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### A Study of the Compatibilizing Effect of High-speed Stirring on the Poly-(Ethylene Oxide)/Polyacrylamide System

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## **A Study of the Compatibilizing Effect of High-Speed Stirring on the Poly-(Ethylene Oxide)/Polyacrylamide System**

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### **ABSTRACT**

The compatibility of the poly(ethylene oxide) (PEO)/polyacrylamide (PAM) system and the compatibilizing effect of PEO-PAM block copolymer formed during high-speed stirring of the PEO/PAM mixture in aqueous solution were studied. Thermodynamics predicts that PEO/PAM is incompatible; contrast microscopy, TEM, SAXS, and stress-strain behavior testing verify this. It is found that PEO-PAM block copolymer is an effective compatibilizer, which decreases the dimension of the domains, reduces the heterogeneity of the system, increases the thickness of the boundary layer, and improves the mechanical properties of the polyblend.

### **INTRODUCTION**

Polymer-polymer compatibility is a question of considerable interest in polymer science. As viewed from thermodynamics, polymers are rarely compatible because of their high molecular weights. How to find an effective compatibilizer for an incompatible system is the key to preparation of new multicomponent materials with polyfunction-

ality. The compatibility of a polymer blend may be enhanced by a block or graft copolymer having segments of structure or solubility parameter similar to the polymers being mixed [1-3].

Poly(ethylene oxide) (PEO) and polyacrylamide (PAM) are two water-soluble polymers widely used in gas and oil field exploitation. PEO-PAM block copolymer can be produced in aqueous solution of PEO/PAM during high-speed stirring [4]. In this paper the compatibilizing effect of PEO-PAM block copolymer upon a thermodynamically incompatible PEO/PAM system has been studied by means of contrast microscopy, transmission electron microscopy, small-angle x-ray scattering, and stress-strain determination.

## EXPERIMENTAL

### Materials

One percent aqueous solutions of PEO ( $\bar{M}_\eta = 5.81 \times 10^5$ ) and of PAM ( $\bar{M}_\eta = 3.60 \times 10^5$ ) were prepared.

Sample A: A mixture of PEO and PAM solutions (1:1, v/v).

Sample B: PEO and PAM solutions were added to the high-speed stirring reactor (Fig. 1), stirred for 10 min at 20 000 rpm and  $20 \pm 3^\circ\text{C}$ , then mixed (1:1, v/v). The molecular weights of the samples after stirring were: PEO,  $\bar{M}_\eta = 2.45 \times 10^5$ ; PAM,  $\bar{M}_\eta = 9.68 \times 10^5$ .

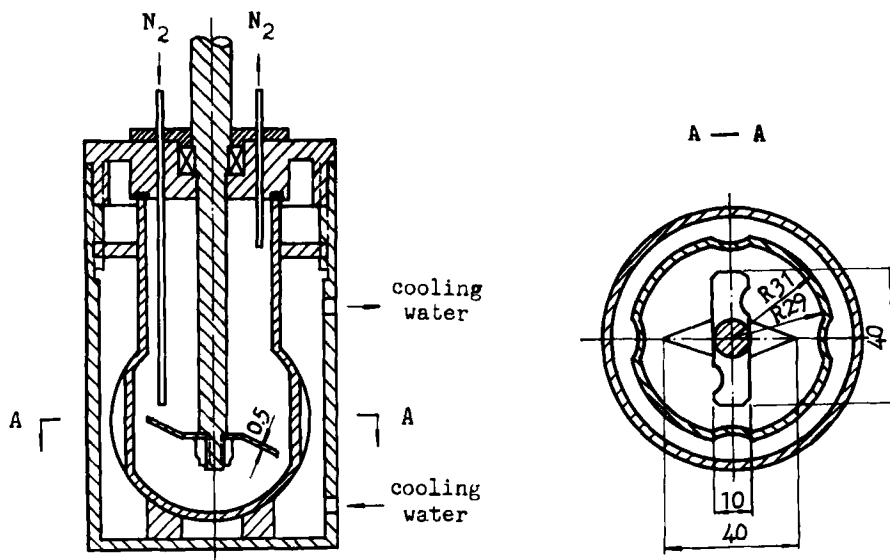
Sample C: PEO and PAM solutions (1:1, v/v) were mixed and stirred for 10 min at 20 000 rpm and  $20 \pm 3^\circ\text{C}$  under nitrogen. The yield of PEO-PAM block copolymer produced by stirring was 66.6% [4].

### Analysis and Characterization

(1) Contrast microscopy. Films of the above-mentioned samples were cast on a flat glass and examined through a BH-2 contrast microscope.

(2) Transmission electron microscopy. Films cast from 0.5% solution of the above-mentioned samples were dyed with 1%  $\text{OsO}_4$  and observed under a TEM 100CX electron microscope. The accelerating electrical voltage was 80 kV.

(3) Stress-strain behavior. The tensile curves of the samples were measured with a YG-001 fiber electronic strong force apparatus, the clamped length was 10 mm, and the drawing speed and moving speed of the recording paper were 1 and 24 mm/s, respectively. The cross-sectional area of the samples was determined by a JTT fiber projection apparatus.



Material: 1Cr18Ni9Ti, Max rpm: 24000

FIG. 1. High-speed stirring reactor.

(4) Small-angle x-ray scattering. The films were laminated to a given thickness and examined with a 3015 x-ray diffraction fluorescent spectrometer, 2203 E1 x-ray small-angle detector with automatic step scanning ( $\text{CuK}_\alpha$ , filtered by nickel foil). The first slit was  $0.08 \times 15$  mm, the second one  $0.06 \times 20$  mm.

## RESULTS AND DISCUSSIONS

### Contrast Microscopy and Transmission Electron Microscopy

Figures 2 and 3 show that there are striking differences in the domain dimensions of different samples. In Sample A the two polymer phases are quite distinct. In Sample B the heterogeneity is also remarkable, indicating the poor compatibility of this system. In Sample C, however, the domain dimension is much smaller due to the presence of compatibilizing copolymer. All of these observations are consistent with theory.

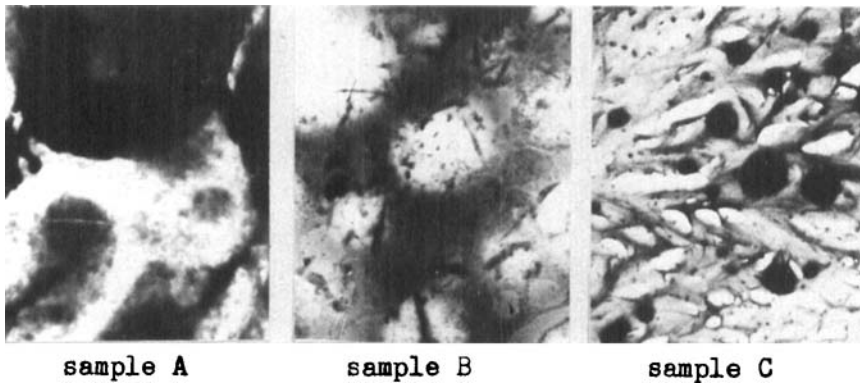
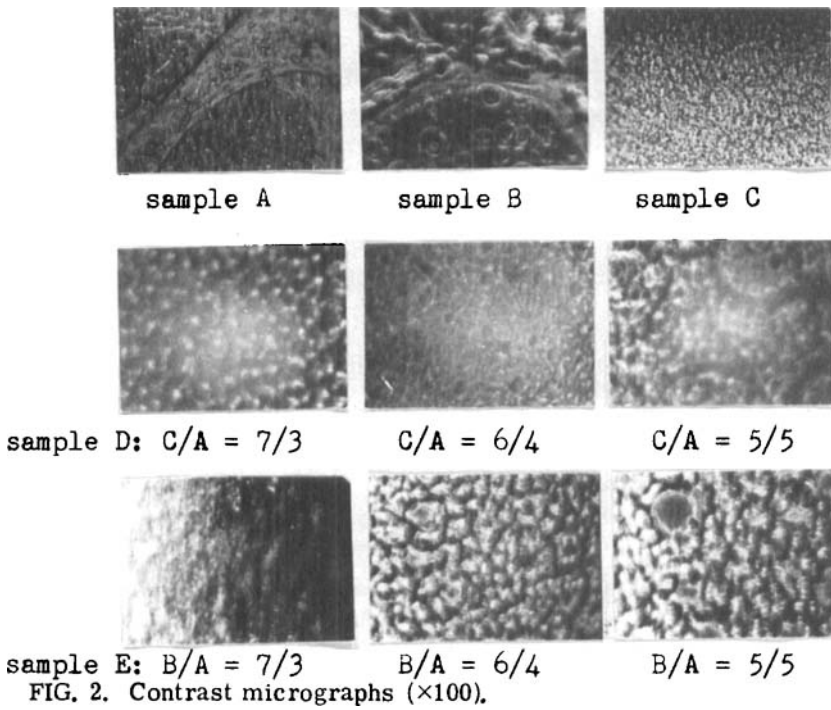


FIG. 3. Transmission electron micrographs ( $\times 4000$ ).

Compared to that of Sample E (Sample A blended with Sample B), the homogeneity of Sample D (Sample A blended with Sample C) is much better. This indicates that the block copolymer in Sample C is an effective compatibilizer of PEO/PAM blend.

### Small-Angle X-ray Scattering

For very small scattering angle, the scattering intensity may be expressed as [5]

$$I(\theta)^{-\frac{1}{2}} = K[1 + 4\pi^2 (L_c^2/\lambda^2) \theta^2],$$

where  $I(\theta)$  is the scattering intensity,  $K$  is a constant related to the nature of the sample and instrument,  $\lambda$  is the x-ray wavelength,  $2\theta$  is the scattering angle, and  $L_c$  is the correlation distance characterizing the heterogeneity of the system. The scattering data were desmeared for slit broadening in a MV/6000 computer. Figure 4 is the Debye-Bueche plot of the processed data. From the ratio of the slope to the intercept, the correlation distance  $L_c$ , characterizing the heterogeneity, was obtained. The  $L_c$  are 12.1, 10.8 and 9.3 nm for Samples A, B, and C, respectively.

From the scattering curve the invariant  $\tilde{Q}$  may be evaluated by integrating the equation  $\tilde{Q} = \int_0^\infty s \tilde{I}(s) ds$ , where  $s$  is the scattering vector and  $\tilde{I}(s)$  is the smeared intensity [6]. According to the method proposed by Vonk [6], we used the Gauss function  $P \exp(-qx^2)$  to fit the first five experimental data, then extrapolated the integral from the minimum angle of observation to  $2\theta = 0$ . In the tail region of the scattering curve,  $Y = (C_1/x) + (C_2/x^3)$  was used as the fitting function. The mean-square electron density fluctuation  $\langle \eta^2 \rangle$  was evaluated by the equation  $\langle \eta^2 \rangle = (60/d_0 a) \tilde{Q}$  (where  $d_0$  is the thickness of the sample, and  $a$  is the distance between the sample and the detector). For an ideal homogeneous system,  $\langle \eta^2 \rangle = 0$  [7].

Vonk [8] suggested that, in the tail region of small-angle x-ray scattering, the slit-smeared intensity  $\tilde{I}(s)$  may be approximated by

$$\tilde{I}(s) = \frac{\pi C}{2} [(-2\pi^2 E^2/3s) + (1/s^3)],$$

where  $c$  is a constant and  $E$  is the thickness of the boundary layer. By comparison with the tail-fitting function mentioned above,  $E$  can be

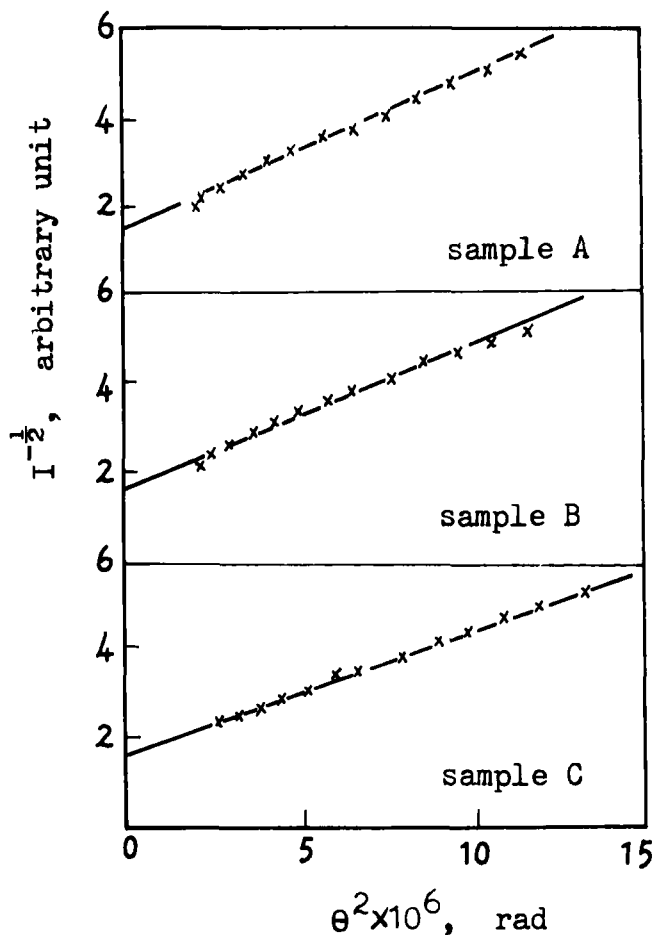


FIG. 4. Variation of  $I^{-\frac{1}{2}}$  with  $\theta^2$  (Debye-Bueche plot).

computed from the fitted values of  $C_1$  and  $C_2$ . The higher the  $E$  value, the better the compatibility of the system [9].

The  $E$  and  $\langle \eta^2 \rangle$  values listed in Table 1 are based on the scattering data of the samples. The data were processed in a MV/6000 computer. The program mainly consists of subtracting the background scattering, fitting the scattering curve in the smaller angle region and the tail region by the Gauss function as well as  $\tilde{I}(s) = (C_1/s) + (C_2/s^3)$ , respectively, finding  $\tilde{Q}(s)$ ,  $E$ , and  $\langle \eta^2 \rangle$ . The values of  $L_c$  and  $\langle \eta^2 \rangle$  of Samples A, B, and C decrease in order, while  $E$  of the samples increases successively, indicating that the compatibility of Sample A is poor, of

TABLE 1. The Values of E and  $\langle \eta^2 \rangle$ 

Sample	Fitting in head region, $\tilde{I}(s) = P \exp(-qs^2)$		Fitting in tail region, $\tilde{I}(s) = (C_1/s) + (C_2/s^3)$				$\langle \eta^2 \rangle^a$ (relative)	
	P	q	Error, %	C <sub>1</sub>	C <sub>2</sub>	Error, %		E, nm
A	$3.27 \times 10^4$	$1.76 \times 10^5$	0.3	-0.223	$6.05 \times 10^{-4}$	1.4	0.75	$6.64 \times 10^{-2}$
B	$2.41 \times 10^4$	$1.49 \times 10^5$	0.6	-0.838	$8.80 \times 10^{-4}$	1.3	1.20	$5.26 \times 10^{-2}$
C	$3.36 \times 10^4$	$1.82 \times 10^5$	0.9	-2.540	$8.17 \times 10^{-4}$	1.5	2.17	$4.51 \times 10^{-2}$

<sup>a</sup>Not calibrated against Kratky sample.



TABLE 2. Stress-Strain Behavior

	Sample		
	A	B	C
Cross-sectional area, mm <sup>2</sup>	0.0200	0.0180	0.0196
Breaking tensile force, g	2.8	14.8	50.0
Breaking tensile stress, g/mm <sup>2</sup>	140	822	2 551

Sample B is a little better than A due to the smaller molecular weight, and of Sample C is more compatible because of the presence of the block copolymer produced by high-speed stirring. These are in accord with the theory that lowering molecular weight will permit miscibility of polymers [10] and the conclusion drawn by Roovers [9] that the covalent bond of the block copolymer may increase the thickness of the boundary layer.

### Stress-Strain Behavior

The stress-strain behaviors of the samples are quite different due to the heterogeneity of their structure (Table 2). Sample A and B are poor in compatibility, and their breaking tensile stresses are low. The block copolymer present in Sample C makes the polymers miscible, and the breaking stress of the blend is high.

### CONCLUSIONS

The PEO-PAM block copolymer produced during high-speed stirring is a compatibilizer for the thermodynamically incompatible PEO/PAM system. It could cut down the dimension of domains, reduce the heterogeneity of the system, increase the thickness of the boundary layer, and improve the mechanical properties of the polyblend.

The method of preparing compatibilizer by high-speed stirring has the merit of producing it in situ and needs no separation. It is an economical and effective way to improve the compatibility of a multi-component system.

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