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Compatibility

The Compatibility in the Poly(Methyl-α-Cyanoacrylate) /Poly(Allyl-α-Cyanoacrylate) System

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Summary

Mixtures of poly(methyl-α-cyanoacrylate), PMCA, and poly(allyl-α-cyanoacrylate), PACA, were precipitated or casted from solutions and their compatibility was estimated by optical microscopy and thermogravimetry. The paper establishes the range of optimum compatibility ratios and discusses the thermal behaviour of the obtained PMCA/PACA blends and of copolymers of similar composition.

Experimental

Materials. PMCA and PACA were synthsized by the anionic polymerization of corresponding monomers (1). Solutions in dimethyl formamide, DMF, or nitromethane, NM, good solvents for both polymers, were prepared by mixing at room temperature exact volumes of previously made solutions of PMCA and PACA in DMF or NM so that the individual polymers were taken in the ratio (w/w) 90/10, 75/25, 50/50, 25/75 and 10/90, respectively, and the total polymer concentration was always 8%. Solid polymer mixtures were obtained by precipitation in methanol containing NaCl aqueous solutions (the precipitate was thouroughly washed with water and methanol and dried for 24 hr at 50°) or by deposing thin layers of polymer mixture solution on glass lamellae for optical microscopy examinations (the lamellae were dried at 70° for 24 hr, the remaining solvent was then extracted with ethyl ether and the drying process was repeated).

Investigation methods. The microscopic examination of films was made with an IOR MC-1 optical microscop (Bucharest), in phase contrast (12 sec), magnification 600. The thermal behaviour of all samples was folowed using a Paulik-Paulik-Erdey (MOM Budapest) derivatograph with a heating rate of 10°/min. The activation energy was determined according to Levi and Reich (2,3) and represents the activation energy of the first thermal decomposition step extrapolated to zero transformation degree, $\alpha=0$, where $\alpha = w_t/w_\infty$ (w_t stands for the weight loss at the time t and w_∞ is the weight loss at the end of the process).

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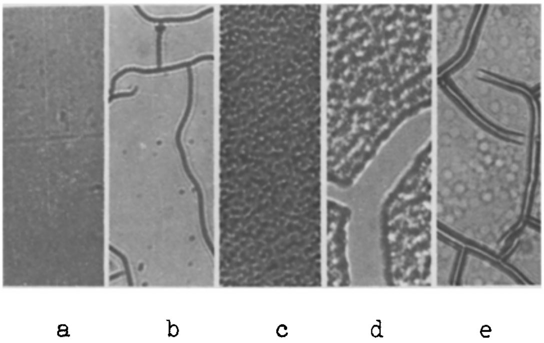

Fig. 1. Microscopic aspects of PMCA/PACA blends casted from DMF (a and b) and NM (c and d) solutions. Blend composition, w/w: a, 10/90
b, 50/50
c, 10/90
d, 50/50;
e represents a 50/50 copolymer casted from DMF. Magnification, x 600.

Results and Discussion

The microscopic aspects of films (Fig. 1) render evident the thermodynamic incompatibility of PMCA/PACA blends. It can be seen that the nature of the solvent used for casting has an influence on the film aspect, i.e. the films obtained from DMF are transparent and continuous (Fig. 1a) while the films casted from NM solutions are less homogeneous (Fig. 1c). In both cases the homogeneity increases for extreme blending ratios, the best results being obtained for PACA rich samples. For a mean composition the films are cracked, irrespective of the casting solvent (Figs. 1b and 1d). Similar observations were made in the case of copolymers but as expected they are more homogeneous than the corresponding blends (Fig. 1e).

The incompatibility of PMCA/PACA blends results also from the shape of their DTG curves (Fig. 2) which roughly are sums of respective curves of the two components. However, the fact that the peaks of DTA curves of samples precipitated from DMF are larger and less evidenced (Fig. 2a) indicates

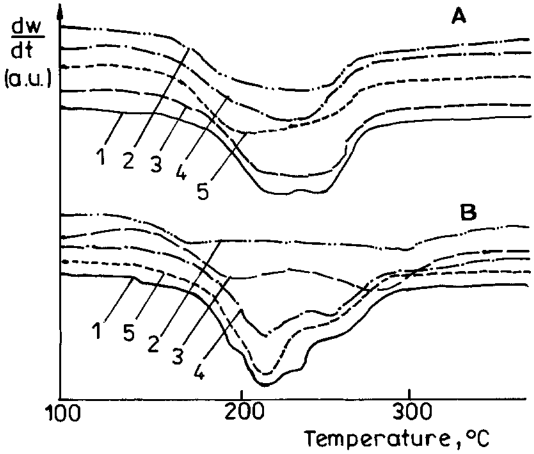

Fig. 2. DTG curves of PMCA/PACA blens and homopolymers precipitated from DMF (A) and NM (B):
1- PMCA
2- PACA
3- 50/50 blend
4- 75/25 blend
5- 90/10 blend.

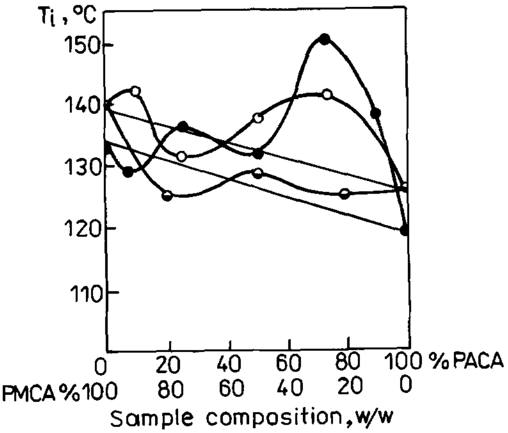

Fig. 3. The dependence of the initial decomposition temperature on composition

(o) blends precipitated from DMF
(●) blends precipitated from NM
(◉) copolymers

again that the blends obtained from DMF are more homogeneous.

From the dependence between the composition and the initial decomposition temperature, T_i (Fig. 3), or the maximum decomposition temperature, T_m, i.e. the temperature at which the decomposition rate is maximum (Fig. 4), one can observe that PACA rich blends decompose at temperatures higher than that predicted by the additivity rule (straight line). The deviations are more pronounced for samples precipitated from DMF indicating that these blends have a higher degree of compatibility. The negative deviations observed in the case of copolymers (Fig. 3) point to a "chain" type compatibility (4).

Different results were also obtained from the variation of weight loss with sample composition (Fig. 5): as compared with the weight loss deduced from additivity, the weight loss at the same composition is lower for blends and higher for copolymers. These differences, especially for PACA rich blends, may be explained through the formation crosslinks between allylic groups (5) which make more difficult the "unzipping" of chains in the first thermal decomposition step.

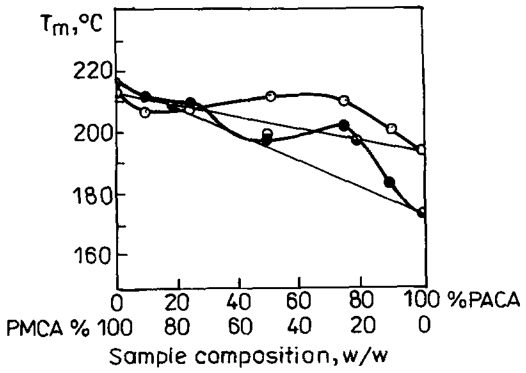

Fig. 4. The dependence of the maximum decomposition temperature on composition

(o) blends precipitated from DMF
(●) blends precipitated from NM
(◉) copolymers

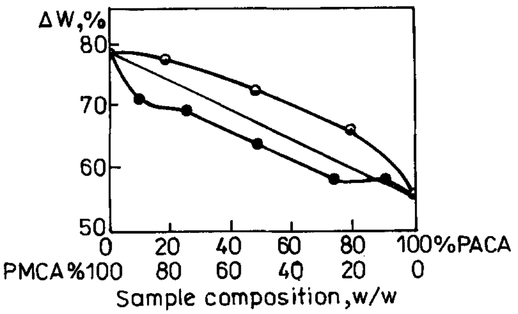

Fig. 5. The dependence of weight loss on composition:
(●) PMCA/PACA blends
(⊙) copolymers

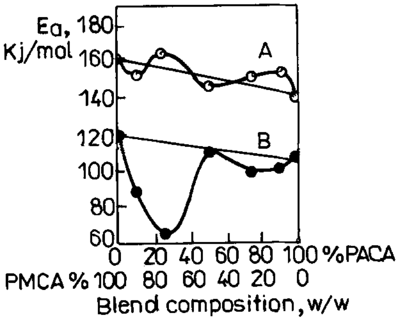

Fig. 6. The change of activation energy of thermal decomposition extrapolated to $\alpha=0$ with composition for PMCA/PACA blends precipitated from DMF:
A- first stage, $\alpha=0.0$ - 0.3
B- second stage, $\alpha=0.3$ - 0.6

The compatibility diagrams activation energy (extrapolated to $\alpha=0$) versus composition (Fig. 6) confirm the increase of thermal stability of PACA rich blends. For low thermal transformation degrees, $\alpha=0$ - 0.3 (curve A), the activation energy is higher or close to that given by additivity but it is always lower than this for advanced decomposition steps, $\alpha=0.3$ - 0.6 (curve B).

Conclusions

The poly(methyl-α-cyanoacrylate)/poly(allyl-α-cyanoacrylate) blends are not thermodynamically compatible.

The homogeneity of samples increases for extreme blending ratios.

The PACA rich blends are most thermally stable.

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