Journal of Thermal Analysis, Vol. 26 (1983) 23–30

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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(Received June 4, 1982)

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.