

Miscibility and Specific Interactions in Blends of Poly(vinyl phenyl ketone hydrogenated) with Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: The miscibility behavior of poly(vinyl phenyl ketone hydrogenated) (PVPhKH) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) are studied by differential scanning calorimetry, thermomechanical analysis, and FTIR spectroscopy. Two miscibility windows between 10 to 40 and 60 to 90 wt % PPO are detected. Only the blend with 50 wt % PPO is immiscible. The best fit of the Gordon–Taylor equation of the experimental glass-transition temperatures for miscible PVPhKH/PPO blends is shown. A study by

FTIR spectroscopy suggests that hydrogen bonding interactions are formed between the hydroxyl groups of PVPhKH and the ether groups of PPO. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1887–1892, 2004

Key words: poly(vinyl phenyl ketone hydrogenated); poly(2,6-dimethyl-1,4-phenylene oxide); specific interactions; hydrogen bonding; miscibility blend

INTRODUCTION

Mixtures of polymers, also known as polyblends, are an important class of materials that exhibit a variety of mechanical, thermal, optical, or electrical properties, depending on the characteristics of the parent homopolymers and the blend composition.¹ Blending different polymers can result in new materials with advantageous properties that have great potential for new applications.² However, the entropy of mixing for long molecules (i.e., polymers) is usually small and in many cases the enthalpy of mixing is positive, so many polymers blends are immiscible. In fact, the majority of industrial polymer blends are immiscible and have limitations in their end uses.^{3,4}

However, miscibility is understood as the penetration of components on the molecular level, analogous to low molecular weight substances. For amorphous polymers, the miscibility is usually associated with the presence of a single glass temperature for the blend.⁵

Many reported miscible blends involve polymers with dissimilar chemical structures that are capable of establishing specific interactions between their chains, causing a negative enthalpy of mixing and a negative Gibbs free energy of mixing.^{6–12} Of the various specific interactions among polymers, hydrogen bonding is the most effective and common.¹³ Through hydrogen bonding, polymers containing proton-donor groups, such as carboxylic, phenolic, or hydroxyl groups, frequently form miscible blends with polymers with proton-acceptor groups, such as carbonyl, amide, and ether groups.^{14–18}

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a rigid polymer with high heat resistance and good dimensional stability, but it is relatively expensive.¹⁹ It is well known that PPO is miscible with polystyrene (PS) over the whole composition range and accessible temperatures.^{20–24} In similar way, PPO is miscible with poly(α -methylstyrene)²³ and poly(*p*-methylstyrene),²⁵ but it immiscible with halogenated PSs such as poly(*o*-chlorostyrene), poly(*p*-chlorostyrene), and poly(*p*-fluorostyrene).^{26–28}

This work reports the miscibility behavior of blends of PPO with poly(vinyl phenyl ketone hydrogenated) (PVPhKH). Both polymers contain complementary groups (see structures in Fig. 1); therefore, specific interactions can be formed between these polymers. Specific interactions can decisively influence the behavior of PPO/PVPhKH blends. PVPhKH is a proton-

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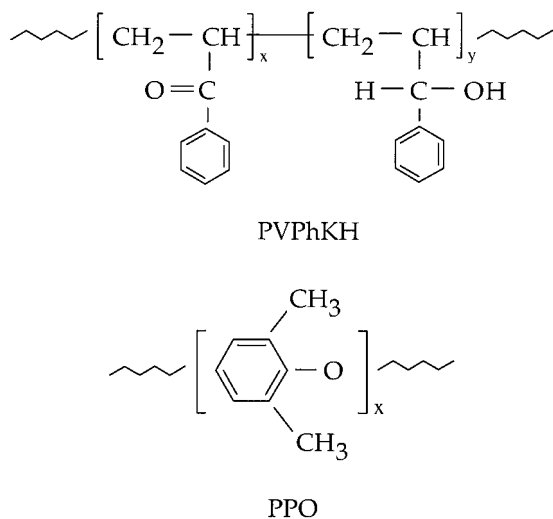


Figure 1 The structural formula of PVPhKH and PPO.

donor polymer with carbonyl and hydroxyl groups, so a competitive self-association (hydroxyl–hydroxyl and hydroxyl–carbonyl) is carried out in this polymer. IR spectroscopy suggests that hydrogen bonds are formed between the hydroxyl groups of PVPhKH and the ether groups of PPO.

EXPERIMENTAL

The PVPhKH (ratio of ketone/alcohol groups $\approx 0.3:1$, according to the supplier) and PPO (viscosity-average molecular weight = 15,500 g/mol) were used as received from Aldrich. Blends of PVPhKH and PPO were prepared by dissolving both polymers in chloroform, followed by casting at 75°C in an oven provided with air flow.

A differential scanning calorimetry (DSC) analysis of the PVPhKH/PPO blends was carried out in a PerkinElmer DSC 7 calorimeter at a heating rate of 20°C/min. Before making the measurements, the instrument was calibrated with indium. In every case, the second scan is reported. The glass-transition temperature was estimated from the peak of the heat flow curve derivative.

Thermomechanical analysis (TMA) of the blends was performed in a PerkinElmer TMA 7 analyzer at a heating rate of 10°C/min. In TMA, the curve of the sample thickness change as a function of temperature is obtained. The thermal calibration of the instrument was performed with indium and zinc. A height standard (3.8 mm) and weight standard (100 g) were used to make height and force calibrations. Again, the second scan is reported. The value of the glass-transition temperature was obtained from the peak of the sample thickness change curve derivative.

The IR spectra were recorded with a PerkinElmer Spectrum One FTIR spectrophotometer. Spectra were taken with a resolution of 2 cm⁻¹ and were averaged from 50 scans. Samples were prepared by dissolving the blends in chloroform (0.02 g/mL). A few drops of each solution were added directly onto NaCl pellets. Films of the polymer blends were obtained after solvent evaporation. All films were annealed for 15 min at 220°C in order to avoid nonequilibrium effects.

RESULTS

Figure 2 shows the calorimetric curves and the sample thickness change curves derivative of the parent polymers obtained by TMA. Both are amorphous polymers. The glass transition for PVPhKH is at about 105°C and for PPO is at about 219°C. The measurements obtained by DSC gave similar results (Table I).

Table I depicts the glass-transition temperatures (T_g) of PVPhKH, PPO, and their blends. The table compares the measurements obtained by TMA with those obtained by DSC. The blends with 10 to 40 and 60 to 90 wt % PPO depict only one glass transition. On the contrary, a blend with 50% PPO exhibits two glass-transition temperatures. The last blend is immiscible. There are small differences between the values of the glass transition measured by DSC and those measured by TMA, but this could be due to different techniques and heat rates.

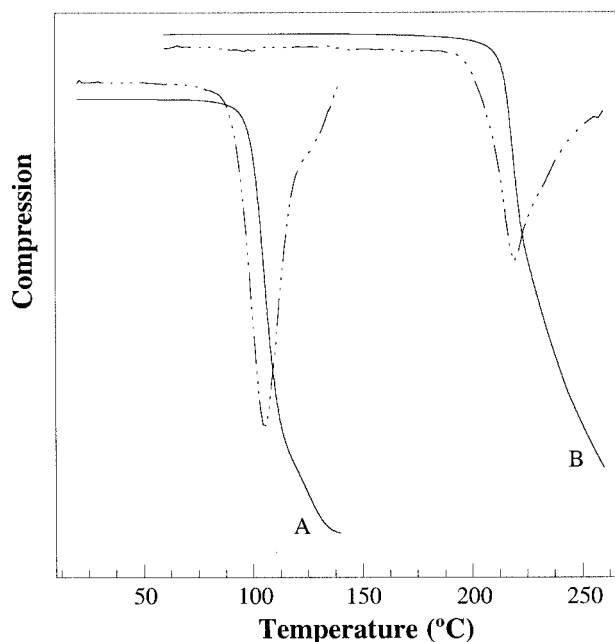


Figure 2 The (—) TMA curves of PVPhKH (curve A) and PPO (curve B). (– · · –) The derivative curve of the sample thickness change is included for both polymers.

TABLE I
Glass-Transition Temperatures of PPO, PVPhKH, and
Their Mixtures measured by TMA and DSC

Composition (% PPO)	TMA T_g (°C)	DSC T_g (°C)
0	105	103
10	108	101
20	111	103
30	114	104
40	150	151
50	109, 161	107, 162
60	169	173
70	178	179
80	180	185
90	201	197
100	219	221

The calorimetric curves of the blends with 20, 40, 60, and 80% PPO obtained by TMA are shown in Figure 3(a). The mechanical spectra of these blends show a strong descent because of a change in the thickness of the sample. This change occurs in the glass-transition range temperatures. Afterward, the thickness of the sample changes very little, so the baseline in the calorimetric curve stays constant. Figure 3(b) shows the derivative of the curve of the sample thickness change versus the temperature for the mixtures mentioned in Figure 3(a). Only one peak is detected in the derivative curves of all blends. This means that all blends have only one glass transition and are therefore miscible.

On the contrary, the mechanical spectrum of the blend with 50% PPO (Fig. 4) is very different. Two peaks in the derivative curve are resolved here. This indicates that this blend has two glass-transition temperatures ($T_{g1} = 109^\circ\text{C}$ and $T_{g2} = 161^\circ\text{C}$), so the PVPhKH/PPO (50/50, w/w) blend is immiscible.

The best fit of the prediction of the Gordon–Taylor equation for the values of the glass-transition temperatures for PVPhKH/PPO miscible blends is shown in the Figure 5. For blends with a poor content of PPO, there are appreciable differences between the experimental data findings and the Gordon–Taylor prediction. However, when the quantity of PPO was increased (i.e., blends with >50% PPO), the Gordon–Taylor equation improved the glass-transition fit for the T_g s of the PVPhKH/PPO blends.

Figure 6 shows partial IR spectra ($3120\text{--}3720\text{ cm}^{-1}$) of PVPhKH and its mixtures with PPO. Because the hydroxyl group of PVPhKH can form strong interactions via hydrogen bonding, the analysis of this band makes it possible to clarify the interactions between PVPhKH and PPO. To facilitate the comparison, the maximum intensities of the hydroxyl group of PVPhKH and the blends were normalized to unity in the spectra shown in Figure 6. Two spectral contributions are detected: a wide band (characteristic of polymers) at 3394 cm^{-1} that can be attributed to stretching

of the hydroxyl group, which is associated with intermolecular hydrogen bonding,²⁹ and another band at 3561 cm^{-1} , which intensifies as the PPO content increases. This band is attributable to hydrogen bonding between the hydroxyl groups of PVPhKH and different groups (e.g., the carbonyl groups of PVPhKH or the ether groups of PPO³⁰). Because this band intensifies as the quantity of PPO increases, it is very probable that hydrogen bonds are preferably formed between the ether groups of PPO and the hydroxyl groups of PVPhKH.

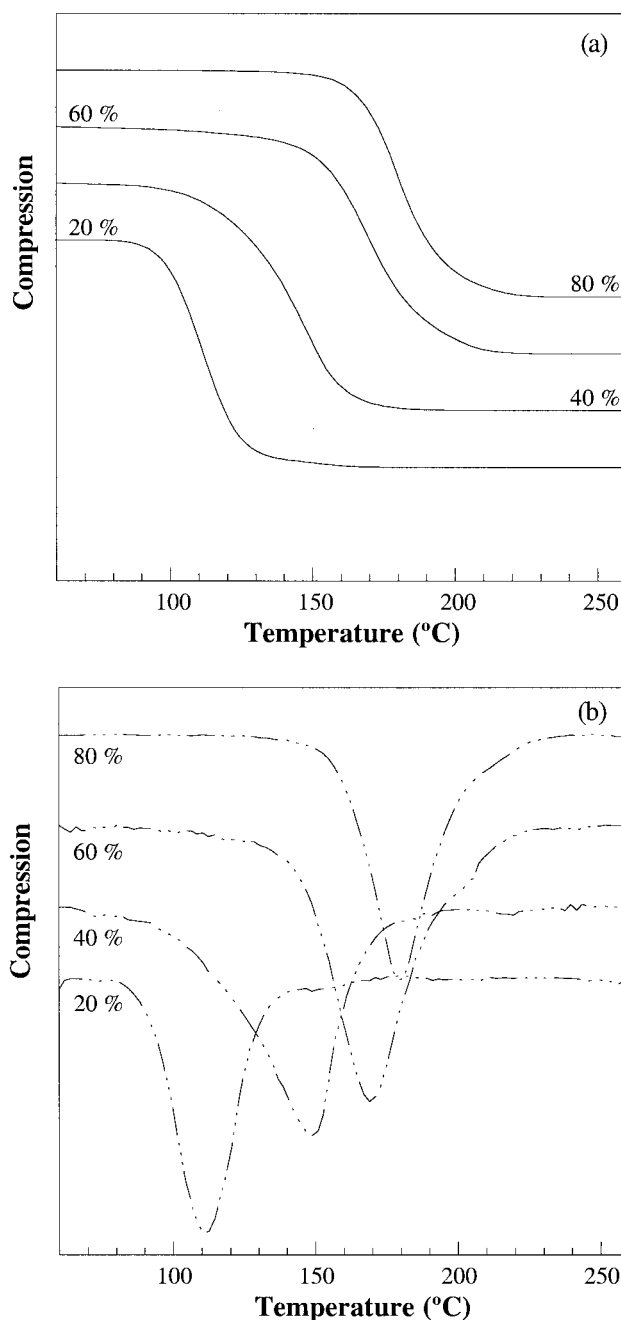


Figure 3 (a) TMA curves of blends with 20, 40, 60, and 80 wt % PPO and (b) derivative curves of the sample thickness change of the TMA curves for these blends.

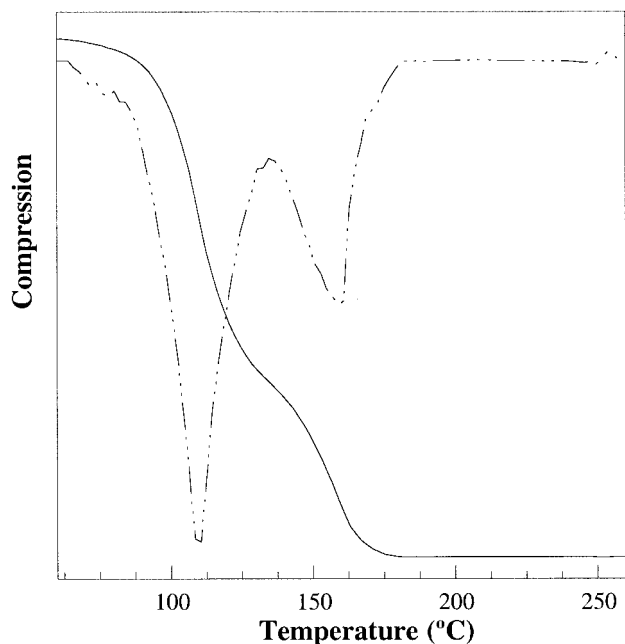


Figure 4 The (—) TMA curve and (---) derivative curve of the sample thickness change of a blend with 50% PPO.

DISCUSSION

PVPhKH is an amorphous proton-donor polymer. Because this polymer has a high content of hydroxyl groups (more than carbonyl groups), it forms mainly hydroxyl–hydroxyl interactions by hydrogen bonding. In contrast, PPO is an amorphous polymer in which the ether groups can interact with other chem-

ical groups of dissimilar polymers. The chemical structure of the two polymers (Fig. 1) shows that the hydroxyl groups of PVPhKH and the ether groups of PPO are complementary. The glass-transition temperature of these polymers is relatively high (major to ambient temperature; Fig. 2). Because there is a big difference between these two glass-transition temperatures, it is possible to study the miscibility behavior of PVPhKH/PPO blends by thermomechanical and calorimetric techniques.

All PVPhKH/PPO blends were transparent as prepared, indicating that they might be miscible. When the glass-transition temperatures of PVPhKH/PPO blends were determined (by DSC and TMA), two-miscibility windows between 10 to 40 and 60 to 90 wt % PPO were resolved. This was because only one glass-transition temperature was detected for these blends (Fig. 3, Table I). Only the blend with 50 wt % PPO has two glass-transition temperatures; therefore, it is immiscible (Fig. 4). This indicates that the $\Delta G_m < 0$ and $(\partial^2 \Delta G_m / \partial \phi^2) > 0$ (where ΔG_m is the Gibbs free energy of mixing and ϕ is the molar fraction of one component) conditions in the composition with 50 wt % PPO are not satisfied.

The Gordon–Taylor equation was originally derived for random copolymers,³¹ but it is frequently used to calculate the T_g of polymer blends:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (1)$$

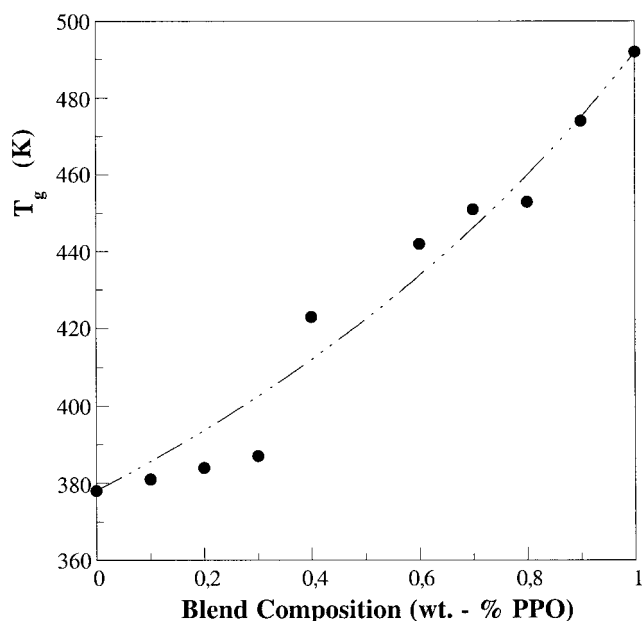


Figure 5 The glass-transition temperatures of the blends as a function of the PPO content and (---) the best fit of the Gordon–Taylor equation.

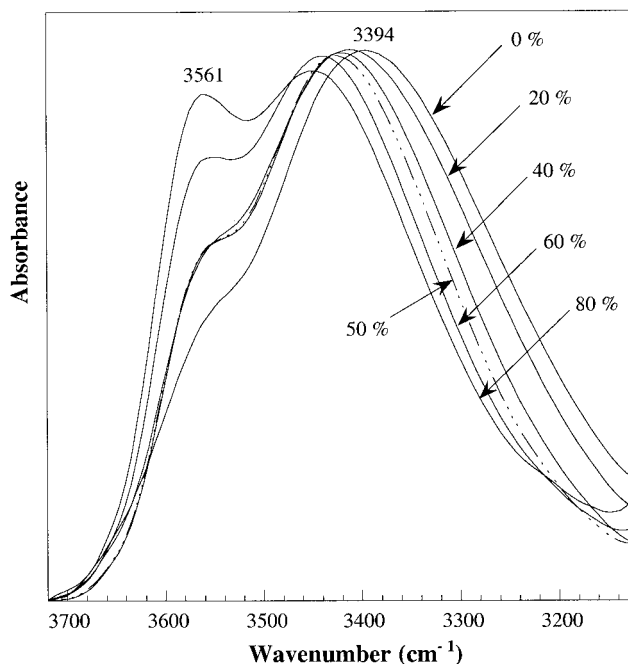


Figure 6 The IR spectra of PVPhKH/PPO blends in the 3120–3720 cm^{-1} region. The blend composition is given as the weight percentage of PPO.

where T_{g1} and T_{g2} are the glass-transition temperatures of the pure components of the blend, w_1 and w_2 are the weight fractions, and k (originally a function of the cubic expansion coefficient and the specific volume) is commonly considered as an adjustable parameter. The evolution of the glass transition of the PVPhKH/PPO blends was described with certain inaccuracy by the Gordon–Taylor ($k = 0.636$) equation (Fig. 5). This equation can successfully describe the T_g behavior for miscible blends with positive or negative deviations if the parameter k is appropriately selected.³² Negative deviations were detected for PVPhKH/PPO blends. The majority of miscible binary polymer blends exhibit negative deviations of the glass temperature from the values predicted by the free volume or flexible bond additive rules. A reasonable explanation is based on the factors that contribute to conformational entropy changes. Several factors could induce an increase of the free volume within the blend: the induced interchain orientation by heterocontact between the components, the mobility in the neighborhood of the contacts, and the probability of related conformational entropy changes.⁵ An increase in the free volume corresponds to a decrease of the blend T_g , which finally can be found below the values predicted by the additive rules, that is, the Gordon–Taylor model.

An IR spectroscopic analysis was performed to study the possible presence of specific interactions in PVPhKH/PPO blends. Because PVPhKH and PPO have complementary groups, the feasibility of hydrogen bond formation between both types of polymers can be suggested. Thus, we highlight the spectral contribution at 3561 cm^{-1} in Figure 6. A weak shoulder is resolved at 3561 cm^{-1} for pure PVPhKH, and this suggests that a self-association via hydrogen bonding is formed between hydroxyl and carbonyl groups in this polymer. When the content of PPO in the blends is increased, this band increases. If only the hydroxyl–carbonyl self-association of the pure PVPhKH contributes to yield the peak at 3561 cm^{-1} , no change would be noted in the spectra of the PVPhKH/PPO blends for this band. Therefore, it is possible that hydrogen bonds were formed between the hydroxyl groups of PVPhKH and the ether groups of PPO. Because a greater quantity of PPO implies more ether groups and the probability of hydrogen bond formation is a function of the quantity of chemical groups, it seems reasonable that the peak at 3561 cm^{-1} increases when the PPO content increases.

The IR spectral behavior of the immiscible blend (50 wt % PPO) is included in Figure 6. A comparison of the peak height at 3561 cm^{-1} of this blend with respect to the same peak of the miscible blend with 40 wt % PPO shows that for the immiscible blend the quantity of hydrogen bonds is not increased. On the contrary, for miscible blends (60 and 80 wt % PPO) a notable

increment is evident in the quantity of hydrogen bonds because the peak at 3561 cm^{-1} is more intense as the PPO content is augmented. Thus, although a hydrogen bond is formed in the immiscible blend, it is very probable that the amount of these is insufficient to create only one phase. This suggests that no completely pure phases form the immiscible blend.

The participation of PPO in forming strong specific interactions in polymer blends has been reported. Opazo et al. reported that in PPO/poly(vinyl pyrrolidone) (PVP) blends there is IR evidence of attractive forces between the ether groups of PPO and the amide groups of PVP.³³ Then, intermolecular interactions have a decisive influence on the phase behavior of PPO/PVP miscible blends.

CONCLUSIONS

With the exception of the blend with 50 wt % PPO, the PVPhKH/PPO blends are miscible in practically the whole range of compositions. The Gordon–Taylor equation fits the experimental PVPhKH/PPO blend T_g s and describes a negative deviation with respect to a simple ruler of mixing. Specific interactions between the chemical groups of PPO and PVPhKH contribute to a negative deviation because heterocontact between the components can produce a change in the entropy of mixing. IR spectroscopy suggests that the hydroxyl groups of PVPhKH and the ether groups of PPO strongly interact via hydrogen bonding.

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