVAc. The thermal behaviour of the freshly prepared PVC/PVAc system was reported by Vasile *et al.* [14].

No matter how the pseudocompatibility was achieved (a fact presented in the previous paper), the system tends towards the phase separation which corresponds to additivity. From a thermodynamic aspect the systems proceed from an initial state characterized by a metastable equilibrium towards a final stationary state [4] characterized by thermodynamic equilibrium.

The variation in time is determined by the initial deviation from additivity:

(a) Mixtures with pseudocompatibility due to the interaction of functional groups display a decrease in thermal properties with time with respect to additivity, characteristic of phase separation, the rate of modification being very slow; for example, the 10 PVC/90 PMMA mixture is not completely separated in phase even after a period of 12 months (Fig. 1).

(b) Pseudocompatible mixtures of "chain" or "fine dispersion" type display an increase in thermal properties with time. For the maximum compatibility degrees, the rate of modification is relatively high (for example, the 80 PVAc/20 PMMA mixture), and for other compositions the equilibrium is reached after four months (for example, the 60 PVAc/40 PMMA system (Fig. 2)).

(c) Incompatible mixtures initially separated into phases do not change in time, for example the 50 PVC/50 PMMA (Fig. 1), 30 PVAc/70 PMMA (Fig. 2) and 60 PVC/40 PVAc (Fig. 3) systems.

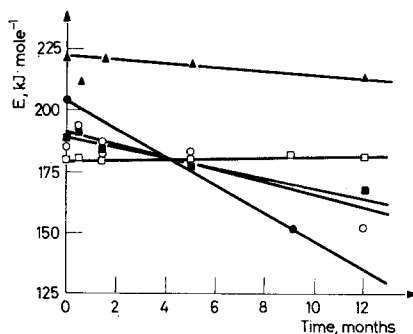


Fig. 1 Variation with time of apparent activation energy for PVC/PMMA system (untreated thermal films)

▲ 10% PVC, ○ 30% PVC, □ 50% PVC, ■ 60% PVC, ● 80% PVC

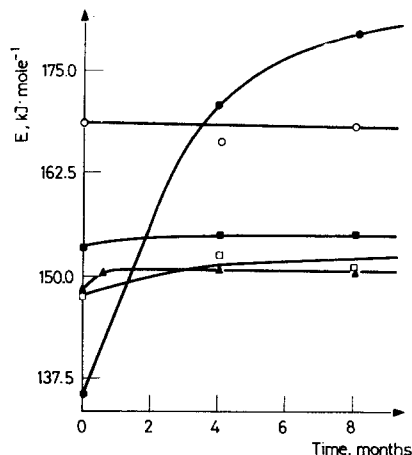


Fig. 2 Variation with time of apparent activation energy for PVAc/PMMA system (untreated thermal films)

▲ 10% PVAc, ○ 30% PVAc, □ 50% PVAc, ■ 60% PVAc, ● 80% PVAc

The same conclusions are obvious from Fig. 4, which presents the variation with time of the initial decomposition temperature (T_i) for untreated samples.

Optical microscopy with phase contrast reveals the morphological changes which take place under the influence of time and temperature. From Fig. 5 the system heterogenization can be seen at all three temperatures of thermal treatment (it should be stressed that for all these samples, the T_g values of the two components were not exceeded) (Fig. 5).

The heterogenization in time (S_d/S_t increase) of the thermally untreated PVC/PVAc system is shown in Fig. 6 for three mixture ratios.

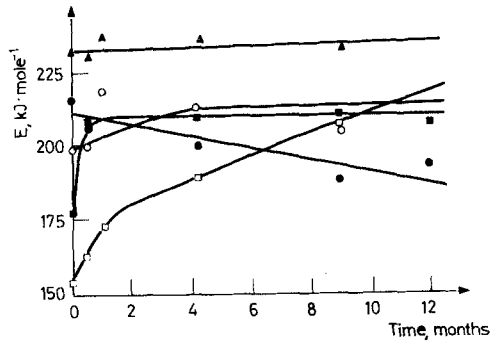


Fig. 3 Variation with time of apparent activation energy for PVC/PVAc system (untreated thermal films)

▲ 10% PVC, ○ 30% PVC, □ 50% PVC, ■ 60% PVC, ● 80% PVC

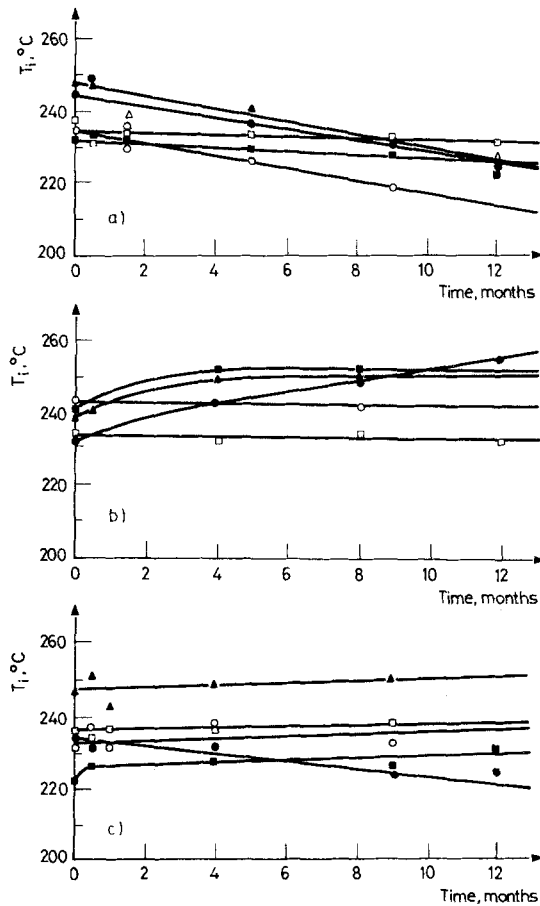


Fig. 4 Variation with time of initial decomposition temperature T_i for a) PVC/PMMA, b) PVAc/PMMA, ▲ 10% PVAc, ○ 30% PVAc, □ 50% PVAc, ■ 60% PVAc, ● 80% PVAc c) PVC/PVAc systems ▲ 10% PVC, ○ 30% PVC, □ 50% PVC, ■ 60% PVC, ● 80% PVC

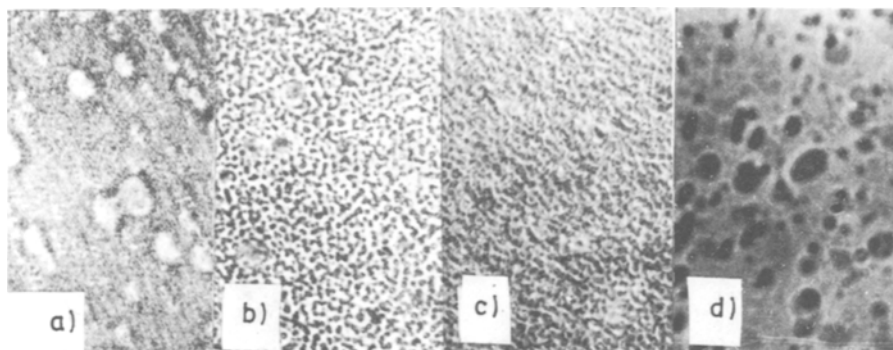


Fig. 5 Microscopic aspects of film of 10 PVC/90 PMMA mixture 5 months after preparation (magnification 600 x, phase contrast) a) initially, b) thermally untreated, c) thermally treated at 70°, d) thermally treated at 135°

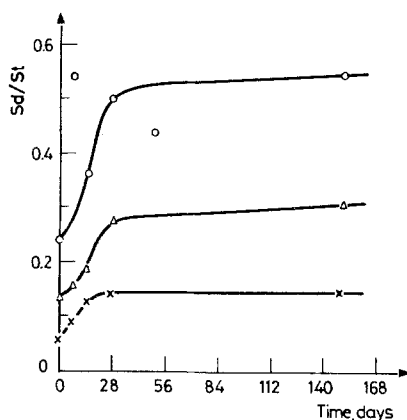


Fig. 6 Variation with time of dispersion degree for PVC/PVAc system thermally untreated, for the following mixtures: (x) 10/90, (Δ) 30/70, (○) 50/50

Figure 7 presents the microscopic modification of the 50 PVC/50 PVAc mixture maintained for four months at room temperature.

The homogenization of the 30 PVC/70 PVAc system immediately after thermal treatment at 135° is shown in Fig. 8. The semiquantitative results are shown in Fig. 9.

The thermal treatment at 135° increases the homogeneity of the systems within 7–14 days, after which the homogeneity gradually returns to the initial state. In comparison with other systems, the 10 PVC/90 PMMA mixture, initially more homogeneous, exhibits a higher stability in time. Similar effects have been observed by other authors: a heterogeneous film can be converted into a homogeneous blend by heating at an appropriate temperature [15].

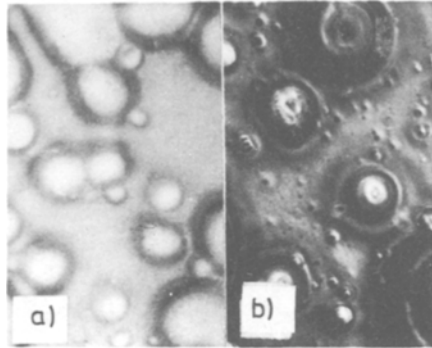


Fig. 7 Microscopic aspects of film of 50 PVC/50 PVAc mixture, thermally untreated (magnification 600 x, phase contrast) a) immediately, b) 4 months after preparation

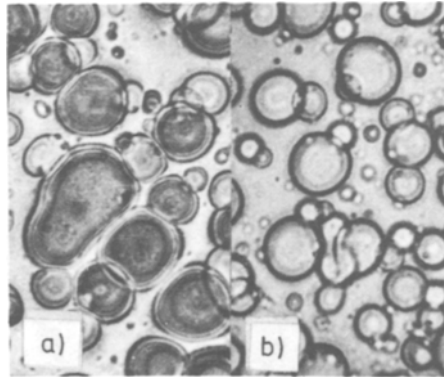


Fig. 8 Microscopic aspects of film of 30 PVC/70 PVAc mixture (magnification 600 x, phase contrast) a) before, b) immediately after thermal treatment at 135°

The results may be interpreted in terms of the conception of Lipatov [16] concerning the role of the transition layer at the separation surface (of variable size) between the phases, that confers different properties at the interphase from those in the bulk.

According to the magnitude of the dispersion degree and the manner in which adhesion is achieved between the phases in the transition layer at the limit of phase separation, the time and temperature exert different influences on the pseudocompatible systems.

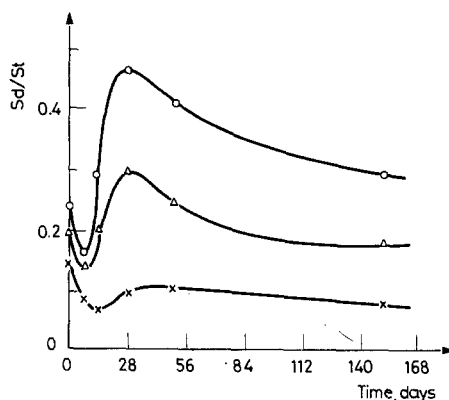


Fig. 9 Variation with time of dispersion degree for PVC/PVAc system, thermally treated at 135°, for the following mixtures: (x) 10/90, (Δ) 30/70, (○) 50/50

For the 10 PVC/90 PMMA maximum compatibility degree, the interaction between the functional groups of the two components at the phase separation boundary probably favours the formation of a system particularly stable in time.

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Zusammenfassung — Der Einfluss der thermischen Behandlung auf den zeitlichen Verlauf der Stabilität des Dispersionsgrades von binäre polymere Gemische (Polyvinylchlorid/Polymethylmethacrylat, Polyvinylchlorid/Polyvinylacetat und Polyvinylacetat/Polymethylmethacrylat) enthaltenden Filmen wurde thermogravimetrisch und mittels optischer Phasenkontrastmikroskopie

untersucht. Der Dispersionsgrad hängt insbesondere von der Zusammensetzung des Polymergemisches ab und kann durch eine thermische Behandlung oberhalb der Glastemperatur beider Homopolymeren verbessert werden. Diese thermische Behandlung scheint ausschliesslich metastabile, im Vergleich zu den ursprünglichen Polymergemischen (als Film) weniger heterogene Strukturen mit einer allgemeinen Neigung zur Phasentrennung kurz nach der thermischen Behandlung zu ergeben.

Резюме — С помощью термогравиметрии и оптической микроскопии с фазовой контрастностью было изучено влияние термической обработки на устойчивость во времени степени дисперсности пленок двойных полимерных смесей поливинилхлорид — полиметилметакрилат, поливинилхлорид — поливинилацетат и поливинилацетат — полиметилметакрилат. Степень дисперсности значительно зависит от состава полимерной смеси и может быть улучшена термической обработкой при температурах, выше температуры стеклообразования обоих гомополимеров. Очевидно, что такая термическая обработка дает исключительно метастабильные структуры, способные к фазовому разделению за короткое время после термической обработки. Вследствии этого гетерогенность исходных полимерных смесей (в виде пленок) является более выраженной.