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

I. Thermogravimetric, infrared spectroscopic and microscopic studies

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The compatibility of binary polymer mixtures of poly(vinyl acetate) and poly(vinyl chloride) or poly(methyl methacrylate) was studied by thermogravimetry, infrared spectroscopy and phase contrast microscopy.

The poly(vinyl chloride)/(poly(methyl methacrylate) system is characterized by pseudocompatibility, due to the interaction of functional groups, with two maximum compatibility ratios, at 10 PVC/90 PMMA and 80 PVC/20 PMMA. For the poly(vinyl acetate)/(poly(methyl methacrylate) system evidence was found of "chain" pseudocompatibility for the composition range 40–90 wt% PVAc, with a maximum degree of compatibility at 80 PVAc/20 PMMA.

The study of the properties of binary polymer mixtures containing poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) or poly(vinyl acetate) (PVAc) has been the subject of numerous reports (PVC/PMMA [1–6] and PVAc/PMMA [7–13].

The results obtained using different methods of investigations have provided evidence of a limited compatibility, depending on the way in which the mixture was prepared and on the polymer characteristics.

The purpose of the present paper was to study the behaviour of these systems by TG and IR methods. Since the properties of the polymer systems depend on the mixture morphology [14], the results were complemented with microscopic observations, with a view to establishing the compatibility ratios.

Experimental

Polymers

The following samples were used:

PVC suspension from Schell, The Netherlands, with 55.62% chlorine content.

PMMA from Research Institute for Organic and By-Products, Medias, Roumania. The unsaturation degree at the ends is expressed by the ratios $A_{840}/A_{1720} = 0.116$, and $A_{985}/A_{1720} = 0.150$, where A_{840} and A_{985} are the band absorbances corresponding to unsaturation and A_{1720} is the absorbance for the internal standard. The structures were also established by NMR measurements: 11.0% isotactic, 38.5% heterotactic and 50.5% syndiotactic.

PVAc from BDH, England, with 100% acetate groups.

The gravimetric average molecular weight was determined by viscometry using the equations:

at 25° for PVC: $(\eta) = 1.1 \times 10^{-6} M_w$ (ml/g) in cyclohexanone [15];

at 30° for PMMA: $(\eta) = 5.2 \times 10^{-5} M_w^{0.76}$ (dl/g) in benzene [16];

at 25° for PVAc: $(\eta) = 1.71 \times 10^{-4} M_w^{0.65}$ (dl/g) in benzene [17].

Preparation of polymer mixtures

The samples of mixed polymers were prepared by solvent evaporation from a common solution obtained by dissolving varying amounts of polymers in tetrahydrofuran (THF) at 10% wt concentration. The solvent was purified by refluxing over iron(II) sulphate in order to remove peroxides, and further distilled under nitrogen between 64.5 and 65°.

PMMA was mixed with PVC or PVAc in ratios of 0–100 wt%. The solutions were stirred for 15–20 min at 60–70° and kept for 24 h to stabilize; films of constant thickness were then obtained by solvent evaporation. The resulting films were dried for 48 h in a vacuum oven at 50°.

Methods

Thermogravimetry

Using constant working conditions, the thermal behaviour of the polymer mixtures (as films) in air was studied with a derivatograph of Paulik–Paulik–Erdey type, on powdered polymer samples with a granulation of 0.1–0.5 mm, admixed with Al_2O_3 (20% sample) freshly calcined at 1100°. The heating rate was maintained constant at 12 degree/min, for all the homopolymers and their mixtures, and in all cases the sample weight was 20 mg.

The apparent activation energies (E_a) of the first degradation step were estimated with the Coats–Redfern method [18], using a programme written in JAL language for a JEC-5 computer.

These values and those of the average gravimetric molecular weights are listed in Table 1.

Infrared spectroscopy

Infrared spectra of constant thickness film samples were recorded between 400 and 800 cm^{-1} using a 557 Perkin–Elmer spectrophotometer.

Table 1 Gravimetric average molecular weights and apparent activation energies of the first degradation process in air for PVC, PVAc and PMMA

Polymers	M_w *	Temperature range °C	E_a, kJ mole^{-1} **
PVC	96,800	233–372	171.76
PMMA	108,000	243–434	126.19
PVAc	360,600	274–397	255.42

* M_w determined viscometrically
** E_a estimated by the Coats–Redfern method [19]

To ensure the plane surface of the films, they were placed in a specially constructed device.

Optical microscopy in phase contrast

The microscopic examination was carried out on monomolecular layer films obtained by solvent evaporation from the common solution using the "frotir" technique. An M-C-1 optical microscope (IOR, Bucharest), equipped with phase contrast and with a magnification of 600 x, was used for microscopic studies. The photographs were taken on X-ray film, the exposure time being 12 s.

Results and discussion

The PVC/PMMA system

Figure 1 presents the variation in the apparent ectivation energy *vs.* composition under constant working conditions for the PVC/PMMA mixture, subjected to thermal degradation immediately after preparation.

The system exhibits two thermal stability maxima, for the mixture ratios 10 PVC/90 PMMA and 80 PVC/20 PMMA; these correspond to an increase of activation energy $\Delta E = +92.84$ and $\Delta E = +49.03$ kJ mole^{-1}, respectively. These values are similar to those found in the study of other polymer mixtures [19, 20] displaying pseudocompatibility due to the interaction of functional groups.

For the ratio mixture 50 PVC/50 PMMA, the system is incompatible.

These results were compared with the microscopic observations on the polymer mixture films.

Figure 2 presents the microscopic images of the films immediately after preparation, for the two maximum compatibility ratios, 10 PVC/90 PMMA and 80 PVC/20 PMMA (Fig. 2*a* and 2*c*), and for the incompatible mixture 50 PVC/50 PMMA (Fig. 2*b*). The mixtures with positive deviations of the apparent activation energies (Fig. 1) at the same time display a high degree of dispersion of the components. As concerns these microscopic distributions, if the films of the mixtures containing the components in

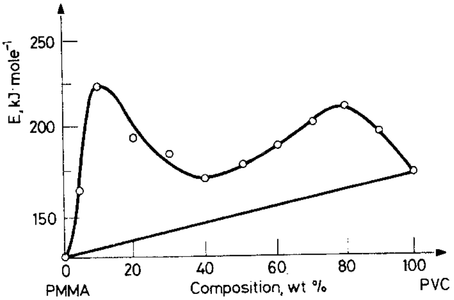

Fig. 1 Dependence of apparent activation energy of first degradation process in air under constant working conditions on PVC/PMMA mixture composition

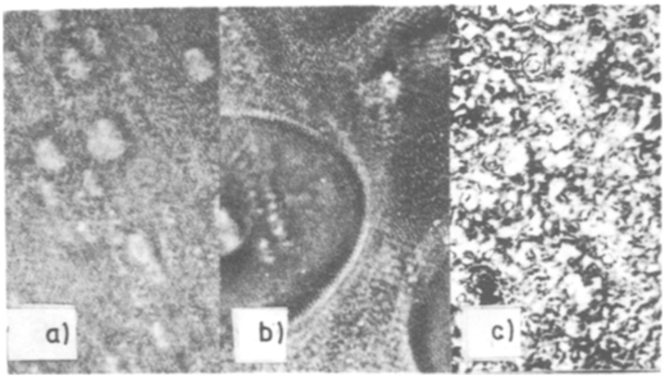

Fig. 2 Microscopic pictures of films immediately after preparation for PVC/PMMA system (magnification 600 x, phase contrast): a) 10/90; b) 50/50; c) 80/20 PVC/PMMA

1 : 1 ratio, are generally opaque immediately after preparation, then the films corresponding to the extreme mixture ratios are clear and transparent.

The absorbances due to the C—C1 bonding were measured by IR sepctroscopy (ν C—C1, 610 and 635 cm^{-1}).

The validity of the Lambert—Beer law for different PVC film thicknesses was previously checked.

Study of the variations in intensity of the two bands *vs.* composition was carried out by means of reduced absorbances (corresponding to 0.001 mm thick film).

Figure 3 shows a well marked minimum for the system rich in PMMA, which suggests the presence of some conformation favourable for intermolecular interactions between the functional groups of the two polymers, a fact which emphasizes the conclusions of the thermogravimetric method.

Similar results have been obtained by other authors [21, 22].

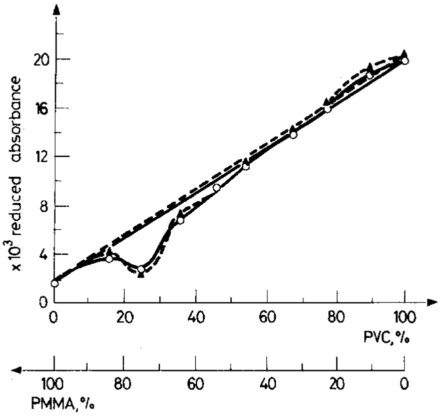

Fig. 3 Variation of reduced absorbance *vs.* PVC/PMMA mixture composition for (○) 610 and (▲) 635 cm^{-1} bands

In the light of the results, the PVC/PMMA binary system is characterized by pseudocompatibility due to functional group interaction, with two maximum compatibility ratios: 10 PVC/90 PMMA and 80 PVC/20 PMMA.

Taking into account the high syndiotactic chain conformation content of the PMMA utilized, there could be intermolecular interactions (dipole—dipole or hydrogen-bond-like) between the ester groups of PMMA (which are considered to be proton-accepting groups) and the α-hydrogen atoms of PVC, leading to a system with a high degree of compatibility. These results are in good agreement with the conclusions of Schurer *et al.* [22] who detected only one T_g for PVC/PMMA systems in the range 0—60 wt% s-PMMA.

The PVAc/PMMA system

The thermogravimetric results for the PVAc/PMMA system are shown in Fig. 4.

The apparent activation energy values for the system rich in PMMA 0—40 wt% lie along the line obtained if there is no interaction between the components, the systems being incompatible.

In the 40—90 wt% range of composition the system exhibits negative deviations from additivity; this is most evident for the PVAc/20 PMMA mixture ratio, for which $\Delta E = -91.12$ kJ mole^{-1}, suggesting "chain" pseudocompatibility.

In our case, the use of THF as a common solvent (whose solubility parameter is $\delta = 19.48 \times 10^{+3}$ $(J/m^3)^{1/2}$ compared with $\delta = 19.62 \times 10^{+3}$ $(J/m^3)^{1/2}$ for PVAc and $\delta = 19.50 \times 10^{+3}$ $(J/m^3)^{1/2}$ for PMMA [23]) probably favoured some interpenetration of the macromolecular chains.

For the same system Schneier [24] theoretically forecasts the compatibility of the mixtures.

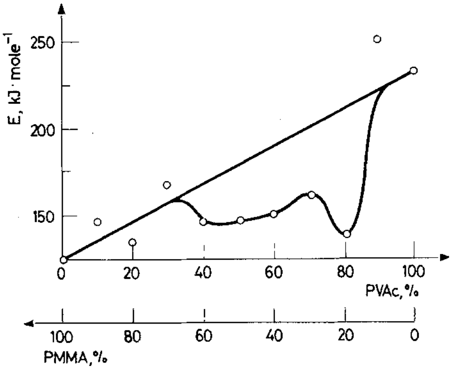

Fig. 4 Dependence of apparent activation energy of first degradation process in air under constant working conditions on PVAc/PMMA mixture composition

Microscopic observations could not be carried out at a magnification of 600 x, for the PVAc/PMMA system, though the difference in refraction indices was about 0.0235 [25].

The infrared spectra could not be obtained because the two components of the mixtures have characteristic absorption bands at the same wavenumbers.

Conclusions

1. Agreeing results were obtained for the PVC/PMMA system by thermogravimetry, IR spectroscopy and optical microscopy in phase contrast.

The system is characterized by pseudocompatibility due to the interaction of functional groups, with two maximum compatibility degrees, at 10 PVC/90 PMMA and 80 PVC/20 PMMA, for which there is a high degree of dispersion of the components. For the 1 : 1 composition, the system is incompatible.

2. The PVAc/PMMA system is characterized by chain pseudocompatibility for the composition range 40–90 wt% PVAc, with a maximum degree of compatibility for 80 PVAc/20 PMMA, at which interpenetration of the two component chains takes place.

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Zusammenfassung – Die Kompatibilität binärer polymerer Gemische von Polymethylmethacrylat mit Polyvinylchlorid oder Polyvinylacetat wurde thermogravimetrisch, infrarotspektroskopisch und phasenkontrastmikroskopisch untersucht. Das System Polyvinylchlorid/Polymethylmethacrylat ist durch eine auf die Wechselwirkung zwischen funktionellen Gruppen zurückzuführende Pseudokompatibilität mit zwei maximalen Kompatibilitätsverhältnissen bei 10 PVC/90 PMMA und 80 PVC/20 PMMA gekennzeichnet. Für das System Polyvinylacetat/Polymethylmethacrylat wurden Beweise für eine "Ketten"-Pseudokompatibilität mit einem maximalen Kompatibilitätsgrad bei 80 PVAc/20 PMMA im Zusammensetzungsbereich von 40–90 Gew.-% PVAc gefunden.

Резюме – Совместимость двойных полимерных смесей полиметилметакрилата (ПММА) и поливинилхлорида (ПВХ) или поливинилацетата (ПВА) была изучена с помощью термогравиметрии, ИК-спектроскопии и фазовой контрастной микроскопии. Система поливинилхлорид – полиметилметакрилат характеризуется псевдосовместимостью. обусловленной взаимодействием функциональных групп полимеров, при двух максимальных соотношениях: 10 ПВХ:90 ПММА и 80 ПВХ:20 ПММА. Для системы поливинилацетат – полиметилметакрилат было найдено доказательство "цепной" псевдосовместимости для состава 40–90 весовых % с максимальной степенью совместимости при 80 ПВА:20 ПММА.