

# Characterization by Fourier Transform Infrared Spectroscopy of Polyethylene Adipate/Cholesteryl Palmitate Blends

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Received 5 June 2003; accepted 25 March 2004

DOI 10.1002/app.21024

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** FT-IR spectroscopy has been employed to study compatibility, melting, and crystallization of the polyethylene adipate (PEA)/cholesteryl palmitate (CP) blends. The changes in FT-IR spectra were followed by controlled rate of heating and cooling. The bands corresponding to the crystalline structure have been assigned. The accuracy of the transition temperature determination has been improved by fitting the curve of the integral absorbance dependence on temperature with a Boltzmann function. From dependence

of the transition temperatures on the composition of the blend, it has been established that for each mixing ratio a certain mass fraction of CP should be dissolved in the PEA matrix. The PEA/CP blends behave as a phase-separated system with partial miscibility. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1156–1163, 2004

**Key words:** FT-IR spectroscopy; polyethylene adipate; cholesteryl palmitate; melting; blend

## INTRODUCTION

Physical blends containing macromolecular compounds and low-molecular-weight liquid crystals (LCs) have important applications: LCs are used as reinforcements for amorphous polymers or in display devices.<sup>1,2</sup>

The addition of LCs to amorphous polymers determines improvements in the mechanical properties of polymeric composites. Due to their mechanical anisotropy, which results from molecular alignment, the LC molecules may orient themselves in the shear field of a processing operation. Upon cooling, this orientation may impart to the composites some improvements in the mechanical properties similar to that found with fibrous reinforcements, but with the advantage that the additive acts also as a plasticizer. The glass transition temperature and the viscosity of the blend are lower than those of the starting polymer.

Liquid crystal displays are interesting due to the characteristics of the obtained devices: low power, low voltage, compactness. In these devices polymer matrices could be used as noninteractive supports. In the dispersions containing polymers and LCs, the polymer content could vary from 80 to 0.5% depending on

the application and the chosen polymer.<sup>4</sup> In our study, cholesteryl palmitate (CP) was chosen because it undergoes phase transitions at moderate temperatures. Thus it was not necessary to heat the blends to temperatures at which polymers might undergo thermal degradation, in particular at ester groups; also at certain domains of composition the degree of compatibility could be higher as a result of intermolecular interactions between compounds.

FT-IR spectroscopy constitutes a valuable technique to study both low-molecular-weight LCs and polymer liquid crystals<sup>5–7</sup> (especially polyurethanes) and also for estimation of interactions and morphological changes in polymer blends such as poly(arylene phosphine oxide)/bisphenol A poly(hydroxy ether),<sup>8</sup> poly(styrene-*co*-vinylphenol)/poly( $\epsilon$ -caprolactone),<sup>9</sup> and polysaccharide/maleic copolymers.<sup>10</sup> To combine the properties of the components of a blend it is necessary to investigate the phase behavior.

In our previous papers polyethylene adipate/cholesteryl palmitate (PEA/CP) blends were studied by differential scanning calorimetry<sup>11</sup> and thermogravimetric analysis<sup>12</sup> and found to behave as a phase-separated system due to the presence of weak interactions between the two components, but a certain partial miscibility was found for each composition varying between 0.9 and 0.2 wt % CP in the PEA matrix.

In the present article the methodology previously applied for the study of physical and chemical interactions in polymer systems<sup>10</sup> is applied also for the

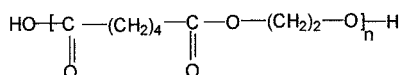
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PEA/CP system, emphasizing the evidencing of the melting and crystallization phenomena.

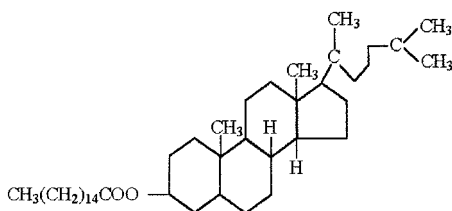
## EXPERIMENTAL

### Materials

As semicrystalline isotropic polymeric compound, PEA, was used, with endcapped hydroxyl groups, is a commercial product purchased from Fiberx SA Savinesti, Romania ( $M_n = 2000$  g/mol) with the following chemical formulae:



CP was used as a low-molecular-weight additive. It was purchased from Nopris SRL, Cluj Napoca, Romania, and used as received. It has the following structure:



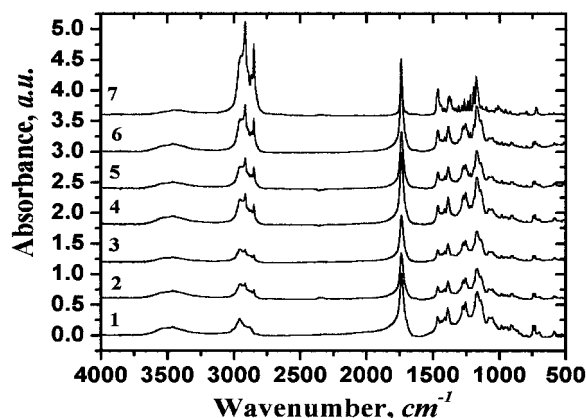
CP is a compound with liquid crystalline properties characterized by two types of mesophases, i.e., cholesteric (Ch) and smectic (S) mesophases. Monotropic phases are obtained out from isotropic melt (I) in agreement with DSC (4°C/min) determinations.<sup>11</sup> The transitions between this phase are (C→Ch) 74.5°C, (Ch→I) 80°C, and (Ch→S) 73.5°C.

### Blends preparation

Semicrystalline PEA and CP were separately dissolved in 1,2-dichloroethane (DCE) to form 0.8 g/dL solutions. Then the solutions were mixed to the final CP/PEA ratios (wt/wt): (1) 2/98, (2) 4/96, (3) 6/94, (4) 10/90, (5) 16/84, (6) 32/68, (7) 64/36, and (8) 80/20. The mixtures of solutions were stirred for 5 h. After that, the solvent was slowly evaporated at room temperature. To remove the residual solvent and moisture, the samples were dried in a vacuum oven at 50°C for 2–6 days and total removal of the solvent was checked by IR spectroscopy.

### Investigation method

FT-IR spectra at different temperatures were recorded on solid samples in KBr pellets by means of a FT-IR Bomem MB-104 spectrometer (Canada) with a resolution of 4 cm<sup>-1</sup>. The concentration of the sample in the



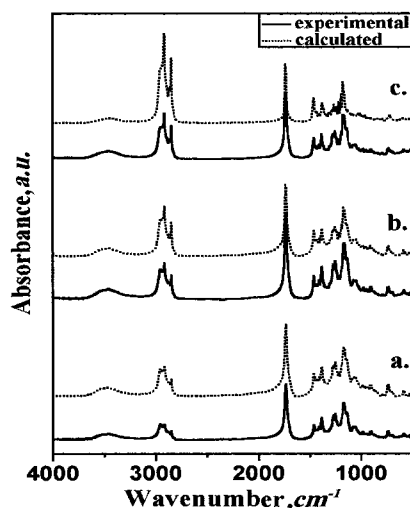
**Figure 1** FT-IR spectra of the pure components and blends recorded at room temperature: (1) PEA, (2) 10 CP/90 PEA, (3) 16 CP/84 PEA, (4) 32 CP/68 PEA, (5) 64 CP/36 PEA, (6) 80 CP/20 PEA, (7) CP.

tablets was constant at 3 mg/500 mg KBr. The behavior of the samples was followed both on heating and on cooling using a heating/cooling rate of 1°C/min. Processing of the spectra was done by means of Grams/32 program (Galactic Industry Corp.).

## RESULTS AND DISCUSSION

As expected, the spectra of the blends obtained at room temperature contain all bands corresponding to the two components (Fig. 1). A detail examination evidences changes in the 2750–3000, 1300–1600, and 1000–1300 cm<sup>-1</sup> regions. Upon increasing CP content in the blends, an increase of the absorbances of the bands at 2915 and 2850 cm<sup>-1</sup> corresponding to the stretching vibrations ( $\nu$ ) of aliphatic groups was observed and also an overlapping of the bands at 1459 and 1464 cm<sup>-1</sup> corresponding to the deformation vibrations ( $\delta$ ) of aliphatic groups forming a single band centered at 1464 cm<sup>-1</sup>. In addition, an increase of the absorbances of the bands at 1221 and 1196 cm<sup>-1</sup> corresponding to the stretching vibrations ( $\nu$ ) of C-O-C group and -OH deformation is noticed. No changes were seen in the 1600- to 1850-cm<sup>-1</sup> region.

With the aim of establishing whether the blending determined spectral changes, the pure components spectra were taken into account and on the basis of additivity law the calculated spectra of the blends were obtained and compared with the experimental ones recorded at room temperature (Fig. 2). For an immiscible blend the additive spectrum is overlapped with the experimental one, while for a miscible or partially miscible blend differences such as frequency shifts, band broadening, and changes in the intensity of some bands caused by intermolecular interactions between components could appear. The differences

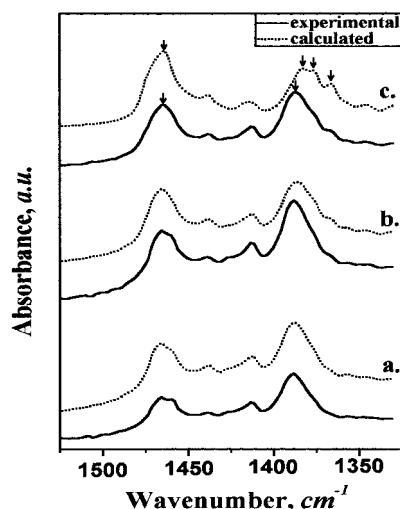


**Figure 2** Experimental and calculated spectra in the 500–4000  $\text{cm}^{-1}$  region of (a) 10 CP/90 PEA, (b) 32 CP/68 PEA, and (c) 80 CP/20 PEA.

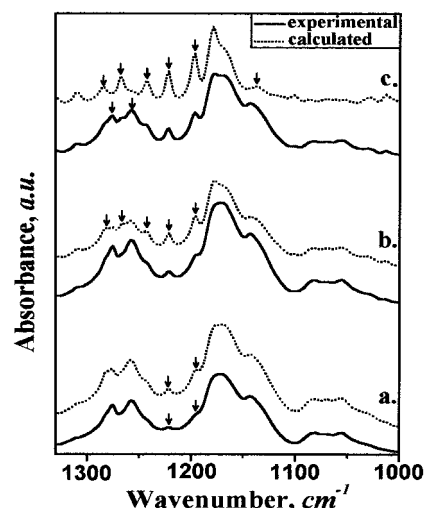
could be attributed to some conformational changes too.<sup>3</sup>

For most of the studied blends one can remark upon the differences between experimental and calculated spectra in the 2750–3100, 1350–1500, and 1000–1350  $\text{cm}^{-1}$  regions. For all the studied compositions in 2750–3100  $\text{cm}^{-1}$  region of the experimental spectra a pronounced decrease of the absorbances of the bands can be seen at 2915, 2942, 2863, and 2850  $\text{cm}^{-1}$  (stretching vibrations ( $\nu$ ) of aliphatic groups) with respect to the calculated ones (Fig. 2).

In the case of the blends with a concentration of CP higher than 32% (wt) (Fig. 3b and c) in the experimental spectra, a decrease of the absorbance can be seen at



**Figure 3** Experimental and calculated spectra in the 1350–1550  $\text{cm}^{-1}$  region of (a) 10 CP/90 PEA, (b) 32 CP/68 PEA, and (c) 80 CP/20 PEA.



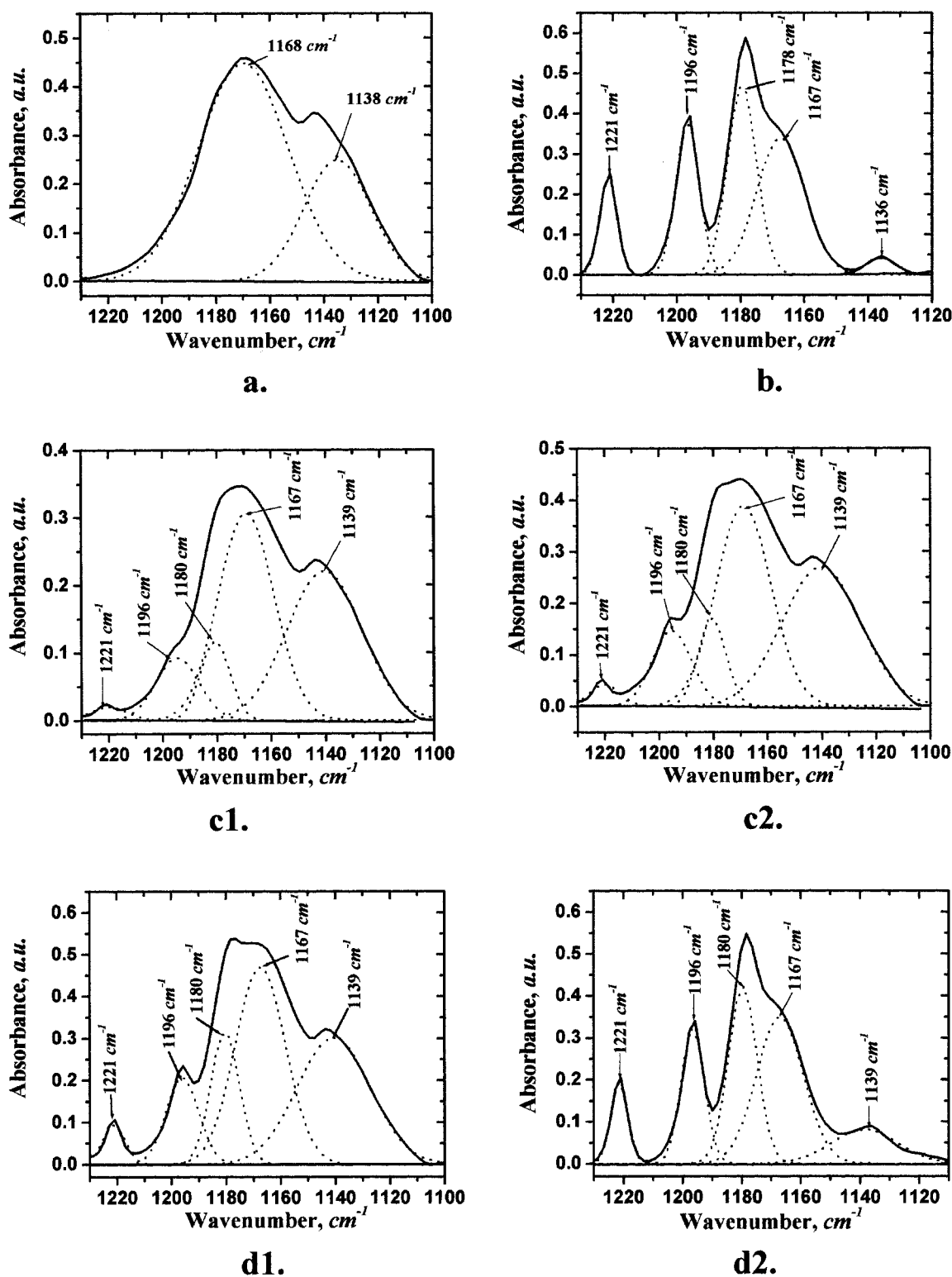
**Figure 4** Experimental and calculated spectra in the 1000–1350  $\text{cm}^{-1}$  region of (a) 10 CP/90 PEA, (b) 32 CP/68 PEA, and (c) 80 CP/20 PEA.

1465  $\text{cm}^{-1}$  accompanied by a slight shift of the band at 1388  $\text{cm}^{-1}$  to lower wavenumbers and also the shoulder at 1377  $\text{cm}^{-1}$  and band at 1367  $\text{cm}^{-1}$ , which disappear.

For some blends (32 wt % CP) in the 1100–1350  $\text{cm}^{-1}$  region in the calculated spectra the bands at 1283, 1267, 1242, 1221, 1196, and 1178  $\text{cm}^{-1}$  are much more pronounced than in the experimental spectra and a gradual disappearance of the bands at 1276, 1257, 1172, and 1143  $\text{cm}^{-1}$  is observed. The experimental spectrum of the blends with prevalent content of CP is a composed spectra of the overlapped bands of components, those of PEA being much better evidenced, while the calculated spectra is, as expected, similar to that of CP (Fig. 4).

To reveal more clearly the changes appearing in the 1100–1350  $\text{cm}^{-1}$  region, the deconvolution of the constitutive bands corresponding to this region was performed (Fig. 5) both for the experimental and for the calculated spectra. It is well known that this region of the IR spectra contains relative broad bands sensitive to the distribution of conformations and change markedly as a function of temperature. These bands can be assigned to the mixed vibrations containing contributions from –O–H deformation and C–O stretching vibration. The changes observed with temperature may be attributed to two main factors: conformational sensitivity and intermolecular interactions<sup>13</sup>

By analyzing the deconvolutions it can be noticed that the deconvoluted peaks are much better separated in the calculated spectra than in the experimental ones and their absorbances differ. The absorbance of 1220, 1195, and 1180  $\text{cm}^{-1}$  bands slightly increases with increasing CP content in the blends both in experimental and in calculated spectra. As for the bands



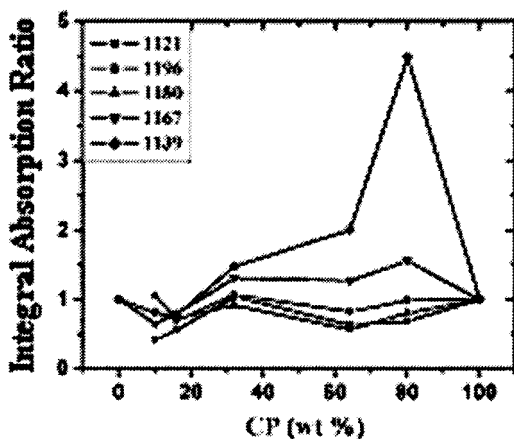
**Figure 5** Deconvolutions for experimental and calculated spectra in the  $1100\text{--}1250\text{ cm}^{-1}$  region of (a) PEA, (b) CP, (c1)10 CP/90 PEA experimental, (c2)10 CP/90 PEA calculated, (d1) 80 CP/20 PEA experimental, (d2) 80 CP/20 PEA calculated.

at  $1170$  and  $1140\text{ cm}^{-1}$  in the case of the calculated spectra the absorbances slightly decrease while for the experimental spectra they are almost constant.

The modifications of these bands are better evidenced by the dependence of the ratio of the integral absorbance

from experimental spectrum to that in the calculated spectrum at corresponding wavenumbers as a function of CP concentration (mass fraction) (Fig. 6).

The deviation from unity is much more important for the CP-rich blends and for absorption bands as-



**Figure 6** Composition dependence of the ratio of the integral absorption of the experimental and calculated spectra, corresponding to the bands determined by deconvolutions in the 1100–1230  $\text{cm}^{-1}$  regions.

signed, as mentioned above, to C-O and -OH groups, which could be involved in intermolecular interactions.

The spectral modifications could be attributed to the interactions between components, conformational changes, or phase transitions.

To elucidate this aspect, further information was obtained from the spectra recorded on heating up to 100°C followed by cooling down to room temperature (heating/cooling rate 1°C/min).

The spectral changes with temperature were followed both for the components and for the blends in the following regions: 2700–3100, 1300–1500, and 1000–1300  $\text{cm}^{-1}$ .

With increasing temperature, the changes of the bands corresponding to the stretching and deformation vibrations of aliphatic groups are taking place: an overlapping of the two bands with maxima at 2959 and 2949  $\text{cm}^{-1}$  with the formation of a band centered

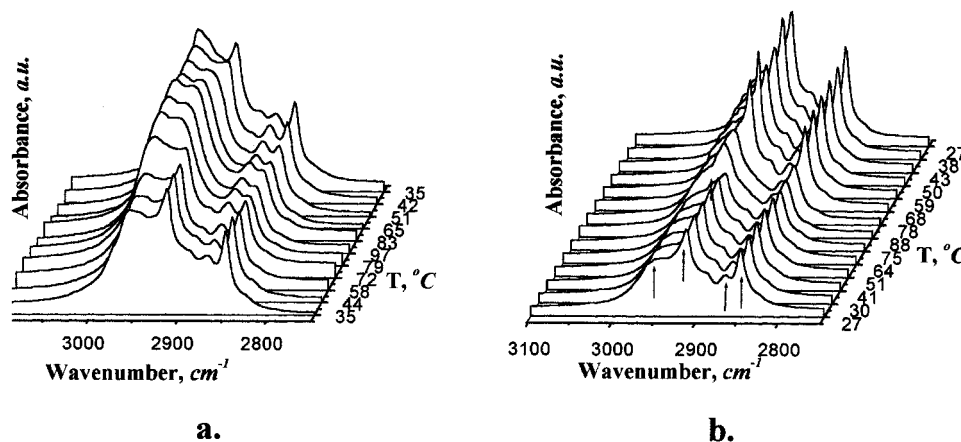
at 2954  $\text{cm}^{-1}$ , decreasing of the intensity of the band at 2915  $\text{cm}^{-1}$  with the formation of a shoulder at 2933  $\text{cm}^{-1}$ , and a decrease of the intensity of the band at 2850  $\text{cm}^{-1}$ . These changes can be observed both in the blends (Fig. 7a) and in the CP spectra (Fig. 7b).

The different sensitivity at temperature of the functional groups is put into evidence also by plotting the dependence of integral absorption on temperature. By analyzing these dependences a sudden variation of the absorbance can be seen as a function of temperature (Fig. 8), associated with transition temperatures.

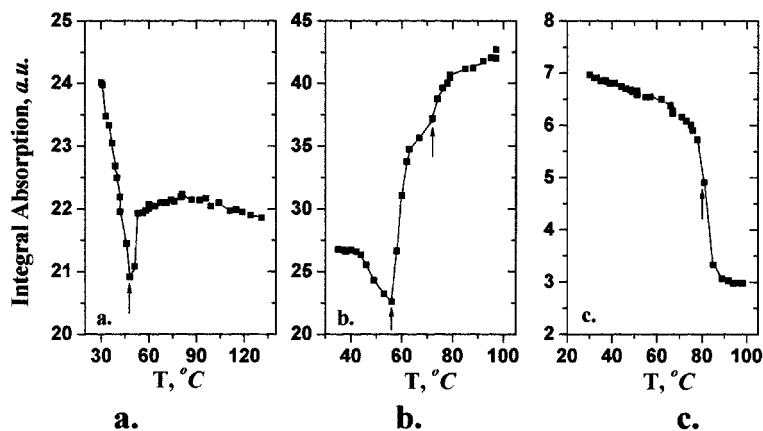
PEA exhibits a melting temperature of 46°C, while the CP transition appears at 76°C. Two transition temperatures, ranging between 46 and 51°C and 68 and 76°C intervals corresponding to the melting of PEA and of CP, respectively, are found for the blends revealing a phase-separated behavior of this system. These temperature ranges do not correspond exactly with transition temperatures of the components for all compositions of studied blends.

The most sensitive bands to the variation of temperature are the bands at 1257 and 1275  $\text{cm}^{-1}$  for PEA (Fig. 9a, arrows) and 1267, 1242, 1221, and 1196  $\text{cm}^{-1}$  for CP (Fig. 9c, arrows), which are also present in the blends (Fig. 9b). These bands disappear by heating at the transition temperature and reappear on cooling, at approximately the same temperature, with the phenomenon being reversible.

Correlating these data with those obtained by DSC,<sup>11</sup> we might assign these bands to the crystalline structure of the two components and of the blends. The melting of the crystalline phase is thus the phase transition evidenced by IR spectroscopy. In addition, it can be noticed the different shape of the blends spectra in the 1100–1300  $\text{cm}^{-1}$  region compared with those of the neat components which might be explained with the appearance of particular crystalline phases or a pronounced mutual influence of the cat-



**Figure 7** Spectral changes appeared in 2700–3100  $\text{cm}^{-1}$  at different temperatures: (a) 32 CP/68 PEA, (b) CP.



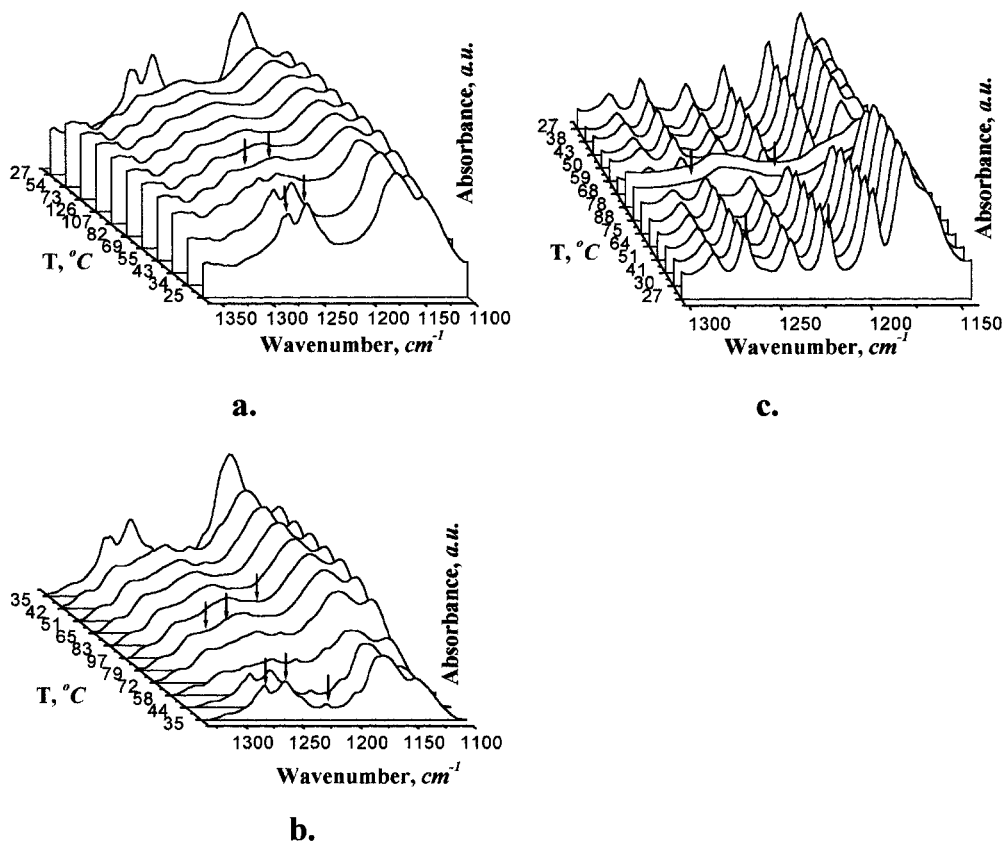
**Figure 8** The variation of the integral absorbance as a function of temperature for 1200–1100  $\text{cm}^{-1}$  region evidencing the transition temperatures (arrows): (a) PEA, (b) 32 CP/68 PEA, (c) CP.

enar segments (especially alkyl segments), which can be aligned in ordered conformations.

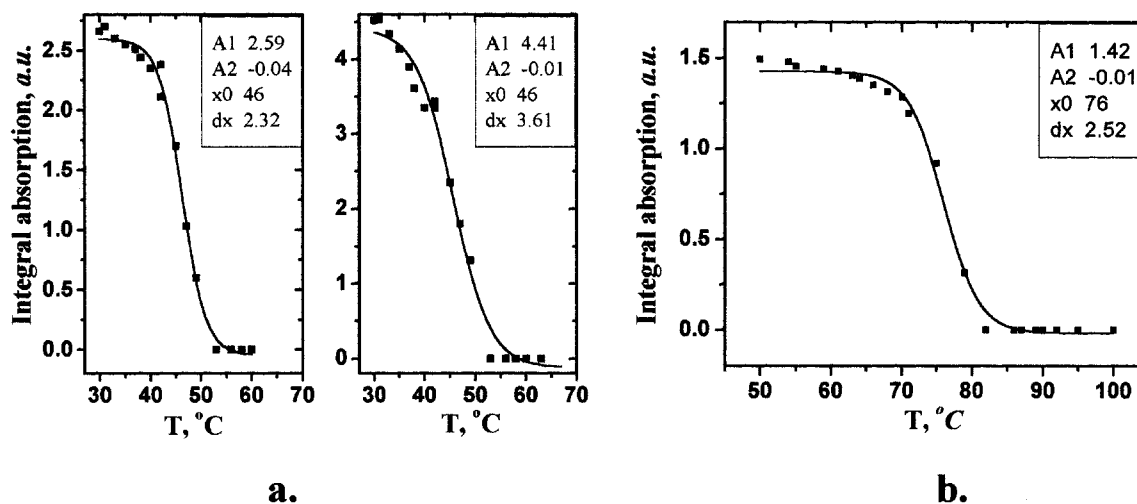
By analyzing it can be seen that at transition temperature they exhibit a sudden variation. For an accurate determination of the transition temperature, the curves of the dependence of integral absorption of these bands on temperature were fitted by a Boltz-

mann function (using Origin 6.1 program) given by the following equation:

$$y = \frac{A_1 - A_2}{1 + e^{\frac{(x-x_0)}{dx}}} + A_2,$$



**Figure 9** Spectral changes appeared in the 1100–1350  $\text{cm}^{-1}$  region at different temperatures: (a) PEA, (b) 32 CP/68 PEA, (c) CP.



**Figure 10** Dependencies on temperature of the integral absorption of the bands at 1257 and 1275  $\text{cm}^{-1}$  of: (a) PEA, (b) 1221  $\text{cm}^{-1}$  (CP).

where  $A_1$  is the minimum value of the function;  $A_2$  is the maximum value of the function;  $x_0$  is the value on the  $x$  axis corresponding to the inflection of the curve, equivalent to the transition temperature; and  $dx$  is the domain in which this value is found.

The reduced  $\chi^2$  for all the fitted curves was  $\chi^2 \leq 0.1$ ; therefore the use of this function is a good approach.

In Figure 10 the values of the integral absorbances at different temperatures of the bands at 1257 and 1275  $\text{cm}^{-1}$  for PEA and 1221  $\text{cm}^{-1}$  for CP are represented by dots, with the solid line representing the Boltzmann fitted curve. By fitting procedure  $A_1$ ,  $A_2$ ,  $x_0$ , and  $dx$  parameters are obtained. The value corresponding to  $x_0$  is the value of transition temperature. These above-mentioned bands appear at the blends, too. Following the same procedure, the values of transition temperatures of the blends were obtained and are shown in Table I

It can be observed that the first transition temperature increases due to the incorporation of CP in PEA, while the second one decreases due to the incorporation of PEA in CP; these results are in agreement with DSC

**TABLE I**  
Transition Temperatures of the PEA/CP Blends

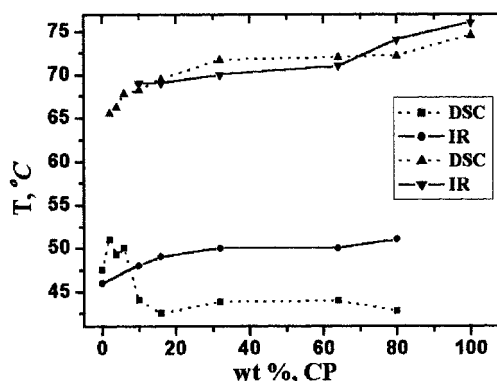
Sample wt % CP	$t_1$ , °C	$t_2$ , °C	$t_3$ , °C
0	46		
16	49	69	46
32	50	70	48
64	50	71	50
80	51	74	54
100		76	72

Note.  $t_1$  and  $t_2$ , transition temperatures determined by heating of the samples (melting);  $t_3$ , transition temperatures determined by cooling of the samples.

data.<sup>11</sup> (Fig. 11). By DSC determinations it was established that for each composition there is a mass fraction of CP dissolved in the PEA matrix, which varies between 0.9 (2 CP/98 PEA blend) and 0.2 (64 CP/36 PEA blend); therefore the blends exhibit a partial miscibility.

The data obtained by DSC and IR are in good agreement in the case of the transition temperatures of CP and differ slightly in the case of the transition temperatures of PEA. In the case of CP, the values of the transition temperatures at the incorporation of the second component are in agreement with the theoretical considerations regarding the melting point depression, but the increase of the values for PEA indicates a somewhat strong interaction or different conformation at lower temperatures, with this result being obtained from the spectral modifications, too.

Because the bands at 1257, 1275, and 1221  $\text{cm}^{-1}$  were attributed to the crystalline structure of PEA and CP, respectively, a value proportional to the relative degree of crystallinity was estimated by the ratio between inte-



**Figure 11** Concentration dependence of the transition temperatures obtained by DSC (dotted line) and IR (solid line).

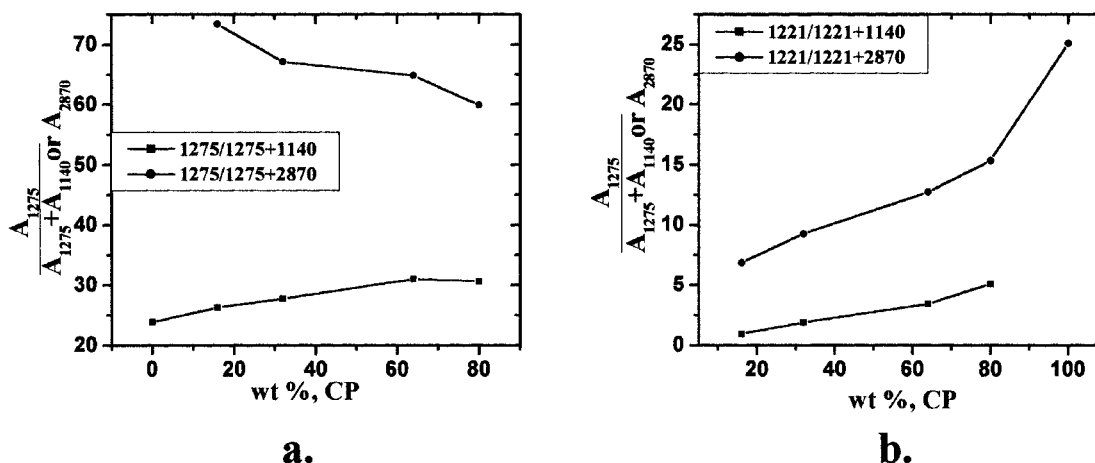


Figure 12 Concentration dependence of the relative degree of crystallinity for (■) PEA and (●) CP.

gral absorption of these bands and the integral absorption of the bands at 1140 and 2870  $\text{cm}^{-1}$ , which don't exhibit significant changes with the variation of temperature. The band at 1140  $\text{cm}^{-1}$  is found in the spectra of the blends and PEA and is absent in the spectrum of CP, while the band at 2870  $\text{cm}^{-1}$  is found in the spectra of the blends and CP and is absent in the spectrum of PEA. The integral absorption of the bands at 1140 and 2870  $\text{cm}^{-1}$  was obtained by deconvolution for the 2700–3100 and 1100–1200  $\text{cm}^{-1}$  regions. The dependencies from Figure 12 show the variation of the relative degree of crystallinity as a function of CP concentration. These values are given only for comparative purpose (they are not absolute significance).

For the band at 1275  $\text{cm}^{-1}$  the relative degree of crystallinity was calculated at 30°C (a lower temperature than the transition temperature of PEA) and for the band at 1221  $\text{cm}^{-1}$  both at 30°C (lower than transition temperature of PEA) and 50°C (lower than the transition temperature of CP). It can be observed that in the case of the band at 1275  $\text{cm}^{-1}$ , the band characteristic to PEA, with increasing of CP concentration in the blends the relative degree of crystallinity decreases, while for the band at 1221  $\text{cm}^{-1}$ , which is characteristic to CP, increasing the CP concentration in the blends also increases the relative degree of crystallinity; thus the presence of the second component affects the morphology and the transitions of the other one. Therefore the changes of the order in both polymers is evidenced by FT-IR spectra.

### CONCLUSION

Compatibility of the PEA/CP blends was followed by FT-IR spectroscopy, establishing that the interactions between the components are more pronounced for the blends with higher CP content.

The bands at 1257 and 1275  $\text{cm}^{-1}$  were attributed to the crystalline structure of PEA and the bands at 1267,

1242, 1221, and 1196  $\text{cm}^{-1}$  to the crystalline structure of CP. Partial miscibility of the components was proved by the dependence of melting temperature on composition.

The transition temperatures of pure components and of the blends were determined, with the accuracy of the determination increasing if the fitting of the curves is carried out with Boltzmann functions. From the dependence of the transition temperatures on composition of the blend, it has been established that for each mixing ratio a certain mass fraction of CP should be dissolved in the PEA matrix. Therefore the PEA/CP blend behaves as a phase-separated system with partial miscibility.

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