

A STUDY ON POLY(ETHYLENE OXIDE)/ POLY(VINYL ACETATE) BLENDS*

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ABSTRACT

Melt blends of poly(ethylene oxide) (PEO) and poly(vinyl acetate) (PVAc) were prepared and studied by Torsional Pendulum Analysis (TPA) and Fourier Transform Infrared (FTIR). Two glass transitions were found in these blends. The lower T_g corresponds to the segmental motion in the pure PEO. The dependence of the position and broadness of the higher T_g on composition of the blends indicates that the two components are compatible in the amorphous phase with micro-heterogeneity. These T_g values observed from mixed PVAc/PEO phase are much higher than that calculated from Fox equation. The comparison of the blends quenched and annealed from melt implies that PVAc mixed with PEO at the segmental level on molten state and the deviation of T_g values from Fox equation could be due to variation of the blend's composition by crystallization of part of the PEO component.

Further indication that the blends are compatible down to the level of chain segments and that there are specific interactions between PVAc and PEO molecules comes from the analysis of FTIR spectra of the blends and the solution of PVAc in diethylene glycol dimethyl ether.

Although the amorphous-amorphous polymer blends have been the subjects of numerous studies in the past, only a few studies on the amorphous-crystalline polymer blends have been reported. Based upon enthalpy consideration, Bohn^[1] indicated that compatible blends of one crystalline polymer with any other polymer were unlikely except for the remote possibility of mixed crystal formation. However, soon after 1968, several studies showed compatible or conditionary compatible polymer blends could be obtained in the amorphous state in which one component was crystallizable, such as poly(vinylidene fluoride)-poly(vinyl acetate)^[2], polycaprolactone-poly(vinylidene chloride)^[3, 4], isotactic polystyrene poly(phenylene oxide)^[5-7], poly(vinylidene chloride)-poly(methyl methacrylate)^[8], polyester-polycarbonate^[9-12] etc. . According to the solubility parameter method and Flory theory, Sanchez predicted that PEO was compatible with PVAc^[13]. Elorza et al. reported an average interaction parameter of $-0.538 (\pm 0.053)$ for 50/50 weight ratio PEO/PVAc blend at 100°C by inverse gas chromatography^[14].

In this paper the dynamic mechanical properties-temperature spectra of PVAc/PEO blends with varying composition and thermal history were obtained by using Torsional Pendulum Analysis (TPA) and showed the compatibility of PVAc and PEO in amorphous state. Also the intermolecular interactions between these two polymers, which caused the blend compatibility, were characterized by Fourier Transform Infrared (FTIR) spectra.

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EXPERIMENTAL

1. *Materials and blends preparation*

PVAc ($M. W. = 146,000$) was obtained from Beijing Organic Chemicals Co. and the PEO sample, from Dupont, has $M. W.$ of 300,000. Thin films of PVAc, PEO and their blends containing 0.9–0.1 weight fraction of PEO were prepared by casting their 1,2-dichloroethane solution (about 5% by weight) onto glass plates. After the majority of the solvent had slowly evaporated, the films were transferred to a vacuum dessicator to remove residual solvent completely. The thickness can be adjusted by quantity of the solution. The films were sufficiently thin so that the IR band intensities are within the absorbance range for which Beer-Lambert law is obeyed. For TPA, the films were about 0.3 mm thick and melted for 15 min in the oven at $100 \pm 2^\circ\text{C}$, then annealed at room temperature or quenched in liquid nitrogen. As soon as the quenched sample was hold in the clips which had been previously cooled by liquid nitrogen, the measurements started immediately.

2. *TPA measurement*

The shear modulus G' and the logarithmic decrement Δ of these samples were determined with a home-made TPA instrument at 1–5 cps (the frequency near glass transition temperature is about 1 cps). A heating rate of $1^\circ\text{C}/\text{min}$ was used in all cases.

3. *DSC*

A Shimadzu DT-30 differential scanning calorimeter was used to measure PEO melting point and melting endotherms. DSC conditions were $20^\circ\text{C}/\text{min}$ on a 20 mJ/sec with about 6 mg sample. All measurements were calibrated against indium.

4. *FTIR spectra*

Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were obtained on a Nicolet 7199B FTIR spectrometer. Thirty-two scans at a resolution of 1 cm^{-1} were signal-averaged. The frequency scale was calibrated internally with a reference helium-neon laser to an accuracy of 0.2 cm^{-1} . Absorbance subtraction technique was applied to eliminate the spectrum of a pure component from the spectra of the blends. The resultant difference spectra was then compared with that of another pure component to extract the information about spectral changes of the components after blending. In order to prove the variations of the band frequency, shape and intensity in these difference spectra reflecting the existence of specific interactions between PEO and PVAc molecules, a concentrate solution of PVAc in diethylene glycol dimethyl ether (DGDE) with about 50% weight concentration was prepared and its FTIR spectrum was obtained. By subtracting the spectrum of pure solvent DGDE from that of the solution, the difference spectrum was obtained and compared with that obtained by eliminating the spectrum of pure PEO from that of PVAc/PEO blends.

RESULTS AND DISCUSSION

1. *Dynamic mechanical properties*

Dynamic mechanical properties of PEO are affected strongly by methods of film preparation and thermal history of samples. Table 1 lists T_g values and melt endotherms of PEO films casting from solution or melting followed by annealing or liquid nitrogen quenching. The heat of fusion of crystalline PEO is taken to be 196.6 J/g to calculate the degree of crystallinity which is listed in Table 1 also. It is clear that the effects of different methods in film preparation and thermal history on T_g are mainly due to variation of degree of crystallinity in different samples. The stress occurring in the amorphous molecular chains during crystallization may elevate T_g value. Besides, higher regularity of aggregates, higher restriction for the segmental motion of amorphous parts between the micro-crystalline regions and therefore higher glass transition temperature is observed. In addition, because of the very high crystallization rate of PEO and film thickness, the quenched film still exhibits a considerable degree of crystallinity^[15].

Table 1 Effect of methods of film preparation on T_g and crystallinity of PEO

Film preparation	Quenching	Annealing	Casting from solution
T_g (°C)	-62	-55	-41
H_m (J/g)	90.9	105.5	141.0
X_c (%)	45.8	53.7	71.7

Figure 1 shows $G'-T$ (1a) and ΔT (1b) curves for melted followed annealing PEO/PVAc blends with various compositions. As can be seen in Figure 1, each blend of PEO/PVAc melted and then annealed shows two distinct glass transitions. One of them locates at -55°C and is not a function of blend composition. This transition is very weak and almost unable to be detected in case of PEO content less than 50%. It appears as a "shoulder" only in case of PEO content above 50% and is getting rather significant with increase of PEO content. This transition can be associated with the segmental motion in the amorphous parts between or inside PEO micro-crystalline regions. In addition, the magnitude of this dynamic mechanical loss peak is much less than that in pure polymer even though the weight percentage of PEO in the blends has been considered. However, thermal analysis indicates that the crystallinity of PEO in the blends is basically a linear function of weight percentage of this polymer in the blends^[15]. Therefore, only a few fraction of amorphous PEO segments exists in the amorphous phase of pure PEO and most of them mix with PVAc segments to form a miscible amorphous phase.

The relationship between another glass transition and composition of PEO/PVAc blends is more complicated. When PEO content is less than 50%, this transition in the blends locates at the same position as the loss peak in unblended PVAc, or even a little higher for

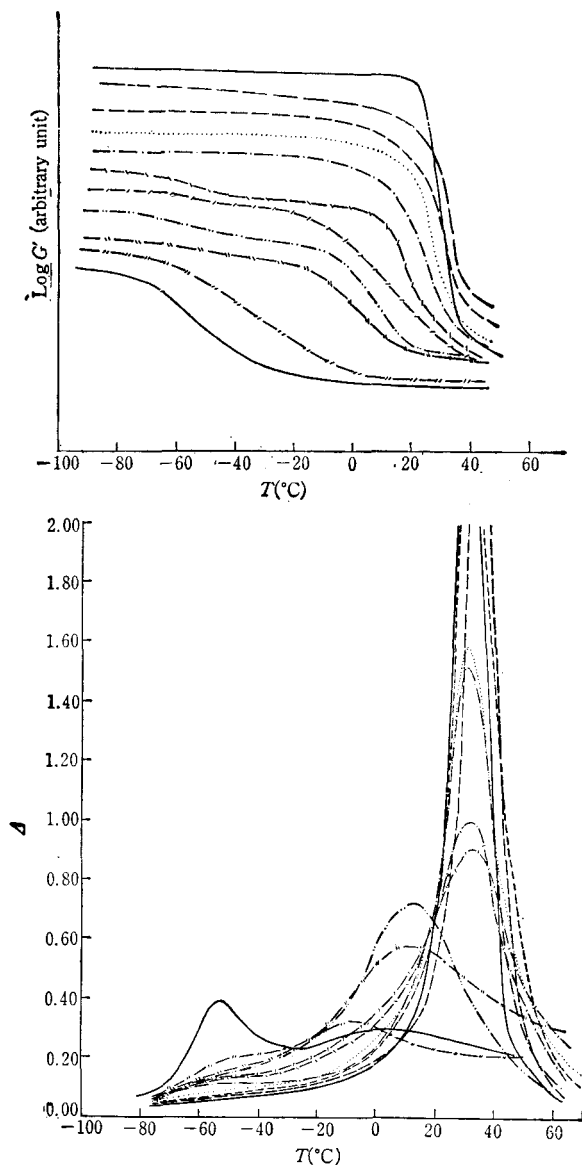


Fig. 1 Dynamic mechanical behavior of PEO/PVAc blends
(a) $G'-T$ spectrum (b) $\Delta-T$ spectrum

10–20 wt% of PEO component. Its width also shows a little increase with increasing PEO content. However, for the blends with more than 50% of PEO component, the position of this dynamic mechanical loss peak shifts towards lower temperature from the T_g of unblended PVAc component as PEO content in the blends increases. This result is interpreted as evidence for existence of a compatible phase in which PEO and PVAc mixed on segmental scale. In this case, common or cooperative motion of PEO and PVAc chain segments in the mixed amorphous phase results in the shifting of T_g values of the blends towards lower temperature from the T_g of unblended PVAc component. However, it was observed that the width of

this T_g peak increases with increasing PEO blend composition which suggests the existence of micro-heterogeneity in composition in the mixed PEO/PVAc phase. The micro-heterogeneity may be related to the crystallization process of PEO from melted blends. Figure 2 shows the glass transition temperature as a function of composition for PEO/PVAc blends. The broken curve was drawn from Fox equation $\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$ while the solid curve was from experiments. It is clear that the experimental T_g -composition curve is far above that calculated from Fox equation. In their studies on poly(vinylidene fluoride)/poly(methyl methacrylate) blends and poly(butylene terephthalate)/poly(hydroxy ether of bisphenol A) blends respectively, Nishi^[16] and Robeson et al.^[17] found the similar deviation from Fox equation and attributed to increasing the content of high T_g component in the amorphous phase resulting from crystallization of a great deal of low T_g component from the mixed amorphous phase. However, Akiyama et al.^[18], in the study on the blends of nitrocellulose and PVAc or EVA resins, and Smith et al.^[19] in their study on the PEO/poly(acrylic acid) blends, found the existence of the maximum in the T_g -composition curves for above blends. These observations have been attributed to the existence of the specific strong interactions between two components in the blends.

In order to estimate the effects of above two factors on the glass transition temperature, the ΔT spectra of the quenched and annealed samples of the blend containing 30 wt% PEO are shown in Figure 3 and have been compared with each other. For the quenched sample, which was obtained by quenching the melted blend into liquid nitrogen and immediately meas-

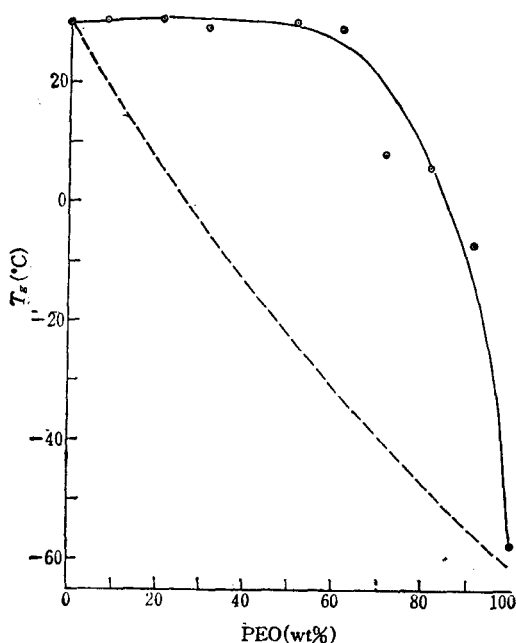


Fig. 2 Glass transition temperature as a function of composition for PEO/PVAc blends
Solid curve: experimental values
Broken curve: calculated values from Fox equation

ured its $\Delta-T$ spectrum started from about -100°C , a broad transition with a distinct shoulder at the lower temperature side, suggesting two overlapping peaks, has been observed. The higher temperature peak may appear due to change of the amorphous composition after rapid crystallization of partial PEO component while the temperature was elevated above the lower temperature peak. When the $\Delta-T$ spectrum of this sample was re-determined after slowly cooling it from temperature above PEO melting point, the lower temperature peak (shoulder) vanished and the higher temperature one shifted to even higher. The results indicated that,

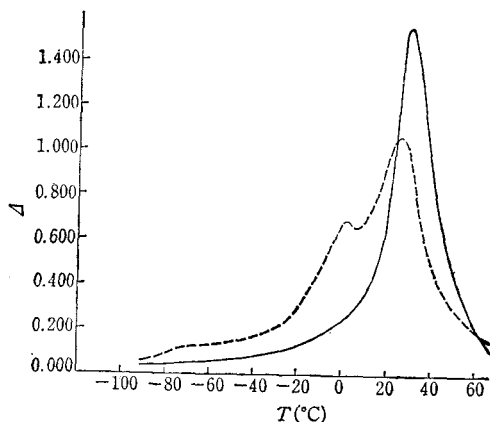


Fig. 3 $\Delta-T$ spectra for PEO/PVAc (30/70 by weight) blends from melt followed by quenching (---) or annealing (—)

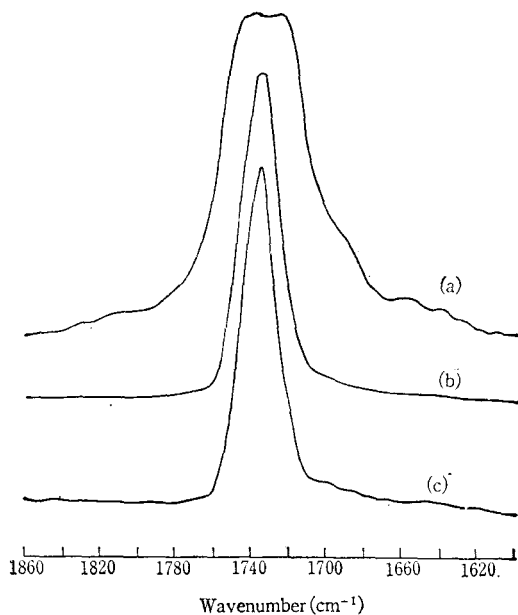


Fig. 4 Carbonyl stretching band for
(a) Pure PVAc; (b) PEO/PVAc=30/70 by weight;
(c) PEO/PVAc=70/30 by weight

in the case of low PEO content, change of amorphous composition due to crystallization of PEO component, besides the specific interaction, really is one of the factors shifting the glass transition temperature of the blends.

2. FTIR

The specific strong interchain interactions between PEO and PVAc components may be the origin favouring the compatibility on segmental scale for the two components and another factor raising the T_g of the blends. In order to prove and characterize the existence of the specific interaction, the infrared spectra of PEO/PVAc blends containing 30 and 70 wt% PEO from melt followed by annealing were measured by using FTIR spectrometer. Figure 4 (a), (b) and (c) show the carbonyl stretching band in the spectra of unblended PVAc and the blends containing 30 and 70 wt% PEO respectively. No frequency shift for the carbonyl band of the PVAc for the blends is observed. However, the band shape is much sharper for the blended than the unblended sample. The width at half-height of the carbonyl band for the blends changes to about 23 cm^{-1} from about 44 cm^{-1} for pure PVAc. Similar variation in carbonyl band shape was observed for the vinyl acetate-vinyl chloride random copolymers^[20]. The FTIR spectra in the range $1600\text{--}600\text{ cm}^{-1}$ for (a) pure PVAc (b) pure PEO and (c) their blend (PEO/PVAc = 30/70) are shown in figure 5.

Figure 6 shows the difference spectra obtained by the digital subtraction of the absorbance spectra in figure 5. Figure 6 (a) is the FTIR difference spectrum obtained by subtracting the spectrum of pure PVAc (Figure 5 a) from that of the blend (Figure 5c) until the bands at 1435 , 796 , 631 and 605 cm^{-1} were reduced to the base line. The following differences are noticed by comparing the difference spectrum Figure 6 (a) with that of pure PEO (Figure 5b): First of all, the intensity of the band at 1241.1 cm^{-1} in Figure 6 (a) is much higher than the corresponding band in Figure 5 (b). It can be attributed to the great changes of shape, position and absorbance of the —C(O)—O— stretching band for the blended PVAc component from the unblended PVAc. The band frequency shifts to 1241.1 cm^{-1} for the blended PVAc from 1243.8 cm^{-1} for pure PVAc. The band shape is much shaper and the absorbance increases for the blends. The second difference in the spectra of PEO for blended and unblended samples is that the absorbance of C—O stretching band (1111.9 cm^{-1}) of PEO increased after blending with PVAc. The third difference between the blended and unblended PEO spectra is that there are two bands at 1023.2 and 1373.3 cm^{-1} appearing in the blended PEO spectra, which can be attributed to —O—CH— stretching and methyl deformation vibrations in the ester groups of PVAc component. Obviously, the above results all indicate that the —C—O— stretching band for blended PEO component, the C=O stretching, —O—CH— stretching and the —CH_3 deformation bands for the ester groups in blended PVAc component, change their intensity position and (or) shape from the corresponding bands in unblended components. Also these changes were proved by subtracting the spectrum of unblended PEO (Figure 5b) from the blended PEO spectrum (Figure 5c) and comparing the obtained blended PVAc spectrum with unblended PVAc spectrum.

Besides the variations in group vibrational force field due to compatibility, the variations in refractive index also may result frequency shifts observed in the spectra of polymer blends.

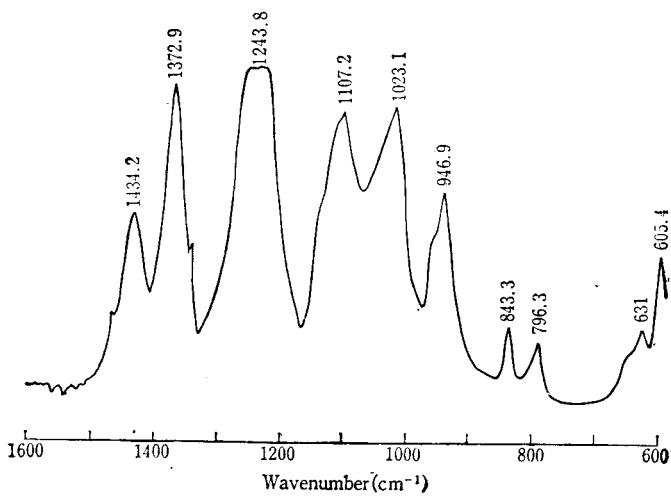
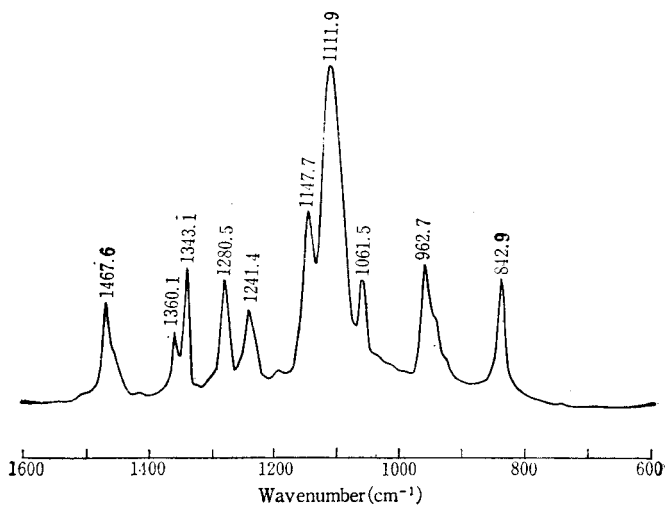
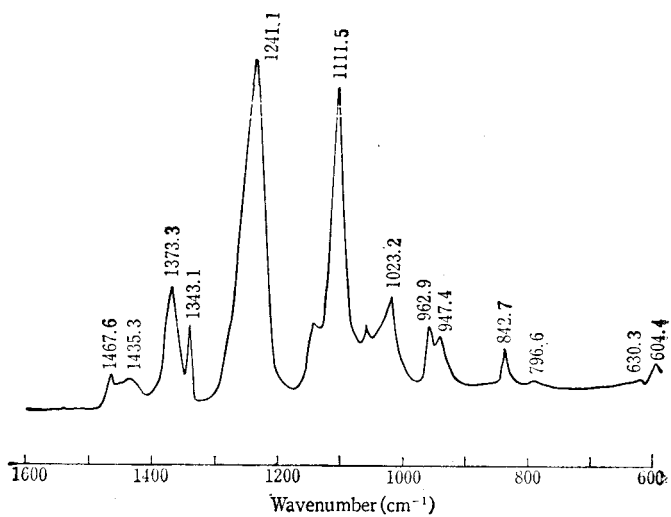


Fig. 5 FTIR spectra in the range 1600–600 cm^{-1}
 (a) Spectrum of pure PVAc; (b) Spectrum of pure PEO;
 (c) Spectrum of PEO/PVAc blend (30/70 by weight)

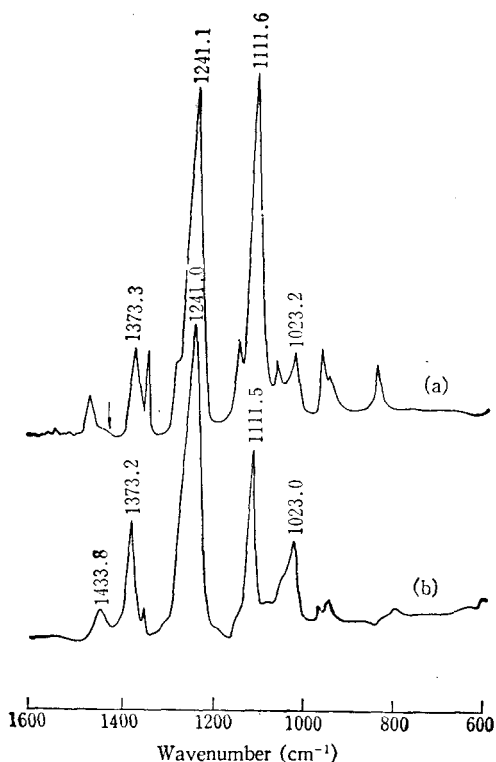


Fig. 6 FTIR difference spectra in the range 1600–600 cm^{-1}

- (a) Difference spectrum of PEO component in the blend containing 30 wt% PEO;
 (b) Difference spectrum of PVAc component in the blend containing 30 wt% PEO

Therefore, the frequency shifts will not be indicative of intermolecular interactions. In order to prove that the frequency shifts observed in the spectra of the blended are due to the inter-chain interactions existed in the compatible PVAc/PEO blends, the solution containing 50 wt% PVAc was prepared by dissolving PVAc in organic solvent diethylene glycol dimethyl ether (DGDE), whose structure is similar to PEO, and used to obtain FTIR spectrum.

By subtracting the solvent DGDE spectrum from that of the solution, the obtained difference spectrum is shown in Figure 7 and compared with pure PVAc spectrum (Figure 5a). A shift of $-\text{C}(\text{O})-\text{O}-$ stretching band to 1240.2 cm^{-1} from the original 1243.8 cm^{-1} in unblended PVAc and a decrease of band width can be observed clearly. These changes occurring in the spectrum of PVAc/DGDE solution were consistent with that of PVAc/PEO blends. Therefore, in conclusion, the strong intermolecular interactions between ester groups of PVAc chains and $-\text{CH}-\text{O}-$ groups of PEO chains in the blended amorphous phase exist and cause the compatibility of the two components on segmental scale and raise the T_g values of the blends from Fox equation.

In the study of the FTIR difference spectrum of the blends containing 70/30 wt% PEO/PVAc, same results have been obtained.

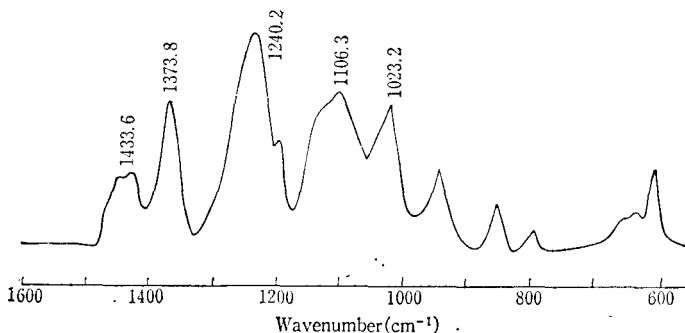


Fig. 7 The difference spectrum obtained by subtracting the spectrum of pure solvent DGDE from the spectrum of the solution

CONCLUSION

1. In the PEO/PVAc blends obtained from melt exist a PEO crystalline phase and an amorphous phase exhibiting two glass transition temperatures.
2. The position of the weak glass transition at lower temperature is independent on the composition of the blends. This transition can be associated with the segmental motion in the PEO amorphous phase between micro-crystalline regions.
3. The main transition is that at higher temperature, whose intensity, broadness and position varied with the composition of the blends. The T_g -composition curve is far above that calculated according Fox equation. This glass transition indicates that the amorphous phase in the blends mainly consists of partial compatible PEO and PVAc.
4. The results obtained from FTIR difference spectra of PVAc/PEO blends and PVAc/DGDE solution indicate the existence of specific intermolecular interactions between ester groups of PVAc chains and $-\text{CH}-\text{O}-$ groups of PEO chains in the blended amorphous phase, which may be the origin causing the compatibility of the two polymers on segmental scale and one of the factors raising the T_g values of the blends.

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