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Characterization and morphology of Novolak or poly(vinyl phenol)/poly(ethylene oxide) blends

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With the aim of obtaining a route for polymeric blends, the behaviour of semi-crystalline poly(ethylene oxide) (PEO) and amorphous Novolak mixtures was studied. The crystallization of the semi-crystalline blend component at different compositions was evaluated by transmission microscopy with crossed polarizers. Infra-red data, thermal analyses and the determination of the Flory–Huggins parameter indicate both that the hydroxyl groups of Novolak are hydrogen bonded to the etheral oxygen of PEO and that the system is miscible. The miscibility of polymer–polymer blends of PEO and poly(vinyl phenol) (PVPh), through the component PEO and poly(vinyl phenol) (PVPh), which has a similar structure to Novolak, but higher molar weight, was also studied. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Many studies of physical mixtures of polymer/oligomer or polymer/polymer pairs have been reported in the literature in the past few years. These blends of polymer pairs exhibit a miscible or partially miscible phase within a concentration range[1]; e.g., poly(vinylidene fluoride) (PVDF)/poly(vinyl methyl ketone) (PVMK)[2], poly(vinyl phenol) (PVPh)/PVMK[3], PVDF/poly(methyl methacrylate) (PMMA)[4,5] and poly(4-vinyl pyridine)/zinc acetate[6] represent some examples. Physical homogeneous mixtures can occur due to entropy contribution or different kinds of intermolecular association such as ion–dipole, hydrogen-bonding or dipole–dipole interactions that provide a favourable energetic contribution to the mixing process. In many cases, when the components have proton donor and proton receptor capabilities, hydrogen bonding is sufficient to obtain miscible blends.

Kwei *et al.* studied Novolak resins mixed with polymers which contain carbonyl or carbonate groups[7,8]. These systems are miscible, with intermolecular hydrogen bonding as a dominant driving force. To obtain a blend of Novolak with other polymers as the dominant driving force, Inoue *et al.* studied the miscibility of poly(oxymethylene) (POM) with Novolak[9], and *FT*i.r. analysis revealed the presence of hydrogen bonding interaction between POM and Novolak resin. Blending of Novolak with other polymers is a simple, economic and effective method of changing the properties of undiluted components and obtaining new materials with specific functions. In the present work, we intend to continue the studies of miscibility and physico-chemical parameters of the mixture of phenolic resin with a poly(ethylene oxide) (PEO) or PEO with poly(vinyl phenol) (PVPh).

The strength of ethoxy–hydroxyl hydrogen bonds was evaluated by infra-red spectroscopy in the system of PEO and Novolak, which are respectively a proton acceptor and donor. The temperature–composition phase diagram of these blends, constructed from differential scanning calorimetric thermograms, exhibit a single melting transition which depends strongly on the nature of the hydrogen bonds and the potential for co-crystallization. PEO was chosen as the proton acceptor because there is only one oxygen site in the monomer unit that can compete with the hydroxyl oxygen of Novolak for the available proton and there is not a pendant group in the backbone to shield sterically the hydrogen interaction. These structural considerations make PEO very attractive as a potential hydrogen-bonding component in blends with 'proton-donor' polymers.

Our laboratory has been applying macroscopic and site-specific probes to identify strongly interacting polymer/small-molecule blends that exhibit unusual phase behaviour in the solid state. This contribution extends this research on 'model systems' to polymer–polymer blends in which conformational entropy of mixing provides virtually no driving force for miscibility.

EXPERIMENTAL

Novolak resin, of molecular weight 675 daltons with an average of 63 phenolic rings per chain, was purchased from Mitsui Toatsu. Its chemical structure consists of phenol rings randomly linked *ortho–ortho*, *ortho–para* and *para–para* by methylene groups in the proportion of 10, 18 and 72% respectively, as determined by n.m.r. in
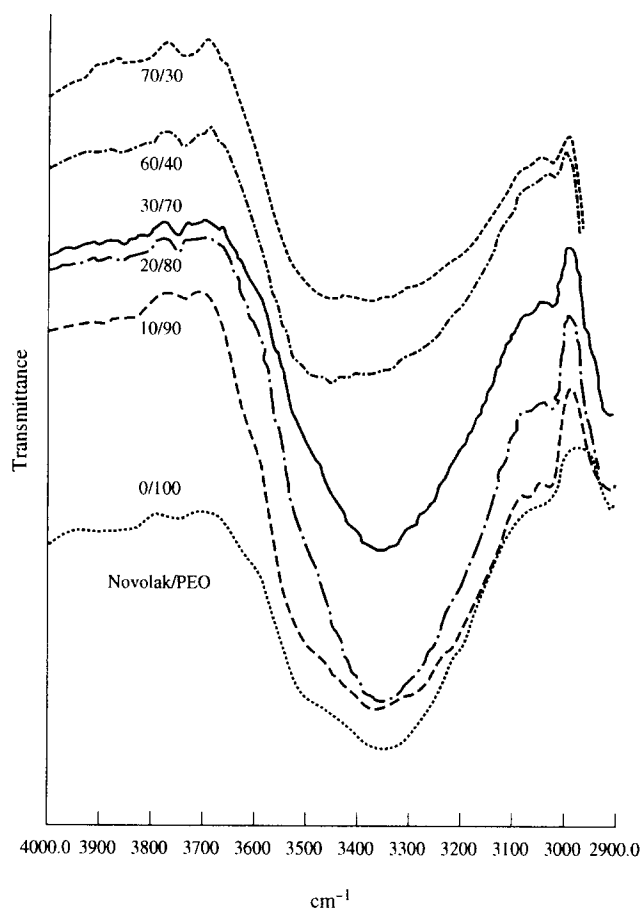
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Figure 1 Fourier transform infra-red spectra of binary mixtures containing poly(ethylene oxide) with Novolak at different mass percentages of each component, as indicated at the left infra-red spectrum

deuterated acetone. Poly(ethylene oxide) (PEO), obtained from Aldrich Chemical Co., has nominal molecular weights of 10 000 and 5 000 000 daltons; poly(vinyl phenol) (PVPh), donated by Maruka Lyncur, had a molecular weight of 10 000 daltons. The components were dried in vacuum for 48 h at 130°C before use. To obtain the PEO /Novolak blends: (i) pure PEO was melted at 160°C; (ii) Novolak resin was added slowly with thorough mixing; and (iii) finally, the mixture was pressed at 160°C and allowed to cool to room temperature.

Thermal analysis

Thermal analysis was carried out on a Shimadzu 50 differential scanning calorimeter. The transition enthalpies were measured, at a heating rate of $10°C\,min^{-1}$, through the glass transition temperature (T_g) and the melting point to 160°C. The samples were then quenched in liquid N_2 to $-100°C$ and the heating process was repeated at the same rate. The values of T_g for the first and second run were very similar. To obtain the Hoffman–Weeks graph[10], pure PEO and the blend samples were annealed at 40, 45, 50, 52 and 55°C for 48 h and the melting temperature determined by d.s.c.

Fourier transform infra-red spectroscopy (FT i.r.)

For *FT* i.r. analysis, thin films of different composition were melted over sodium chloride windows. The infra-red spectra were recorded on a Perkin Elmer, Model 16 PC *FT* i.r. spectrometer. A minimum of 6 scans was
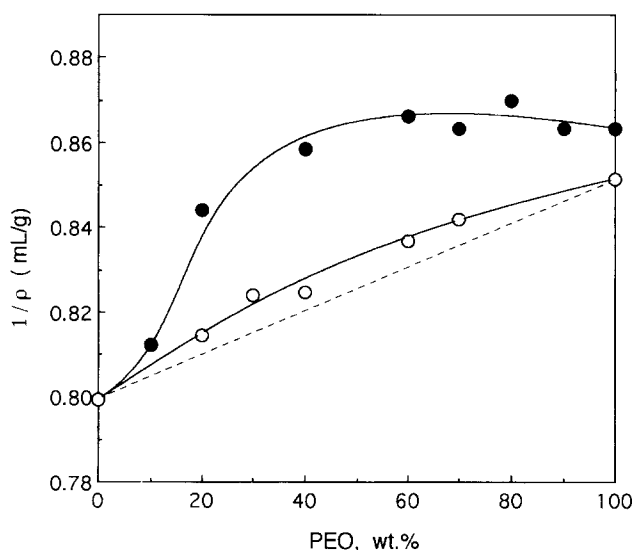

Figure 2 Behaviour of density inverse as PEO percentage in the mixture PEO/Novolak with PEO molecular weight of (O) 10 000 daltons and (●) 5 000 000 daltons. The dashed straight line represents the values obtained by equation (1)

signal-averaged at a resolution of $4\,cm^{-1}$. The experiments were carried out at room temperature and all of the films used in this analysis were thin enough for the Beers–Lambert law to be obeyed.

Density and partial specific volume measurements

Blend densities were determined by using a 1 m aqueous sucrose density gradient column at 25°C. The density, as a function of column height, was determined from refractive index measurements made during the preparation of the column.

The partial specific volume of PEO and Novolak were determined by using a PAA–DMA 60 densimeter. A weighed quantity of Novolak was added to a known mass of alcohol and the total volume was obtained from the total weight and solution density. PEO was first dried over P_2O_5 under vacuum to constant weight, and its partial specific volume was determined by the same procedure except that water was used as the solvent.

RESULTS AND DISCUSSION

Miscibility of PEO/Novolak blends

The interactions between the ether oxygens of PEO and the hydroxyl protons of Novolak can be analysed by infra-red spectroscopy and provide information on the specific intermolecular hydrogen-bonding interactions between the two components in the blend[11]. *Figure 1* shows a set of *FT* i.r. spectra of different Novolak–PEO blends. The two bands at 3360 and $3525\,cm^{-1}$ are the absorptions of the intermolecular hydrogen-bonding and free hydroxyl groups, respectively. The relative intensity of the band at $3360\,cm^{-1}$ increases with increasing PEO content of the blend and is probably due to specific interactions with PEO ether oxygen. Above 70% by weight of the amorphous component (Novolak), the spectrum approaches that of pure Novolak. These relative peak intensities correlate the contributions of free and associate forms. The conformational effect of macromolecules does not seem to aid interaction between free hydroxyl groups.
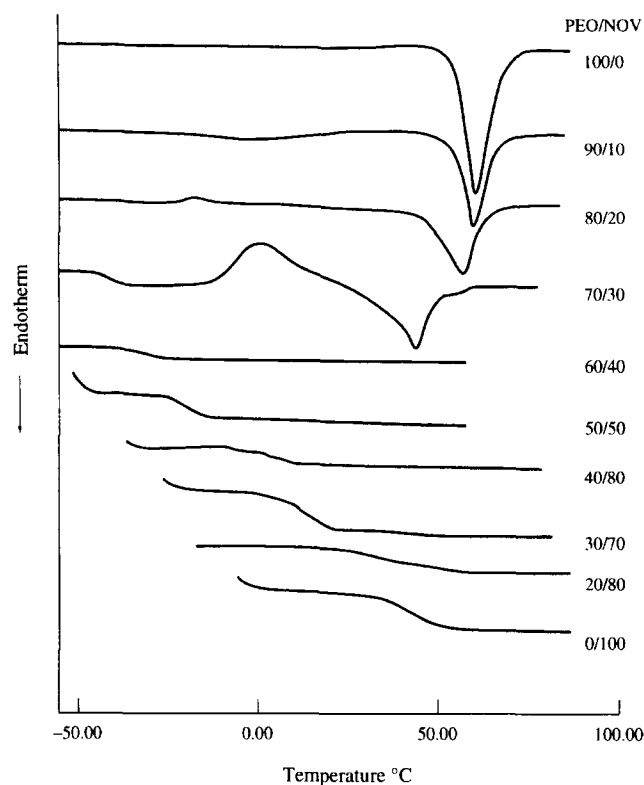
Figure 3 D.s.c. thermograms at a heating rate of $10°C\,min^{-1}$ which illustrate multiple melting peaks for PEO and a single glass transition temperature in the PEO/Novolak blends of different compositions as indicated

Figure 4 Concentration dependences of the melting (T_m) and single glass transition (T_g) temperature during the d.s.c. heating trace. The continuous line represents the values obtained from equation (2)

The reciprocal of the blend density vs weight percentage of PEO is shown in *Figure 2*. In general, the densities of crystalline regions can be as much as 10% greater than those of the amorphous regions[12], so that for a blend with increasing amorphous content the crystallinity of PEO in the mixture decreases, as will be shown in the next section. The dashed straight line represents the behaviour expected when the partial specific volumes in the components are additive (equation (1)), in which w, ρ and subscripts b, 1 and 2 indicate weight, densities of the blend and each component, respectively.

$$\frac{1}{\rho_b} = \frac{W_1}{\rho_1} + \frac{w_2}{\rho_2} \qquad (1)$$

Negative deviations of blend density from equation (1) are observed for PEO/Novolak blends with PEO of molecular weights of 10 000 and 5 000 000 daltons, and suggest a volume contraction of the components in the mixture. The biggest deviation is observed for high
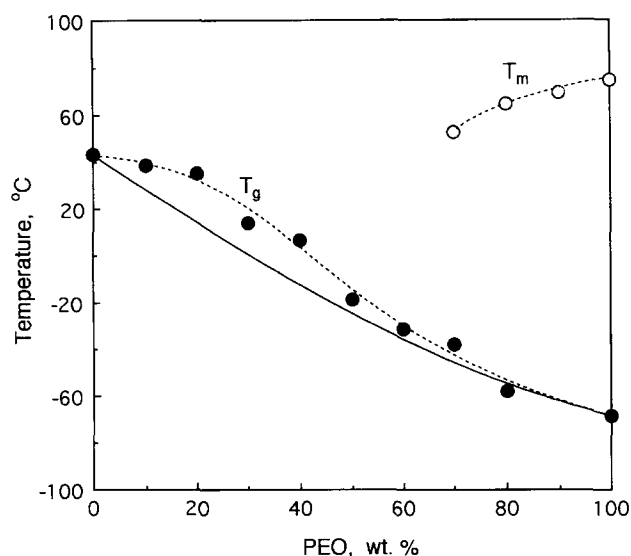
molecular weight PEO. Zakrzewski[12] and Hickman[13] suggested that a density or a negative excess volume of miscible blends is caused by a more favourable macro-molecular packing promoted by strong intermolecular interactions.

D.s.c. curves (second run) of the PEO (MW 10 000 daltons)/Novolak mixtures at different compositions are shown in *Figure 3*. The values of the melting (T_m) temperature and the glass transition (T_g) temperature obtained from each d.s.c. experiment are plotted in *Figure 4*. Semicrystalline PEO samples exhibit both transition temperatures but amorphous Novolak only T_g. The miscibility of binary polymer blends is often ascertained from changes in their glass transition temperatures. Generally, T_g in the amorphous component increases monotonically with added semicrystalline component. A single T_g value in different blend compositions indicates miscibility. Different equations have been proposed to correlate T_g with polymer blend miscibility. However, these expressions, which are derived from the so-called free volume hypothesis or from thermodynamic arguments[14], do not often predict the observed experimental deviations. The solid line in *Figure 4* corresponds to the Fox equation (equation (2)), where subscripts are defined as in equation (1).

$$\frac{1}{T_{gb}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (2)$$

Table 1 Data for the total volume of alcoholic Novolak and aqueous PEO solutions at different concentrations

| Novolak					PEO				
$m_{Novolak}$ (g)(g)	$m_{alcohol}$ (g)	m_{total} (g)	Density (g ml^{-1})	Total volume (ml)	m_{PEO} (g)	m_{water} (g)	m_{total} (g)	Density (g ml^{-1})	Total volume (ml)
0.0153	4.9528	5.0154	0.79912	6.2762	0.0045	5.0161	5.0045	0.99835	5.0127
0.0265	5.1049	5.0260	0.80004	6.2822	0.0117	4.9304	5.0119	0.99866	5.0186
0.0490	5.2694	5.0465	0.80142	6.2969	0.0170	4.9187	5.0173	0.99902	5.0222
0.0807	5.0369	5.0801	0.80359	6.3228	0.0337	4.9162	5.0343	0.99948	5.0369
0.1288	4.9832	5.1292	0.80796	6.3483	0.0485	4.9151	5.0493	0.99996	5.0496
0.2284	4.9063	5.2328	0.81446	6.4249					
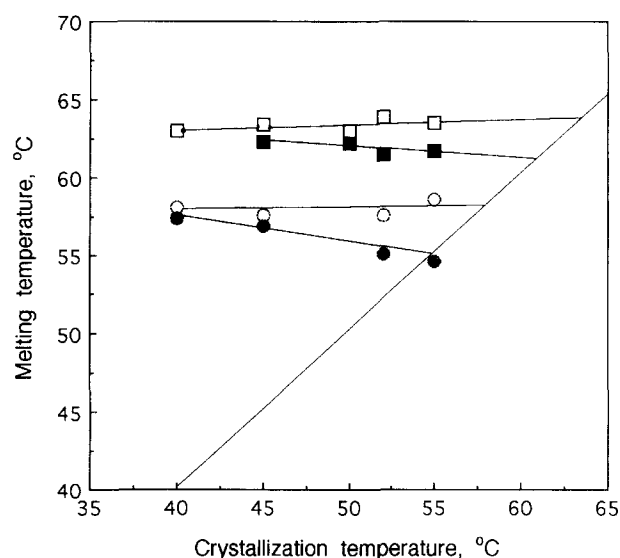
Figure 5 Hoffman–Weeks plot for calculating the equilibrium melting temperature of pure PEO and PEO/Novolak blends. Wt% PEO in the mixture: (□) 100/0, (■) 90/10, (○) 80/20 and (●) 70/30

Table 2 Equilibrium melting temperature of PEO/Novolak blends at different volume fractions of Novolak

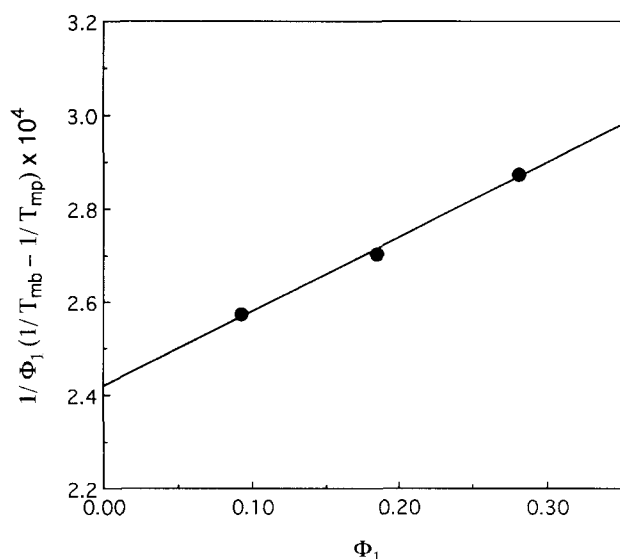| Blend	T_{mb} (°C)	Volume fraction ϕ_1
100/0	63.8	0
90/10	61.0	0.093
80/20	58.2	0.185
70/30	54.8	0.281

Figure 6 Flory–Huggins parameter determined by equation (4), using data from *Table 2*

Blend compositions with PEO weight percentages less than 50% deviate from the Fox equation, probably of strong interaction or the dispersion of one component in the other matrix.

Determination of the partial molar volume of the monomeric unit

The binary solution volume can be written as:
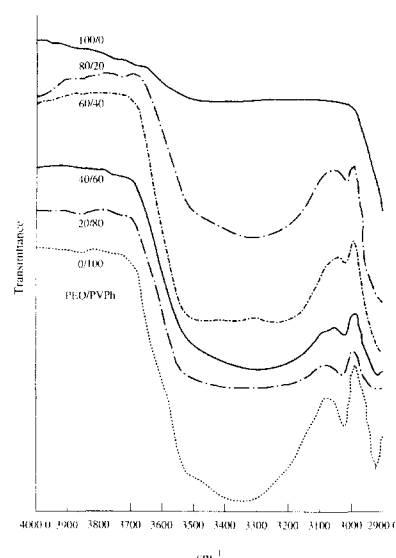
$$\bar{V} = n_1 \bar{V}_1 + m_2 \bar{v}_2 \tag{3}$$

Figure 7 *FT* i.r. spectra of PEO/PVPh mixtures containing different mass percentages of each component

where $\bar{V}_1$ is the partial molar volume of the solvent, $\bar{v}_2$ the partial specific volume and m_2 the mass of the polymer. *Table 1* shows the experimental data and total volumes calculated for Novolak and PEO in alcohol and aqueous solutions, respectively. The total solution mass was corrected to constant mass of 5.0000 g of solvent. To estimate volumes of PEO and Novolak we multiplied their partial specific volumes, $\bar{v}_2$, obtained from a graph of solute mass vs total volume of polymer solutions, by the molecular weights of their monomer units. Values of $0.8422 \, \text{ml g}^{-1}$ and $0.6795 \, \text{ml g}^{-1}$ were obtained for $\bar{v}_2$, which gives molar volumes of 37.0 ml and 72.0 ml for PEO and Novolak. The value of the partial specific volume of PEO is close to $0.834 \, \text{ml g}^{-1}$, as published in literature[15].

Determination of the equilibrium melting temperature of PEO/Novolak blends

Figure 5 shows the Hoffman–Weeks graph in which T_{mp} values are plotted as a function of the annealing temperature and extrapolated to obtain the crystallization temperature, T_m. The equilibrium melting temperatures and volume fractions ϕ_1 of Novolak are shown in *Table 2*. The melting temperature of PEO decreases with increasing volume fraction of Novolak, due to a decrease in the chemical potential of the amorphous phase and the miscibility of the two components.

Determination of the Flory–Huggins parameter

Specific interactions between the two components can be described by the Flory–Huggins parameter (χ_{12}), that distinguishes microscopically the free energy of the mixture and is used like a contribution of excess enthalpy and entropy to render the mixture potentially favourable. The more negative the Flory–Huggins parameter, the stronger the interaction, and this indicates the local variation of random distribution of contact number between the same and different molecular species.

Several techniques have been used to determine the Flory–Huggins parameter of miscible polymer blends, including melting point depression, vapour sorption, reversed phase gas chromatography, small angle neutron
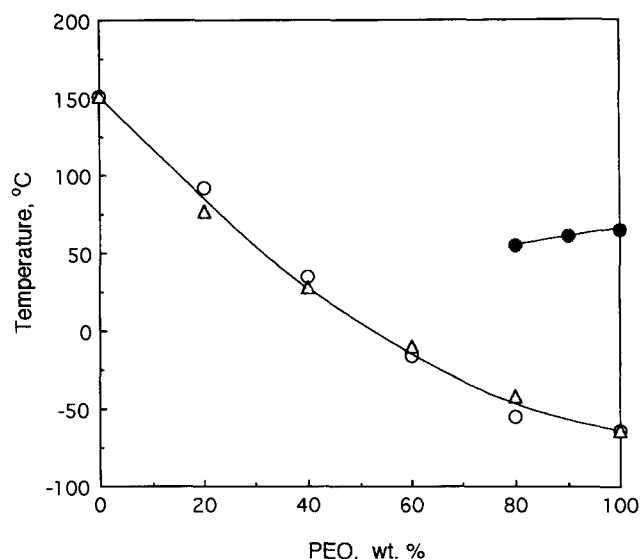
Figure 8 Concentration dependences of melting (T_m) and single glass transition (T_g) temperatures during the d.s.c. heating trace for PEO/PVPh blends. The continuous line represents the values obtained by equation (1)

scattering, small angle X-ray scattering[16] and equilibrium vapour pressure[17]. In this work, we used melting point depression to determine the non-equilibrium melting temperature of blends with more than 60 wt% PEO. The Flory–Huggins parameter can be determined

from equation (4)[18] because the contribution of conformational entropy to the mixing process is assumed to be negligible and because of the high molecular weight of the PEO samples. In equation (4), R is the gas constant, ΔH_f the melting enthalpy of crystalline PEO, T_{mp} and T_{mb} the equilibrium melting temperatures of undiluted PEO and the blend, V_{1u} and V_{2u} the molar volumes of the monomeric units of Novolak and PEO, respectively, ϕ_1 the volume fraction and m_2 the number of monomeric Novolak units.

$$\frac{1}{\phi_1}\left(\frac{1}{T_{mb}} - \frac{1}{T_{mp}}\right) = \frac{R}{V_{1u}}\frac{V_{2u}1}{\Delta H_f m_1} - \frac{RV_{2u}}{V_{1u}\Delta H_f}\chi_{12}\phi_1 \qquad (4)$$

Using the literature value of $\Delta H_f = 2100$ cal mol^{-1},[19] $R = 1.98$ cal K^{-1} mol^{-1} and V_{2u}, $V_{1u} = 37$ and 72 ml, respectively, together with the data listed in *Table 2*, we obtain the graph shown in *Figure 6*. From the slope, we obtained the Flory–Huggins parameter of -0.352. This value is of the same magnitude as that in other similar systems[20,21,22], and the negative value is consistent with a miscible system, as already discussed.

Poly(oxyethylene)/poly(vinyl phenol) (PVPh) system

The same techniques used to study the PEO/Novolak system were applied to PEO/PVPh blends. Novolak and PVPh have similar structures because PVPh also has pendant phenolic groups, but it has a higher polymerization degree than Novolak. *Figure 7* shows the absorption band of the free and bound hydroxyl group of pure PVPh and the effect of increasing PEO content in
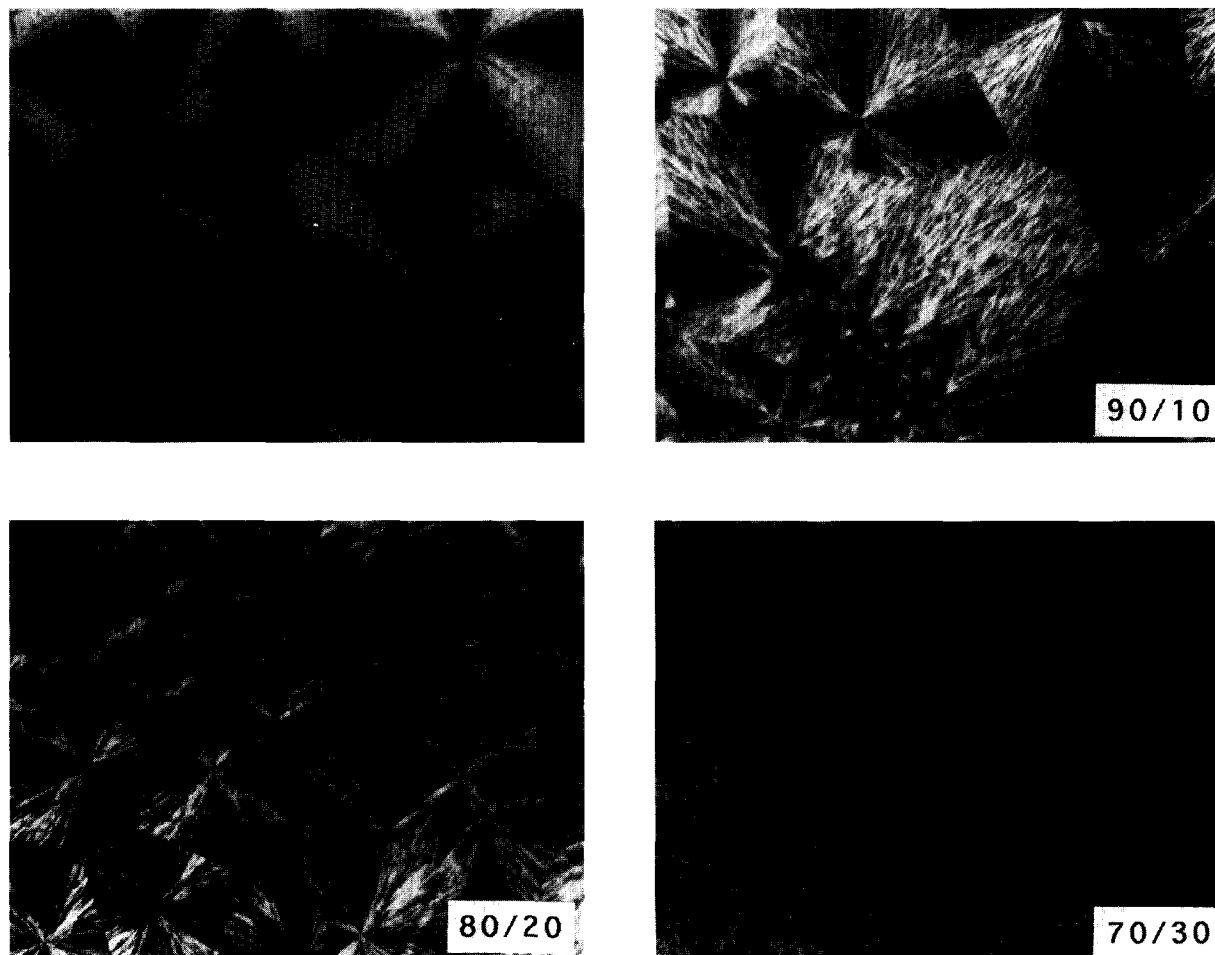

Figure 9 Photomicrograph of pure PEO and PEO/Novolak blends 100/0, 90/10, 80/20 and 70/30 (w/w). — 0.01 mm
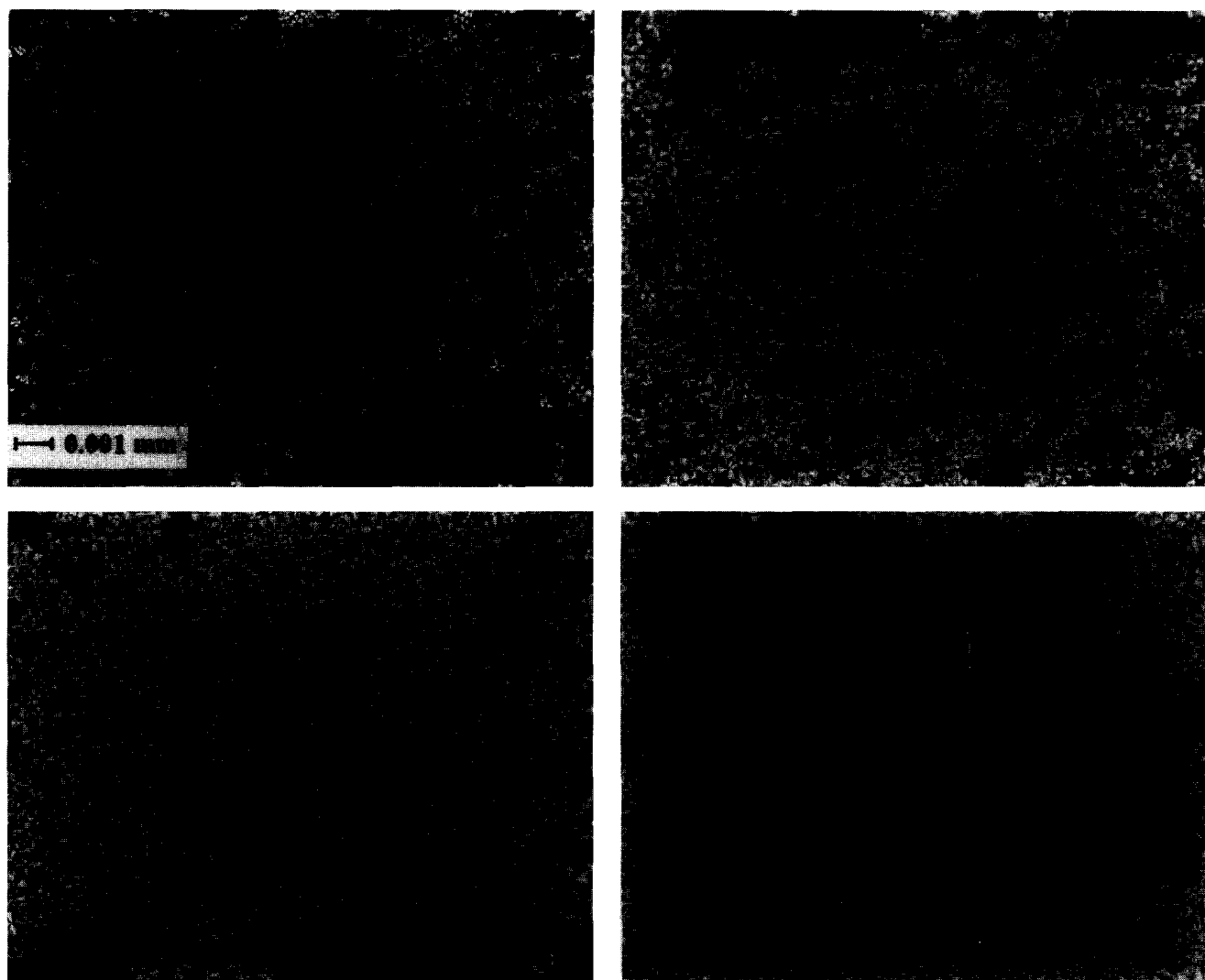
Figure 10 Photomicrograph of PEO/PVPh blend 90/10 (w/w) at 5 min intervals

the blends. We can observe band broadening, with a shift of the band near $3300 \, \text{cm}^{-1}$ due to intermolecular hydrogen bonding. A single glass transition temperature, between 150 and $-67°C$, corresponding to the pure components, was observed for all PEO/PVPh blends by d.s.c. (*Figure 8*). Unlike the results for PEO/Novolak, the values fit the Fox equation, probably because of the high molecular weights of both components. T_m for PEO changes from $64.3°C$ for undiluted PEO to $55.8°C$ for 80 wt% PEO, indicating the influence of the amorphous component on the crystalline structure.

PEO crystallization

The structure of semicrystalline PEO can be evaluated by polarizing microscopy between two cover-slips at low magnification. The experiments revealed the development of spherulites. A characteristic feature of spherulitic structure is the formation of fibrous sub-units that extend radially outward from the central nucleus. *Figure 9* shows a photomicrograph of pure PEO (MW 10 000 daltons) and blends with 10, 20 and 30% (w/w) of Novolak, melted at 150°C and crystallized at 55°C over a period of 48 h. In blends with Novolak percentages above 30% we did not observe spherulites to form. A 90/10 (w/w) PEO/PVPh blend was melted and crystallized at room temperature and photographs were taken

at 5 min intervals. The photographs in *Figure 10* show that the fibrous sub-units radiate as the spherulites grow. Cimmino *et al.*[23] studied poly(ethylene oxide)/poly(ethylene-*co*-vinyl acetate) blends and showed that after crystallization there is no evidence that the copolymers form segregated domains in the inter- and/or intraspherulitic contact zones. In our system, the presence of Novolak disturbs the crystallization kinetics during cooling from the melted state. This is probably due to hydrogen bonding between components, which changes the peripheral superficial free energy of crystalline lamella and upsets the characteristic backbone folding of PEO. These observations are consistent with PEO crystallization from PEO/Novolak solutions with Novolak present in the interlamellar regions, in agreement with the properties of their blends presented above. The same behaviour was observed with PEO/PVPh blends with smaller size of the rays than the PEO/Novolak system.

CONCLUSION

The results presented in this contribution identify the coordination mechanism needed to obtain solid state blends of polymer/oligomer as a route to producing polymer–polymer blends. Molecular spectroscopy

indicates hydrogen bonding between the hydroxyl groups of Novolak and the ether oxygens of PEO. The miscibility and *FT*i.r. results for PEO and Novolak show that the interactions between hydroxyl groups within Novolak molecules are weaker than the intermolecular hydrogen bonds with PEO. This interaction between two dissimilar components is responsible for the exothermic contribution upon mixing. A single value for the glass transition temperatures and the melting-point depression for PEO/Novolak mixtures favour the compatibility of components in the amorphous phase. The negative value of the Flory–Huggins parameter suggests that the miscibility of PEO and Novolak is driven by specific interactions, and the microscopy results suggest that these interactions occur on the periphery of the crystalline phase. The analysis of the PEO/PVPh system by *FT*i.r. and thermal analysis indicates the formation of miscible blends at the microscopic level.

ACKNOWLEDGEMENTS

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