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Compatibility Study of a Blend of Poly(Ethylene Oxide) in Dilute Solutions of Poly(Methyl Methacrylate) in Benzene

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Abstract

Dilute solutions of poly (ethylene oxide), PEO and poly(methyl methacrylate), PMMA blends have been studied at 30°C over an extended range of concentrations using benzene as the solvent. The intrinsic viscosity solutions of PEO have been found to decrease with increasing concentration of PMMA. Viscometric interaction parameter b_{23} and K_{AB} gave positive values of 0.0125 and 0.2109 respectively. These results show that the blend is fairly compatible.

Introduction

Polymer blends are mixtures of structurally dissimilar polymers which interact through secondary forces, with no covalent bond involved (Satsewska et al,1981).The blending of polymer has become a useful approach for the preparation of materials or objects with new desirable properties that the component polymers do not have. The blending of polymer may result in reduction of the basic cost, improved processing and may also enable properties of importance to be maximized (Singh at al 1983).However, the manifestation of superior properties depends upon compatibility or miscibility of the homopolymers at molecular levels. Depending upon the degree of molecular mixing, the blends may be categorized as semi-miscible (semi-compatible blend), immiscible (incompatible blends) and miscible (compatible blends). The extent of compatibility results in different morphologies of the blends.

The viscosity behaviour of two chemically dissimilar polymer blend in a low molecular mass solvent is interesting for three reasons.

- (i) In practice, it is sometimes necessary to predict, at least approximately, the viscosity of solutions of polymer mixtures.
- (ii) Some polymers are prepared by polymerizing a monomer A in a solution containing a low amount of polymer B. It has been shown that the reaction rate and physical properties are changed by the presence of this polymer and that the origin of the effect is physical rather than chemical.
- (iii) Because of its simplicity, viscometry is often used in the investigation of interactions (compatibility) of dissimilar polymers.

The basis for using dilute solution viscosity as a parameter for compatibility characterization and determination of intrinsic viscosity of polymer blends lies in the fact that while in solution, macromolecule of both types may exist in a mutual attraction state, thereby rendering positive influence on viscosity. The interactions among polymer constituents are reflected in the solution viscosity of polymer blends because polymer-polymer interaction usually dominates over polymer-solvent interactions.

This work attempts to determine the extent of compatibility between PEO and PMMA using interaction parameters obtained by viscosity measurements of the blends in benzene solvent.

Experimental

Poly (ethylene oxide), (PEO) (Mw = 91,300, Mn = 48,400) and poly (methyl methacrylate), (PMMA) (Mw=100,000) samples were obtained from Polysciences, U.S.A.

Ubbelohde viscometer was used to measure the viscosities of the dilute solutions. Benzene (BDH) was used as the solvent. The flow time of the pure benzene (t₀) and flow times (t) of various blends were recorded at 30°C±0.02°C.

- (a) Five solutions (30cm³ each) of PMMA were prepared by dissolving the sample in benzene to give various concentrations of 1.0, 0.8%, 0.6% , 0.4% and 0.2% respectively. The average flow time of each concentration was recorded.
- (b) 1.0%w/v solution of PEO in benzene was prepared and the flow time recorded. Various concentrations of PEO in benzene were then prepared by dilution methods to give 0.8, 0.6, 0.4 and 0.2% respectively.
- (c) The blending of PEO and PMMA solutions were prepared by withdrawing a known volume of PEO solution and replacing with the same volume of PMMA solution. The procedure was repeated by gradual increase in the volume of PEO solution removed and corresponding addition of PMMA solution to obtain various concentrations of the mixture.

The polymer solutions under investigation were allowed to flow under gravity through the capillary of the viscometer, and the transit time measured.

Measurements of the viscosity of each solution (blend) was calculated by substituting the flow time values, t₀ and t into the equation:

$$\eta_{rel} = \frac{t}{t_0} \quad \text{and} \quad \eta_{sp} = \left(\frac{t}{t_0} - 1 \right)$$

The specific viscosity (η_{sp}) and relative viscosity (η_{rel}) were then calculated from the various flow times of the solutions(Bilmeyer,1970).

Results and Discussion

Intrinsic Viscosity Plots

The intrinsic viscosity plots gave positive values of 50.76 and 26.03 for dilute solutions of PEO and PMMA respectively, suggesting that PMMA is more viscous than PEO. An initial increase in intrinsic viscosity values was observed as the concentration of PEO in PMMA increase from 0.2 to 0.4 giving intrinsic viscosity values of 37.67 and 49.87 respectively as indicated in Table 1.

Table 1: Intrinsic viscosity values for various concentrations of the blend

Concentration	0.2	0.4	0.6	0.8	1.0
[η]	37.67	49.87	49.98	19.38	20.04

This is indicative of some level of attraction or partial adhesion between two dissimilar polymers, forming aggregates thereby increasing the viscosity of the mixture(Soria et al 1981) A decline in intrinsic viscosity from 37.98 to 19.38 was observed for higher concentration of PMMA solution in PEO. The attraction between the two polymers may be due to the fact that at higher concentration of PMMA, the interaction of similar molecules dominates over that between dissimilar ones.

Interaction Parameter

Sovia et. al(1981) determined the viscometric interaction parameter between the components in solution using the expression:

$$\frac{d[\eta]_3 C_2}{dC_2} = b_{23} - [\eta]_2 [\eta]_3$$

Where C_2 = concentration of polymer (2) in pure solvent, $[\eta]_2$ and $[\eta]_3$ are the intrinsic viscosities of the polymers (2) and (3) in pure solvent respectively. A plot of $[\eta]_2 \cdot C_2$ against C_2 gave a positive slope b_{23} which indicates a degree of compatibility between the polymers.

Applying the same expression to the blend of PEO in PMMA Figure 1 also gave a slightly positive value of 0.0125. This is an evidence to suggest some compatibility between the polymers.

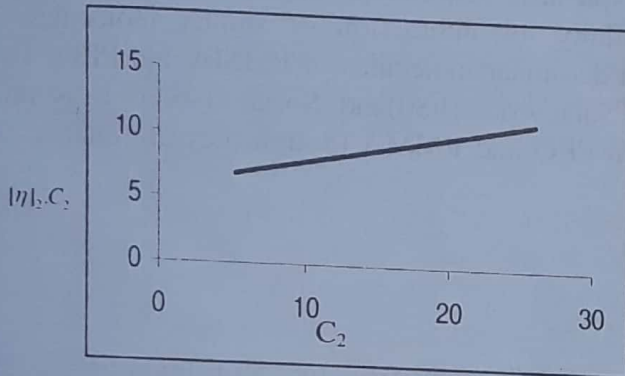


Fig 1: Compatibility plot for the blend of PEO in PMMA

Satzewska et al (1980) employed the expression:

$$p \cdot \eta_r(C_B) = 1 + 2K_{AB} [\eta_B] C_B$$

to evaluate the term K_{AB} which provides some information on the interaction of chemically dissimilar polymers.

Where $P = \frac{[\eta_A]_{CB}}{[\eta_A]}$, η_r is the relative viscosity of PMMA, C_B is the concentration

of PMMA, $[\eta_A]_{CB}$ is the intrinsic viscosity of PEO in PMMA,

$[\eta_A]$ is the intrinsic viscosity of PEO in pure solvent,

$[\eta_B]$ is the intrinsic viscosity of PMMA in pure solvent,

K_{AB} is the interaction coefficient between PEO and PMMA

It was reported that the K_{AB} term can easily be estimated from the slope of the plot of $p \cdot \eta_r(C_B)$ Versus $[\eta_B] C_B$. Setting $\eta_r C_B \cong 1 + [\eta_B] C_B$, a plot of $p[1 + \eta_B C_B]$ versus $[\eta_B] C_B$ was obtained and the slope estimated as K_{AB} .

This relation was used to determine K_{AB} for dissimilar molecules of PEO and PMMA and a positive slope of 0.2109 was obtained as shown in figure 2.

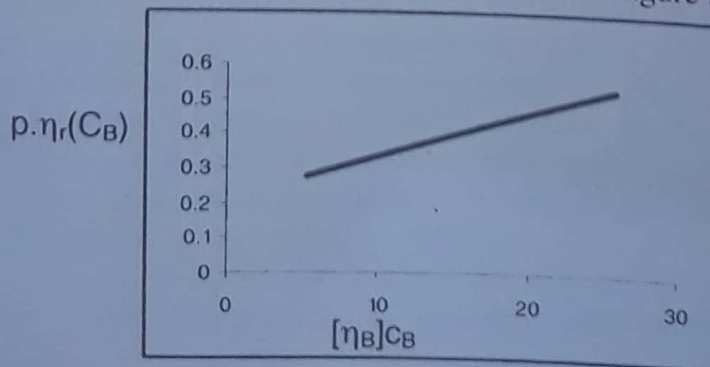


Fig 2: Compatibility plot for a blend of PEO in PMMA

This positive K_{AB} values of 0.2109 is in line with the findings of Sonia et. al(1981). This value may be due to the fact that there is a measure of positive interaction between these two polymers.

Conclusion

The compatibility study using interaction parameter suggests that there exist some degree of miscibility between PEO and PMMA in benzene. The slightly positive values are indicative that two dissimilar polymers may still have reasonable affinity for one another if properly blended. However, the greater affinity for interaction of similar molecules of PMMA remained dominant over that between dissimilar molecules of PMMA and PEO. This recent findings tend to agree with that of Satzewska(1980)and Soria (1981). It is thus concluded that there is an interaction between PEO and PMMA though they are chemically different polymers

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