Secondary Relaxations in a Miscible Polymer System: Poly(hydroxy ether of Bisphenol A)/Poly(ϵ-caprolactone) Blends

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ABSTRACT: Dynamic mechanical measurements have been used to study the α- and β-relaxation in blends of Phenoxy (PH) and poly(ϵ-caprolactone (PCL). Single glass transition temperatures between those of the original polymers are obtained. The crystallinity causes a significant influence on the T_g values, giving rise to a positive deviation from the T_g data obtained from DSC measurements. Regarding the β-relaxation, it is observed that the two polymers relax independently of each other in the blend, although the shift of the Phenoxy β-relaxation to lower temperatures as PCL concentration increases is a symptom of the influence of this polymer on the secondary relaxation of Phenoxy. We discuss this influence by comparing the Phenoxy β-relaxations of PH/PCL blends with those of acetylated Phenoxy, PH/PEO blends, and antiplasticized Phenoxy and analyzing the effect of hydrogen-bonding interactions in the rotation of the hydroxy ether groups of Phenoxy.

Introduction

The degree of miscibility of the components in a blend is of crucial importance with respect to its morphology and physical properties. In thermodynamics terms, miscibility means homogeneity down to the molecular level. However, the techniques to probe blend miscibility can only estimate an upper limit in the degree of dispersion, so, from an empirical point of view, the miscibility is a question of scale.

Several studies have been carried out on the miscibility of poly(hydroxy ether of Bisphenol A)/poly(ϵ-caprolactone) (Phenoxy, PH/PCL) blends. From a thermodynamic point of view, the interaction energy density B_{23} between the two polymers, as determined from melting point depression (mpd) studies, inverse gas chromatography (IGC), and FTIR spectroscopy using a theoretical association model,[1] was in all cases negative, regardless of the method employed, indicating the miscible nature of this blend.

A single T_g has been found by several techniques (DSC, torsion pendulum, DMA)[2–4] which indicates that the domain sizes are, approximately, below 15 nm. FTIR spectroscopy probes miscibility at still smaller dimensions. Infrared spectral changes associated with the PCL carbonyl band and phenoxy hydroxyl band were observed. These changes were attributed to a hydrogen-bonding interaction between the PH pendant hydroxyl and the ester carbonyl of PCL.[5]

Dynamic mechanical measurements have been widely used[6,7] to analyze the miscibility of two polymers at the level of the motions involved in α-relaxations. Often, the damping peaks in the intermediate composition are broader in the transition region, suggesting the existence of microheterogeneity due to the different segmental environments. The case of blends of poly(vinyl chloride) (PVC) and butadiene–acrylonitrile rubbers is a good example. Matsuo et al.[8] found that blends exhibited only one relaxation intermediate between those of the two components, although electron microscopy revealed rubber domains less than 10 nm in size. Within this framework, it should be noted that mechanical relaxations at lower temperatures, such as β-relaxations, can reveal information about the intimacy of mixing between compatible polymer molecules, since these secondary relaxations are more sensitive to the small-scale local environment. From a technological point of view, local motion is a factor contributing to bulk polymer properties such as ductility and impact strength. Thus, studies looking into the effect of blending on the small-scale motions of polymers are interesting for both basic and applied research.[9–17]

This paper investigates the α- and β-relaxations of PH/PCL blends, with the aim of determining the effect of specific interactions on the local molecular motions of two polymers which are miscible at the level of motion involved in α-relaxation.

Experimental Section

Materials and Procedures. The blend involved in this investigation is that of poly(ϵ-caprolactone) (PCL), supplied by Polysciences, with a weight-average molecular weight (M_w) of 17 600, and poly(hydroxy ether of Bisphenol A) (Phenoxy, PH), a condensation polymer resulting from the reaction of epichlorohydrin and Bisphenol A, provided by Union Carbide, of M_w 50 700. The M_w's, in both cases, have been obtained by GPC using adequate Mark–Houwink[18,19] constants and tetrahydrofuran (THF) as a solvent.

The pure polymers and their blends were first prepared by casting a 2% solution (w/v) in THF. The samples were finally dried in a vacuum oven at 130 °C in order to make sure that all residual solvent was eliminated.

Samples for dynamic mechanical testing were heated between two platens of a compression-molding press to 120–180 °C and then rapidly transferred to an oven at 42 °C. After maintaining that temperature for 1 day, the thicknesses of the resultant sheets, from which specimens were cut to proper size, were 0.7 mm approximately. The choice of that temperature was made as a criterion to give the same thermal history to the samples, as it is not possible to obtain amorphous samples by quenching them in liquid nitrogen. All blends prepared in this manner were opaque until 70 wt % PH, with the transparency depending on the level of PCL crystallinity developed.

A Polymer Laboratories Ltd. DMTA was used for dynamic mechanical measurements from −140 °C to the end of the α-relaxation peak (T_α), when the samples were amorphous, or until the melting point of PCL (T_m), when the samples crystallized. The scanning rate used was 4 °C/min.

For several compositions, scans at 50 Hz show two β-relaxation peaks (T_β) and the T_α of the blend, while at 1 Hz, only the T_β corresponding to the higher temperature and the T_α of the blend could be seen.

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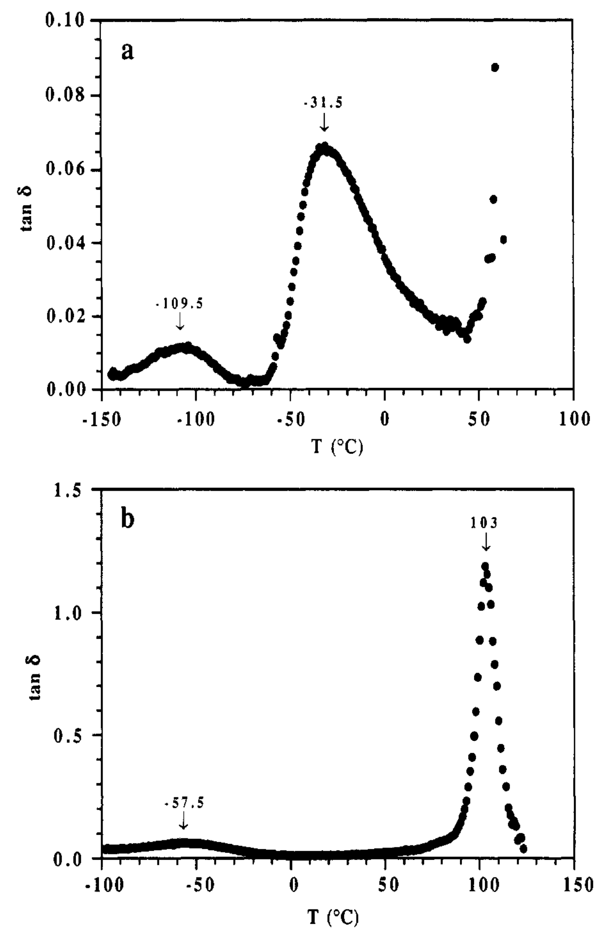

Figure 1. (a) Loss tangent, at 50 Hz, as a function of temperature for pure poly(ε-caprolactone). (b) Loss tangent, at 1 Hz, as a function of temperature for pure Phenoxy.

All of the PH/PCL blends show a single α-relaxation. The temperature location of these peaks varies with blend composition, giving higher temperatures as the amount of PH in the blend is increased. However, samples containing 60 and 70 wt % PH, measured at 1 Hz, and that having 50%, measured at 50 Hz, have such close values of both the T_α of the blend and the T_m of PCL that these peaks appear to split into two overlapping peaks and they can hardly be separated by DMTA measurements.

Additionally, several PH/PEO blends were prepared in order to compare the results with those obtained from DMTA measurements for PH/PCL blends. The PEO was supplied by Polysciences and has a reported M_w of 300 000. The samples were prepared by casting a 2% solution in chloroform. Both the drying conditions and the sample treatment for DMTA studies were identical to those employed for PH/PCL blends. Scans at a frequency of 50 Hz and at a scanning rate of 4 °C/min show a T_β close to that of pure PH and the single T_α of the PH/PEO blend.

Results and Discussion

In Figure 1, the loss tangent, tan δ, is presented as a function of temperature for both of the original polymers, Phenoxy and PCL. The amorphous nature of the Phenoxy is reflected in the high maximum value of tan δ at the α-relaxation which contrasts with the small peak observed for highly crystalline PCL. The Phenoxy and PCL α-relaxations located at +103 and −31.5 °C, respectively, are regarded as the glass transition temperatures, whereas less prominent, lower temperature β-relaxations are due to local molecular motions such as the motion of the methylene sequence in the case of PCL.[9] The Phenoxy β-relaxation at −57.5 °C is due to hydroxy ether groups only, since the diphenyl propane motion is resolved as a separate relaxation taking place at very low temperatures.[20,21] We will return to this subject later in the text.

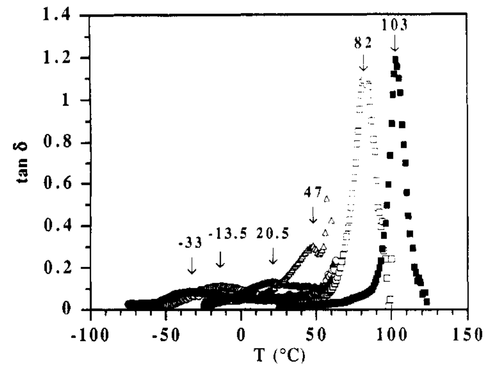

Figure 2. α-Relaxations of PH/PCL blends at 1 Hz: (●) 0/100; (○) 10/90; (▲) 30/70; (△) 50/50; (□) 90/10; (■) 100/0.

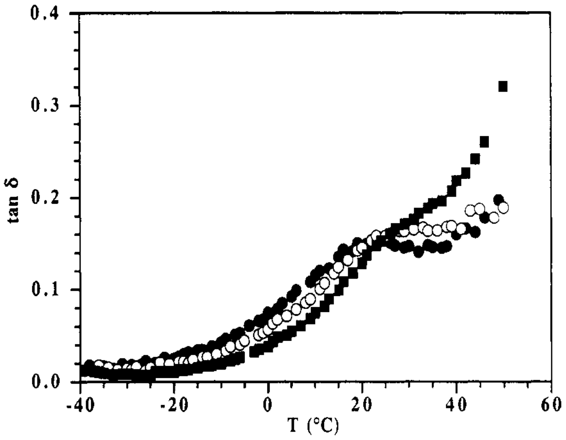

Figure 3. Overlapping of the melting peak of the crystalline phase of PCL with α-relaxation of a 40/60 PH/PCL blend. Temperature scans at frequencies (●) 0.3, (○) 3, (■) 30 Hz.

In order to clarify the presentation of the dynamic mechanical data of the blends, we have separated the range of temperatures corresponding to the glass transition temperatures from that of β-relaxations. In Figure 2, we observe single glass transition temperatures between those of the original polymers, an experimental evidence of miscibility. Other compositions also studied have been omitted for clarity, except blends containing 60 and 70% Phenoxy, which have not been included due to the overlapping of the melting peak of the crystalline phase of PCL with the α-relaxations of the blends. This effect is observed in Figure 3, where we present the spectra of the blend 40/60 PH/PCL at various frequencies. Glass transition temperatures can be detected, although the increase of tan δ as the crystalline phase melts tends to mask them, especially at high frequencies.

Glass transition temperatures are plotted as a function of blend composition in Figure 4, where literature data[2,4] are also presented. For samples ranging from pure Phenoxy to 70% Phenoxy, the differences between the reported glass transition temperatures are not large and can be attributed to the use of different experimental techniques. We emphasize the fact that samples within this range of Phenoxy content do not show a melting peak (crystallization is completely inhibited), as has been shown in a previous work.[2] The circumstances are different for blends with a content of PCL beyond 30%, and the strong deviation of our dynamic mechanical data with respect to the T_g data obtained from DSC measurements after quenching must be interpreted on the basis of the effect of the thermal treatment on the crystallinity of the blends. In previous works[2,3] it has been stated that, if samples are quenched, the crystallinity per unit mass of PCL in the blend is lower than that in the present case, where blends

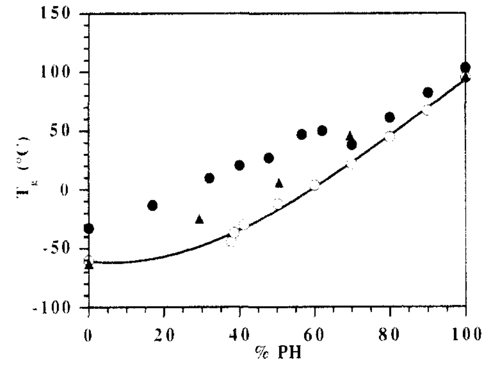

Figure 4. Glass transition temperatures versus composition for PH/PCL blends: (●) this work (1 Hz); (▲) DMTA data ref 4; (-○-) DSC data of ref 2.

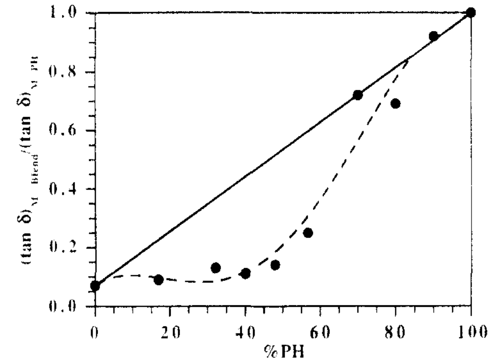

Figure 5. Variation of the values of the loss tangent at the maximum of the α peak, normalized with respect to the maximum of the α peak of pure Phenoxy, $(\tan\delta)_{M\ Blend}/(\tan\delta)_{M\ PH}$, with composition.

have been annealed (see the Experimental Section), which gives rise to an increase of crystallinity; therefore, the PCL concentration of the amorphous phase of the blend is depleted. In our case, we have taken into account this fact, and the real PCL concentration of the amorphous phase of the blend has been calculated. However, we can explain the positive deviation observed in Figure 4 as a consequence of the restriction of the crystallites to the motion of amorphous sequences. Actually the glass transition is a manifestation of the amorphous state, and therefore the glass transition temperatures of the annealed blends are close to those of quenched blends of higher content in Phenoxy. Similar differences between the glass transition temperatures of annealed and quenched blends have been reported by Robeson et al. in the case of PBT/Phenoxy[22] and PEO/Phenoxy[23] blends. The effect of crystallization on the dynamic mechanical properties of the blends is also observed in Figure 5 which shows the variation of the relative peak intensities of the α-relaxation, $(\tan\delta)_{M\ Blend}/(\tan\delta)_{M\ PH}$, with composition. The deviation with respect to the additive rule from 70% Phenoxy downward is a consequence of the reduction of the amorphous phase that, as is known,[7] produces a decrease in the value of $(\tan\delta)_{M\ Blend}/(\tan\delta)_{M\ PH}$.

Regarding the secondary transitions, in Figure 6 it is seen that the two polymers relax independently of one another, so we can assert that these miscible blends behave like two phase systems at the level of the motions involved in β-relaxations. In Figure 7, we note that, whereas the PCL β-relaxation temperature remains unchanged for all the compositions, the Phenoxy β-relaxation shifts to lower temperatures as the PCL concentration increases. These results suggest that the motions involved in the −110 °C transition, typical for polymers containing $(-CH_2-)_n$, $n > 4$, groups such as PCL, are not affected by Phenoxy chains,

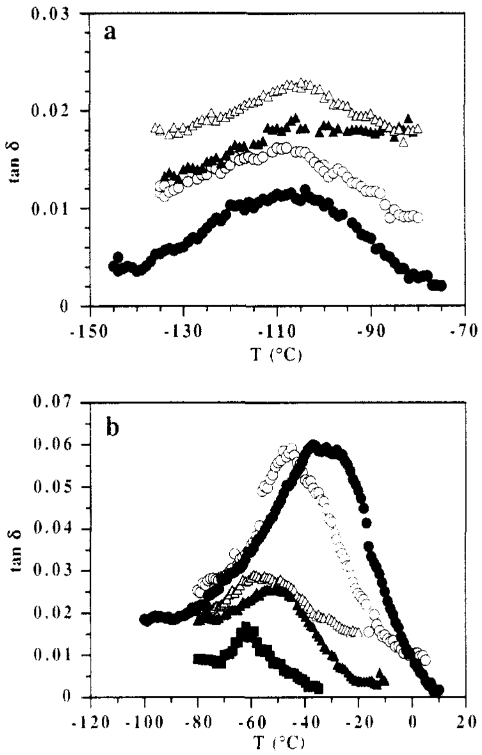

Figure 6. (a) β-Relaxations of PCL at 50 Hz for PH/PCL blends: (●) 0/100; (○) 30/70; (▲) 50/50; (△) 70/30. (b) β-Relaxations of PH at 50 Hz for PH/PCL blends: (●) 100/0; (○) 90/10; (▲) 70/30; (△) 50/50; (■) 30/70.

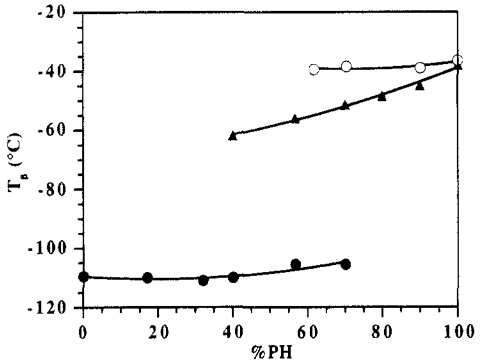

Figure 7. β-Relaxation temperatures, at 50 Hz, as a function of composition: (▲) Phenoxy β-relaxation in PH/PCL blends; (●) PCL β-relaxation in PH/PCL blends; (○) Phenoxy β-relaxation in PH/PEO blends.

notwithstanding that the Phenoxy local chain motions are affected by PCL chains.

In order to discuss this PCL influence on the secondary relaxation of Phenoxy, we have compared in Figures 7 and 8 our experimental results with those of the following cases: *Case I.* Effect of the concentration of hydroxy ether groups upon the β-relaxation peak temperature of Phenoxy.[21] *Case II.* Binary blends of the miscible PH/PEO system.[23] *Case III.* Antiplasticization of Phenoxy by the polar diluent 4′-[(2-hydroxy-3-Phenoxypropyl)oxy]acetanilide.[24]

The hypothesis of a plasticization due to PCL methylene sequences ought to be considered. A dilution effect leads to a decrease in the concentration of hydroxy ether groups, which according to case I (Figure 8) gives rise to a decrease in the Phenoxy β-relaxation temperature. Actually, it is believed that hydrogen-bonding interaction between the pendant hydroxyl group plays an important role in pure Phenoxy β-relaxation, hindering the crankshaft type rotation of the $-CH_2CH(OH)CH_2O-$ group. Within this

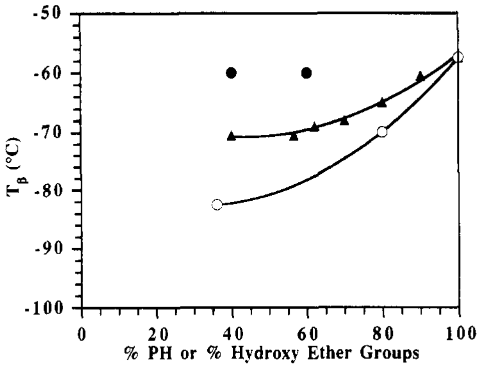

Figure 8. Variation of the β-relaxation temperature, at 1 Hz, with composition or % hydroxy ether group: (▲) Phenoxy β-relaxation in PH/PCL blends (this work); (●) Phenoxy β-relaxation in PH/PEO blends (ref 23); (○) Phenoxy β-relaxation in pure and acetylated Phenoxy (ref 21).

framework blending Phenoxy with PCL should have the same effect as decreasing the concentration of hydroxy ether groups. However, when we compare the data from the PH/PCL blends with those of the acetylated Phenoxy resin, we observe that, for the same hydroxy ether group concentration, the β-relaxation temperatures of the blends are higher than those of the acetylated Phenoxy. This means that the shift of Phenoxy β-relaxation in PH/PCL blends to lower temperatures is not a consequence of a shear dilution effect. Furthermore, cases II and III have in common a temperature-independent Phenoxy β transition with poly(ethylene oxide) and antiplasticizer contents, respectively (see our Figures 7 and 8 and Figure 2 of ref 24). The antiplasticization of Phenoxy by 4′-[(2-hydroxy-3-Phenoxypropyl)oxy]acetanilide (EPPHAA) is attributed by Stevenson et al.[24] to interactions between the polymer and the solvent, probably through hydroxyl groups of the Phenoxy. For their part, Coleman and Moskala[5] have shown that, in PH/PEO blends, hydrogen-bonding interactions are stronger than those occurring in pure Phenoxy. Thus, in both cases II and III, the hindrance of –OH groups is increased as the second component (PEO or EPPHAA) increases, with the crankshaft type rotations being restricted. This can lead to the total suppression of the lower-temperature relaxation of the Phenoxy.

Analyzing the results of Figures 7 and 8, we can see that the variation of Phenoxy T_β in PH/PCL blends is intermediate between case I (shear dilution) and cases II and III where hydrogen-bonding interactions restrict mobility. In fact Coleman and Moskala[5] have demonstrated that there is also an intermolecular hydrogen-bonding interaction between the pendant hydroxyl group of Phenoxy and the PCL carbonyl group, although this is weaker than the interactions in the self-associated Phenoxy. Consequently we envisage the hypothesis that the shift of Phenoxy β-relaxation in PH/PCL blends to lower temperatures is not a shear plasticization effect of the methylene group of the PCL but can be due to the weak hydrogen-bonding interactions between both polymers.

Analysis of the β-relaxation peaks of both PH/PCL and PH/PEO blends allows us to study further the questions posed above. In Figure 9, we compare the relaxation peaks for 50/50 blends of both systems, the only difference being the shift to higher temperatures of T_β in PH/PEO blends. An appropriate measure of the size of the β-relaxation peaks is given by the so-called "relaxation strength",[13,16] which corresponds to the area under the tan δ curves plotted against inverse absolute temperature:

$$R = \int_{\text{peak}} \tan\delta \; \mathrm{d}(1/T) \qquad (1)$$

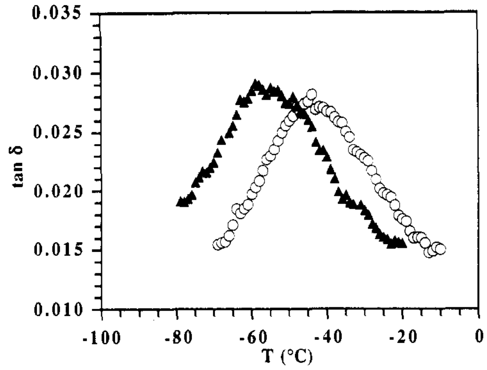

Figure 9. Phenoxy β-relaxations, at 50 Hz, for (▲) 50/50 PH/PCL and (○) 50/50 PH/PEO.

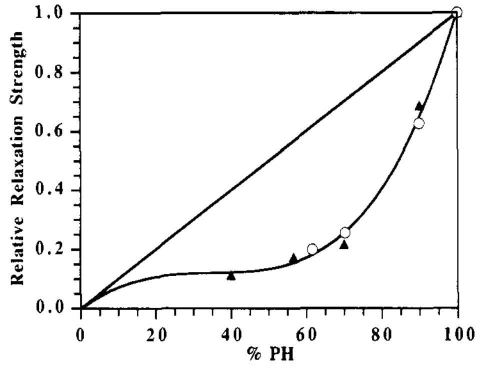

Figure 10. Normalized relaxation strength, defined in eq 1, at 50 Hz, of Phenoxy β-relaxations as a function of composition: (○) PH/PEO blends; (▲) PH/PCL blends.

Measures of R were possible since β transitions for each component were plainly separated from other transitions not to have their areas affected.

Figure 10 shows the relative relaxation strengths, i.e., the ratio of the relaxation strength in the blend to that of the corresponding homopolymer, of the Phenoxy β transition in the PH/PCL and PH/PEO blends. Data of both blends can be adjusted to one curve which deviates negatively from the additive line. The Phenoxy β-relaxation is thus significantly suppressed relative to the additive rule of the simple dilution. This behavior of Phenoxy-based miscible blends involving hydrogen-bonding interactions between the polymers resembles the antiplasticization effect of the polar solvent EPPHAA which, added in a proportion of 30 pph to the Phenoxy, suppresses the β-relaxation.[24]

Concluding Remarks on Secondary Relaxations

Comparing the Phenoxy β-relaxations of PH/PCL blends with those of acetylated Phenoxy resin, PH/PEO blends and antiplasticized Phenoxy, the following features are observed:

(a) The Phenoxy β-relaxation of PH/PCL blends shifts to lower temperatures as the proportion of PCL increases, following an intermediate trend between the dilution effect and the strong hindrance effect on local chain motions observed in PH/PEO blends and EPPHAA/Phenoxy systems.

(b) The relaxation strengths of the Phenoxy β peaks for PH/PCL and PH/PEO blends show a negative deviation from the additive line, displaying a partial β-relaxation suppression effect.

It is proposed that these features are the result of the effect of hydrogen-bonding interactions in the rotation of the hydroxy ether groups of Phenoxy.

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