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Melt Behaviour of Poly(Ethylene Oxide)-Poly(Vinyl Acetate) Blends

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SUMMARY

The compatibility of blends of poly(vinyl acetate) and poly(ethylene oxide) has been studied by rheological and thermo-optical analysis. Results from experiments point to the conclusion that there is extensive mixing between the segments of the two macromolecules in the blend. The interaction between the two polymers is manifested by a decrease in the melting point and a continuous decrease in viscosity with decreasing POE content in the mixture.

INTRODUCTION

Perhaps the most important direction today for obtaining new polymeric materials is the blend of homopolymers. In this sense it is worth noting that the projected production of blends for 1983 is the 13% of the total volume of thermoplastics (POLYMER NEWS 1981).
Blends or "alloys" can be obtained from compatible (miscible) or incompatible (immiscible) polymers. According to some authors (PROGELHOF 1981) miscibility or compatibility would be desirable for technological purposes because in completely immiscible blends components separate into their respective phases limiting the effectiveness of the mechanical behaviour of the blends. Nevertheless other investigators (UTRACKI et al. 1981) (PLOCHOCKI 1978) consider that better results might be obtained from incompatible polymer blends, due to the fact that, in this case, as Utracki says "final properties will be determined by those of pure polymers, geometrical arrangements of the two phases, their morphology, extent of interpenetration and the nature of the interface". We have to point out that between "complete immiscibility" and "thermodynamic miscibility" there exist some different levels of compatibility, for example the so called "technological compatibility" where two phases exist but the blend behaves (in a macroscopic sense) as unique material at industrial processing conditions.
There are different methods in order to evaluate the miscibility of polymer blends (PAUL and NEWMAN 1978) (OLA-

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BISI et al. 1979). In this paper we analyse the miscibility of mixtures of poly(vinyl acetate) and poly(ethylene oxide) by means of rheological measurements and melting point depression.

EXPERIMENTAL

Commercial polymer samples were used. Poly(ethylene oxide) (POE) ($\overline{M}_w$=3.65x10^5) was supplied by Quimigranel. Poly(vinyl acetate) (PVA) ($\overline{M}_w$=9.9x10^4) was obtained from Explosivos Rio Tinto. The samples were characterized by capillary viscometry.

Both polymers were dissolved in chloroform. The ratios of POE and PVA in the mixtures refer to weight proportions. The mixtures of polymers were maintained in solution for a period of 2 weeks with frequent agitation to assure homogeneity.

Films of POE, PVA and their mixtures were cast from chloroform solution on to a glass surface at room temperature; the solvent was allowed to evaporate very slowly under a stream of air. The resulting films were subjected to further drying under vacuum for a week.

In order to achieve a better dispersion of one material in another, the films were extruded in a capillary rheometer at 100°C and low velocity of the piston (V_p=8x10^{-3} cm/s) according to the method described by Schmitt (SCHMITT 1968) and Karam (KARAM et al. 1955).

Melt viscosity measurements were carried out with a Sieglaff-McKelvey capillary extrusion rheometer at 120°C. The lenght to diameter ratio L/D was 26.4 with L=2.54 cm.

Temperatures of fusion were detected using a polarizing microscope Reichert fitted with a Mettler FP 52 hot stage. Heating was conducted at rate of 10°C min^{-1} using a Mettler FP5 programming unit. During measurements the polarizers of the microscope were crossed. The light source, a 6v bulb, was stabilized by a voltage stabilizer. The light output of the optical system was measured by a photomultiplier inserted in the eyepiece tube and recorded on a strip chart recorder Vitatron UR 400 against a time base. The temperature at which birrefringence was lost totally was recorded (SHULTZ and GENDRON 1972).

RESULTS AND DISCUSSION

In order to determine the miscibility of polymer blends, melt viscosity measurements are sometimes used, even when the theoretical aspects of the problem are not still completely developped (OLABISI et al. 1979).

Because the morphology of two phase system can change with extrusion shear conditions it is expected that viscosity of miscible systems will change monotonically with composition, whereas two phase systems will show deviation from monotony. Evidence of this deviation has been observed for two phase systems such as polyethylene-polypropylene

(PLOCHOCKI 1978, 1981) (NOEL and CARLEY 1975); polycarbonate -acrylonitrile butadiene styrene copolymer and polycarbonate- polypropylene (DOBRESCU and COBZARU 1978); polystyrene-polyethylene and polystyrene-polypropylene (HAN 1976). On the other hand monotonic variation was observed for miscibility systems such as poly(phenylene oxide) -high impact polystyrene (SCHMIDT 1979); polycarbonate-poly(methyl-methacrylate) (DOBRESCU and COBZARU 1978); cis 1-4 polyisoprene - natural rubber (OLABISI et al. 1979).

Because the objetive of this paper was to compare viscosities of blends having different composition we did not take into account non-newtonian correction nor ends effect correction (MIDDLEMAM 1968).

Therefore, in fact we obtained an apparent viscosity, η, defined by

$$\eta = \frac{\sigma_{21}}{\dot{\gamma}}$$

where the shear stress σ_{21} is given by:

$$\sigma_{21} = \frac{\Delta PD}{4L}$$

Δ P is the total pressure and the shear rate $\dot{\gamma}$ is given by

$$\dot{\gamma} = \frac{4Q}{R^3 \pi}$$

being Q the volumetric flow rate and R the capillary radius. In figures 1 and 2 we present the viscosity dependence with composition at different shear stress and at shear rate $\dot{\gamma}=50$ s^{-1}, respectively.

It is seen that in all cases viscosity increases continously with increasing POE content and, therefore, we can conclude that there is, at least, a certain degree of solubility between POE and PVA in the melt phase.

Other indication for compatibility in the melt phase is the depression of the melting point of POE by PVA, since, the degree of miscibility of blends where one component is semicrystalline can also be followed by measurement of fusion temperature (NISHI and WANG 1975) (KWEI et al. 1976) (ROERDINK and CHALLA 1977) (AUBIN and PRUD'HOMME 1980) (ZISKA et al. 1981). As shown in table 1, the melting temperature of POE in the mixtures decreases with the POE content. This result can also be interpreted as being due to extensive mixing of the two segments of each blend.

The melting point depression, which is evident in our entire microscopic study, intensifies progressively with the decrease in the POE content. Nishi and Wang (NISHI and WANG 1975) have derived a relation between the melting point de-

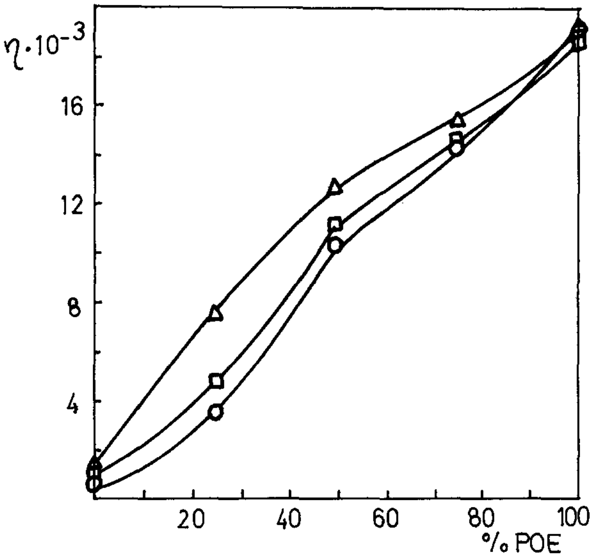

Fig. 1.- The dependence of apparent viscosity on composition for the POE-PVA system at different shear stresses △, σ_{12}=0.9x10^6 dyne/cm^2; □, σ_{12}=1.2x10^6 dyne/cm^2; ○, σ_{12}=1.5x10^6 dyne/cm^2.

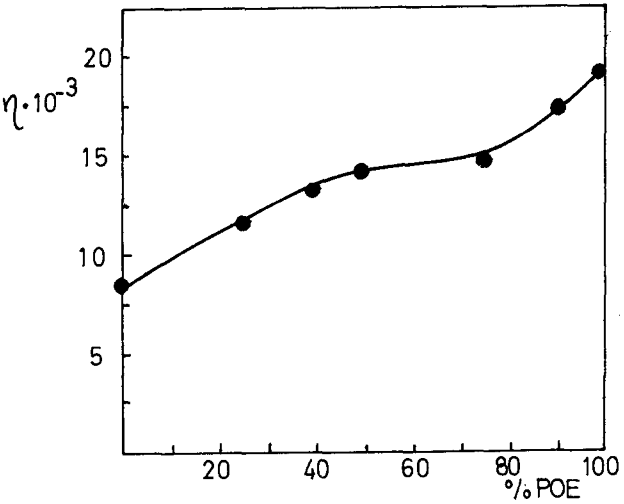

Fig. 2.- The dependence of apparent viscosity on composition for the POE-PVA system at $\dot{\gamma}$=50 sec^{-1}

pression and the interaction parameter for a crystalline-amorphous polymer system based upon Scott's (SCOTT 1949) thermodynamic theory for a mixture of two polymers:

$$\frac{1}{V_1}\left(\frac{1}{T_m} - \frac{1}{T_m^\circ}\right) = -\frac{B\ V_{2u}}{\Delta\ H_{2u}}\ \frac{V_1}{T_m}$$

V_{2u} being the molar volume of the repeating units in POE (39.2 cm^3/mol); V_1 volume fraction of PVA; ΔH_{2u} molar heat of fusion of the repeating units in POE (2016 cal/mol) (VAN KREVELEN 1976); T_m melting point of POE crystals in the mixture; T_m° melting point in pure POE; B the interaction energy density characteristic of the polymer pair, which is related to the binary interaction parameter χ_{12} thus

$$B = RT\frac{\chi_{12}}{V_{1u}}$$

where R is the universal gas constant (1.98 cal/mol K) and V_{1u} the molar volume of the repeating units in PVA (72.35 cm^3/mol) (VAN KREVELEN 1976).

TABLE 1

Melting point of POE, PVA and their mixtures

POE weight content (%)	T_m, °C
100	65.6
90	65.1
80	64.3
70	63.6
60	62.7
50	61.8
40	61.0

A convenient graphical representation of the melting point data makes use of the plot of $(1/T_m - 1/T_m^\circ)/V_1$ vs. V_1/T_m. This is shown in Figure 3.
The experimental results are represented by a straight line. From the slope we obtain:

$$B = -0.739\ cal/(cm^3\ of\ PVA)$$

$$\chi_{12} = -8.12 \times 10^{-2}\ at\ 60°C$$

The negative sign of B indicates that the polymer pair can form thermodynamically stable single phase mixtures at temperatures near the melting point of POE.

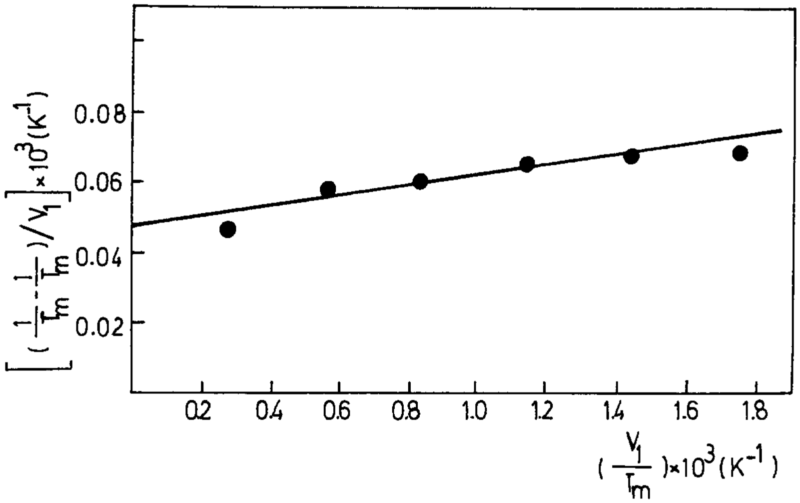

Fig. 3.- A plot of the quantity $(1/T_m-1/T_m^o)/V_1$ against V_1/T_m for the POE-PVA system.

The possibility exists that the depression in melting point may also arise from morphological changes such as imperfections in the crystals and reduction in lamellar thickness (HOFFMAN and WEEKS 1962). Therefore, an analysis of the current data does prove interesting but the results must be regarded as tentative.

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