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Phase Equilibria of PS with PMMA and Poly(co-methyl methacrylate and styrene)mers

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Introduction

The available literature data on the phase equilibrium in the systems PS - PMMA and PS - (MMA-S) copolymers of various compositions are ambiguous. The most contradictory results were obtained for mixtures formed from solutions [1-3]. This fact can result, first, from the low compatibility of the polymers, which borders on the sensitivity of the testing methods used, and second, from specific interactions between the components.

In the present work, the polymer compatibility was studied using an optical interferometer [4]. The sensitivity of this method is limited by the translational mobility of molecules, $\sim 10^{-9}$ cm^2/s, so the measurements were carried out at high temperatures close to the destruction temperatures of PMMA and its copolymers. The specific feature of optical interferometry is that the studies are carried out in thin layer; this enables visual separation and estimation of the effect of the destruction products and the destruction process on the compatibility of polymers. Therefore, the purpose of this work was to study the effect of the thermal destruction products on the interference of the destructed polymer and on the diffusion transition zone of polymers in order to obtain the most complete data on the compatibility of the polymers over a broad composition range.

Experimental

Mixtures of PS (MM 2,350) with PMMA (MM 89,000) or styrene-MMA copolymers in the ratios 17:83 (MM 202,000), 27:73 (MM 228,000), 50:50 (MM 11,000), 70:30 (MM 79,000), 86:14 (MM 69,000) and 90.8:9.2 (MM 58,000) were used as the objects of this study. The polymers were synthesized by radical polymerization in toluene in the presence of azoisobutyronitrileisobutyric acid as the initiator [1]. Toluene was removed as follows: the

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[1] The polymers were synthesized in the A.D.Litmanovich laboratory of the Institute of petrochemical synthesis of the Russian Academy of Sciences.

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polymer was precipitated in methanol; the precipitate was filtered off and dissolved in benzene; the latter was removed by liophilic drying.

Results and Discussion

The plotting of phase state diagrams for polymer mixtures near and above the destruction temperature of one of the polymers is an actual problem [5,6].

The formation of destruction products accompanied by an abrupt change in the optical density and the thermal effects in the system makes it impossible to separate the effects caused by the phase changes in the system from those caused by destruction and makes it impossible to use the most popular optical and calorimetric methods for the plotting of phase state diagrams. Therefore, researchers are forced to limit the studies to temperatures up to the polymer destruction temperature when plotting the phase state diagrams, although some polymers, such as PMMA, maintain their MM and other block characteristics unchanged at small degrees of destruction [5-7]. A technique for plotting the phase diagrams of polymer mixtures in the destruction region of one of the polymers has been reported elsewhere [8].

The interference observations of the concentration profiles of binary mixtures of PS with PMMA and styrene-MMA copolymers can be classified in three groups:

1) In the temperature range below the destruction temperature of the polymer (T_{des}^*) determined experimentally, *the observations are characterized by full reversibility of the interference profiles upon changing the mixture tempeerature;*

2) Near the destruction temperature of the polymer (T ? T_{des}^*), *the inclusions of the destruction products do not change the interference profiles, and reversibility of the concentration profile upon decreasing the temperature is also observed;* let us call this region «the induction zone»;

3) 3) at $T > T_{des}$, *the primary distinction of these observations from the previous ones is that the course of the interference bands is disrupted and the concentration profile changes due to the dissolution of the decomposition products in the polymer matrix and due to the change in the MM of the destructed polymer;* this region is characterized by complete irreversibility of the data.

Fig. 1 presents the experimental phase state diagrams for the systems PS (MM 2350) - (S-MMA) copolymers.

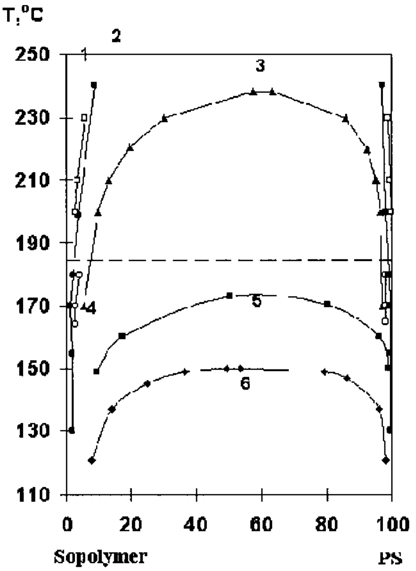


Fig. 1. Phase state diagram for the mixtures of PS (M=2350) with PMMA (1); and MMA styrene copolymers in the ratios: 17:73 (2); 27:73 (4); 50:50 (3); 70:30 (5); 86:14 (6).

The dashed line separates the region of the phase diagram points obtained below T_{des}^* of PMMA from the points obtained above T_{des}^*. One can see that the phase diagrams are characterized by HCST. The binodal curves are asymmetric; the critical points of systems whose positions were determined from the intersection of the diameter with the binodal dome are shifted towards dilute solutions of copolymers in PS. Using the «Termo» software, the phase diagram fragments were completed and the interaction constants of the mixed polymers were determined (Fig. 2).

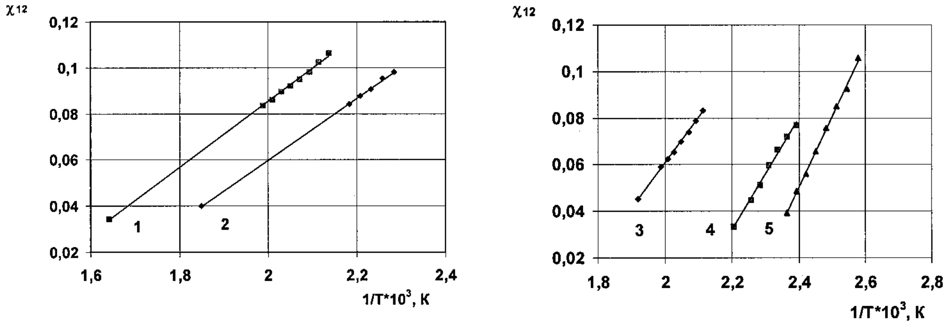
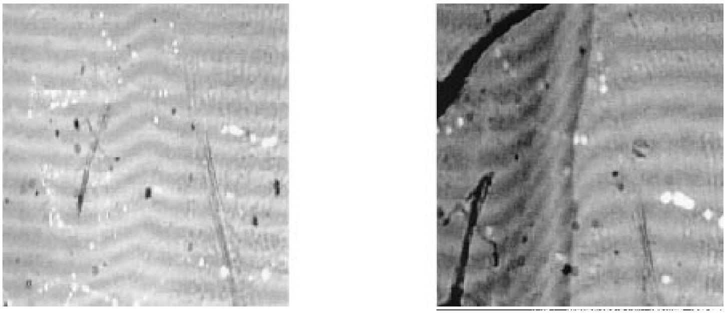


Fig. 2. Influence of temperature on the parameters of interaction of the (S-MMA) copolymers with PS (2350). Styrene-MMA copolymers in the ratios: 1 - 9,2:MMA ; 2 - 17:MMA; 3 - 50:MMA; 4 - 70:MMA; 5 - 86:MMA.



a

b

Fig. 3. Diffusion zone compression in mixtures of PS (M=2350) with a styrene-MMA copolymer in the ratio 86:14 (a). Formation of two interfaces in the mixture: PS (M=2350 with a styrene-MMA copolymer in the ratio 86:14 (b).

A study of the mixture of PS with the MMA:S=14:86 copolymer showed an anomalous increase in the optical density of the transition zone (Fig. 3a) at PS content about 32%. After the composition is cooled to room temperature, the formation of two interfaces is observed (Fig. 3b). Probably, specific interactions occur in this composition range due to enhanced solubility of PS in the microphases of styrene fragments whose molecular mass is close to that of low-molecular PS. A comparison of the IR spectra of pure PS and a MMA-S(86) copolymer with the spectrum obtained for their mixture containing 35% PS showed (Fig. 4) that the observed compression of the diffusion zone is caused by the conformation changes of the polystyrene fragments, *i.e.*, a decrease in the planar deformation vibrations, mostly in the aliphatic part and to a smaller extent in the benzene ring.

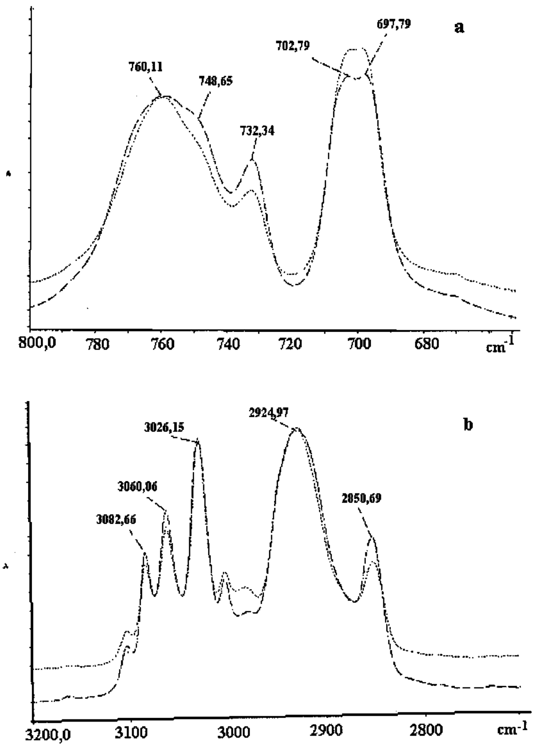


Fig. 4. FT-IR-spectra of MMA-14 copolymer (···· ····) and their mixture with 35% PS (— — –).

These changes in the spectrum of the polystyrene fragments were assigned [7,8] to the transition of iso-tactic polystyrene from the quenched condition to the annealed condition. Thus, the increase in the system specific density in a narrow concentration range results from increased ordering of the styrene fragments in the copolymer if an optimum amount of PS is present, *i.e.*, an associative structure is formed. Therefore, the phase diagram should contain a region corresponding to the existence of such associates.

As the temperature is decreased, the copolymer with ordered styrene fragments behaves as an independent compound due to the lower molecular mobility; this results in the formation of two interfaces: Copolymer - Copolymer «ordered with polystyrene» and Copolymer «ordered with polystyrene» - PS.

Thus, the experimental data obtained suggest the existence of specific interactions between PS and MMA-styrene copolymers. These interactions can be the reason of the discrepancy of the phase diagrams obtained by different authors. In addition, the developed method for plotting the phase equilibrium diagrams in the vicinity of the destruction temperature of one of the components has made it possible to obtain data on the phase equilibrium in this region for the first time.

References

1. J.L.White, R.D.Patel /J.Appl.Polym.Sci., (1975) v.19, №6, p.1775.
2. A.E.Chalykh, N.I.Prokopov, V.K.Gerasimov, I.A.Grichkova /Vysokomol. Soedin. A. (1996) v.38, №11, p.1888.
3. A.J.Malkin, A.E.Chalykh "Diffusion and viscosity. Research techniques". //M: "Chemistry", 1979, 300p.
4. A.E.Chalykh “Diffusion in polymeric systems". //M: "Chemistry", 1987, 312p.
5. “Thermal methods of analysis". //Second Edition W.W.Wendlandt, 1974, by John Wiley & Sons. 528p.
6. S.Madorskii “Thermal decomposition of organic polymers”. //M: “World”, 1967, 328p.
7. I.A.Vishnevskaya, A.E.Chalykh, L.I.Garova, «Investigation of polymer destruction with the help of optical interferometer». In: "Structure and molecular dynamics of polymeric systems". Joshkar-Ola, 1998, part 1, p.4.
8. I.A.Vishnevskaya, A.E.Chalykh, L.I.Garova, Vysokomol. Soedin. A. 2000. In print.