



*Dedicated to Professor Eugen Segal
on the occasion of his 80th anniversary*

TRANSITION TEMPERATURES AND MOLECULAR INTERACTIONS OF POLYTETRAHYDROFURAN/COLESTERIL PALMITATE BLENDS BY PRINCIPAL COMPONENT ANALYSIS

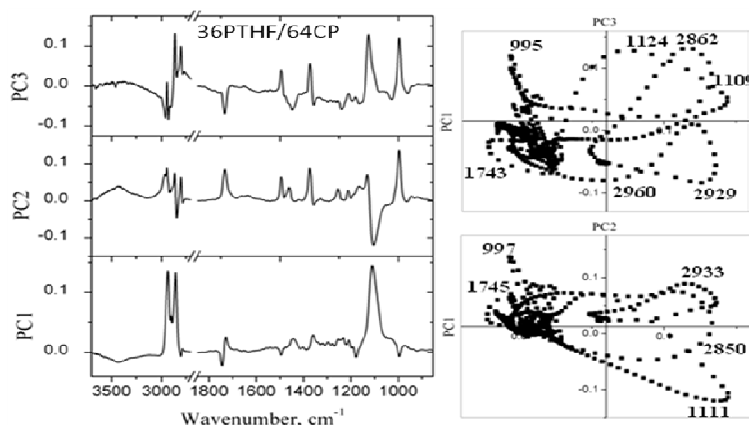
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Principal component analyses (PCA) were applied on spectral data to reveal the transition temperatures and to evidence the molecular nature of spectral variations of polytetrahydrofuran (PTHF), colesteril palmitate (CP) and PTHF/CP blends. The score plots of PCA constructed from temperature-dependent original FTIR spectra illustrate a transition at 38 °C for PTHF, 77 °C for CP and two transition temperatures between 34-37 °C and 67-73 °C for their blends, which are consistent with the results obtained by other techniques. The PC loadings indicate that aliphatic and C-O groups from both components and the carbonyl groups from CP affect the thermal properties of the polymeric blends.



INTRODUCTION

Chemometrics is the field of extracting information from multivariate chemical data using statistics and mathematic tools. It can study and model data gained from complex chemical systems, improve the accuracy of current data interpretation methods, and provide an easier and more efficient way to perform the extensive calculations which result from the analyses of large data sets.

Among the many chemometrics procedures, principal component analysis (PCA) is a widely used technique for evaluating multivariate spectroscopic data. Due to the importance of multivariate measurements in chemistry, PCA is frequently considered as the technique that most significantly changed the chemist's view of data analysis. PCA is used in all forms of analyses – from neuroscience to computer graphics – because it is a simple, non-parametric method of extracting relevant information from confusing data sets. With minimal additional effort, this approach

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provides a roadmap for how to reduce a complex data set to a lower dimension to reveal the sometimes hidden, simplified dynamics that often underlie it.

PCA is a very useful technique for extracting a pure component from different types of spectra such as near infrared (NIR) spectroscopy,^{1,2} UV-vis spectroscopy,³ electron paramagnetic resonance (EPR),⁴ FTIR spectroscopy⁵⁻⁷ or liquid chromatography.^{8,9}

FTIR spectroscopy has shown particular promises as a technique for measuring the transition temperatures of polymers.^{10, 11} The utility of FTIR stems from the specificity of the IR probe to different submolecular and segmental constituents of polymeric systems, which gives a unique capacity to elucidate the molecular origin of transition phenomena.

PCA was applied for many years in analyzing chemical phenomena monitored by infrared spectroscopy. Thus, Hasegawa *et al.*¹² applied PCA to the angle-resolved ATR FTIR spectra of water, and then evaluated the orientation of water molecules using the plots of the loading vectors of the three significant PCs, and to detect minute bands in the FTIR spectrum of a mixture.^{13, 14} Jung and coworkers determined the glass transition temperature from the temperature-dependent FTIR spectra of poly(*tert*-butyl methacrylate) Langmuir-Blodgett films,¹⁵ poly(methyl methacrylate) (PMMA) thin films,¹⁶ and the order-disorder transition of polystyrene-block-poly(*n*-pentyl methacrylate) copolymers,¹⁷ while Sakata and Otsuka studied the relationship between the physical properties and molecular behavior of pullulan films,¹⁸ etc.

PCA is a mathematical manipulation of data matrices that transform original measurement variables into new uncorrelated variables called principal components (PCs). By converting the data into the dimensionally reduced PCA space, the input data set is decomposed into two matrices of interest: scores and loadings. The loadings matrix defines the new axes of the dimensionally reduced data set, while the scores matrix describes the samples in the PC space. The use of a multivariate analysis with polymer systems has been limited. With PCA, the most important features of the FTIR spectra can be identified, and

the band shifts and non-symmetries in the bands between the samples can be quickly determined.

This study is concerned with the application of PCA to the analysis of phase transitions in polymeric blends.

RESULTS AND DISCUSSION

The temperature-dependent IR spectra of PTHF, CP, and PTHF/CP blends, obtained during the heating from 20 to 120 °C, were reported in a previous paper¹⁹ and show that the spectral intensities in the C=O, C-O-C, and C-H stretching vibration regions are markedly changed with temperature. The bands at 1128 and 995 cm⁻¹ were attributed to the crystalline structure of PTHF, and the bands at 1267, 1242, 1221, and 1196 cm⁻¹ to the crystalline structure of CP. The crystalline bands decrease while the amorphous bands increase during the melting process, in both pure components and blends. Partial miscibility of the components was proved by changing the bands position in blends as compared with those in the pure components and by the dependence of melting temperature on composition.

In order to find the values of the transition temperatures and to evidence the sensitivity of different functional groups to temperature, the PCA method was used. This method allows the visualization of the main variability of a data set without the constraint of an initial hypothesis concerning the relationship within samples, or between samples and responses (variables). Each sample has a score on each principal component (PC), which reflects the sample location along that PC. Plotting these scores against one another can reveal patterns or clustering within a data set. After applying the PCA to the temperature dependent FTIR spectra of PTHF, CP and CP/PTHF blends, the original spectral data sets were decomposed into scores and loading vectors. PC1, PC2, and PC3 account for 85-96 %, 2-12 %, and 1-2 %, respectively, of the contribution to the data; thus, the three principal components have essentially all information needed to describe the temperature-dependent IR spectra. Fig. 1 shows the scores of the three principal components *versus* temperature for the temperature-dependent FTIR spectra of PTHF (a), CP (e) and CP/PTHF blends (b-d).

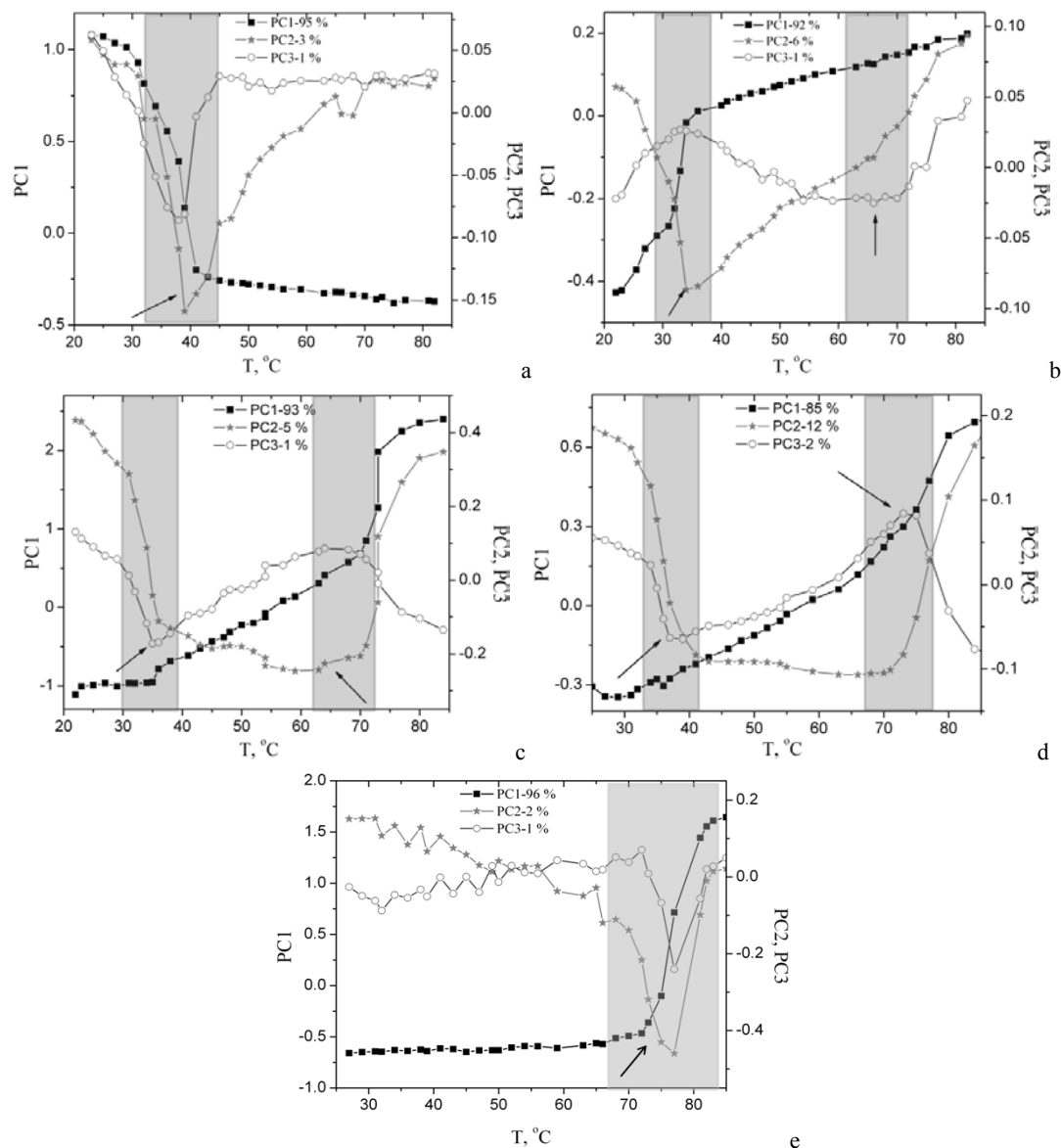


Fig. 1 – Score plots of PC1, PC2 and PC3 versus temperature of the temperature-dependent FTIR spectra of PTHF (a), 84PTHF/16CP (b), 36PTHF/64CP (c), 20PTHF/80CP (d) and CP (e).

The score plots of PC1 in Fig. 1 show a decrease for PTHF and an increase for CP and blends over the investigated temperature region. This reveals that PC1 reflects the overall intensity changes of ordinary character from the beginning to the end of the temperature range. To evidence the transition temperature, the curve can be fitted with Boltzmann function.²⁰ The temperature values which result from the fitting process are 38 °C for PTHF and 77 °C for CP. In the case of the blends the transitions are not clearly evidenced or only one transition appears. To obtain more information, the PC2 and PC3 score plots were calculated. The presence of inflection points, maxima and minima in the scores potentially indicates the presence of transitions and point the temperatures at which the events take place. These

data reveal significant changes at 38 °C for PTHF, 77 °C for CP, 34 °C and 67 °C for 84PTHF/16CP, 35 °C and 72 °C for 36PTHF/64CP and 37 °C and 73 °C for 20PTHF/80CP. These temperatures coincide with the temperatures detected in the dependence of integral absorptions as a function of temperature obtained from FTIR spectra and by DSC.²¹ Thus, the score plots provide a convenient and sensitive indicator of the presence of transitions. The analysis of the dependence of score plots on temperature allows the detection of conformational or structural changes. Each score has an associated “loading”, providing information on the chemical differences between the samples. Fig. 2 shows the loadings plots for PC1, PC2 and PC3 for PTHF, CP and PTHF/CP blends.

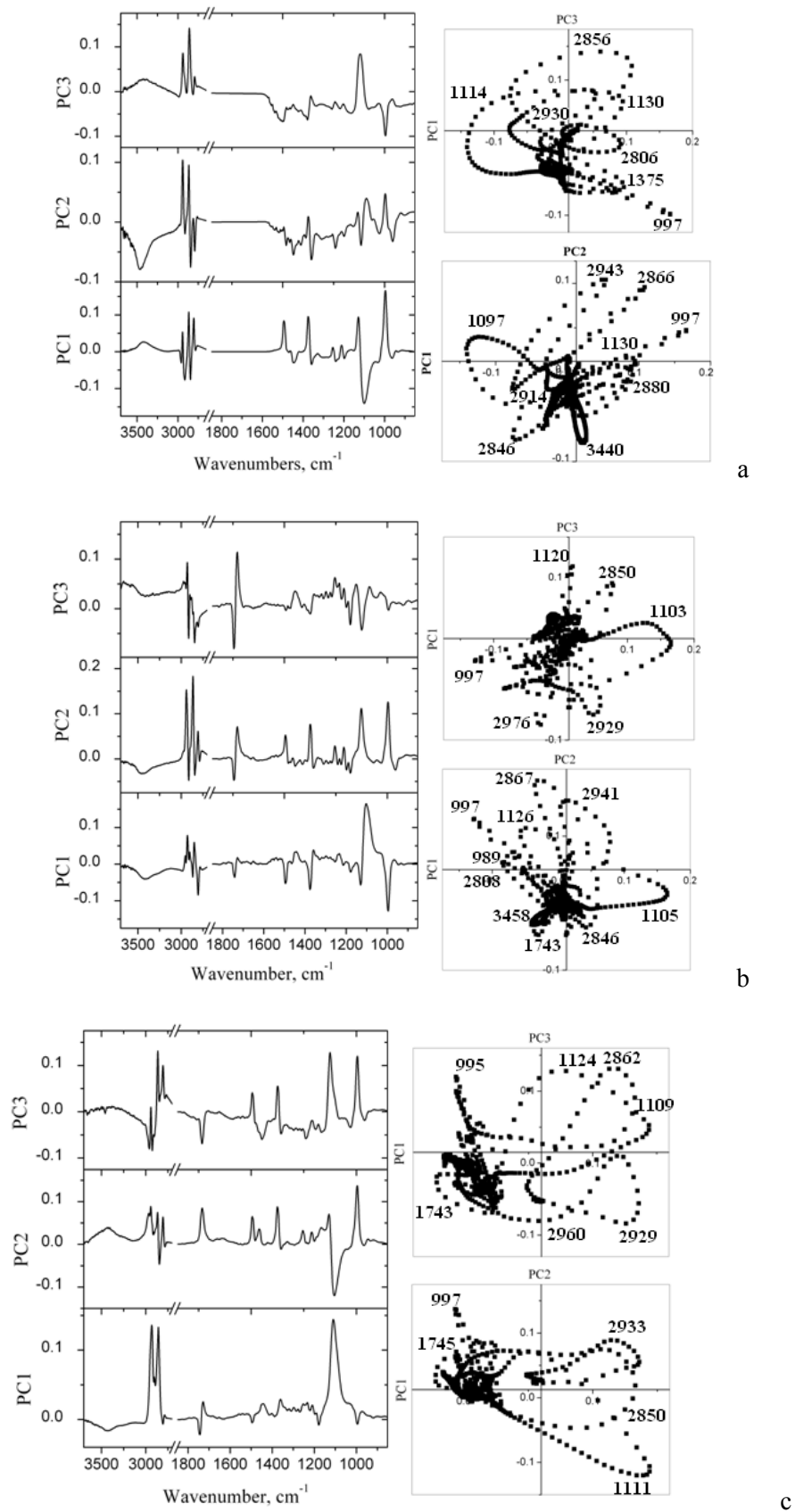


Fig. 2

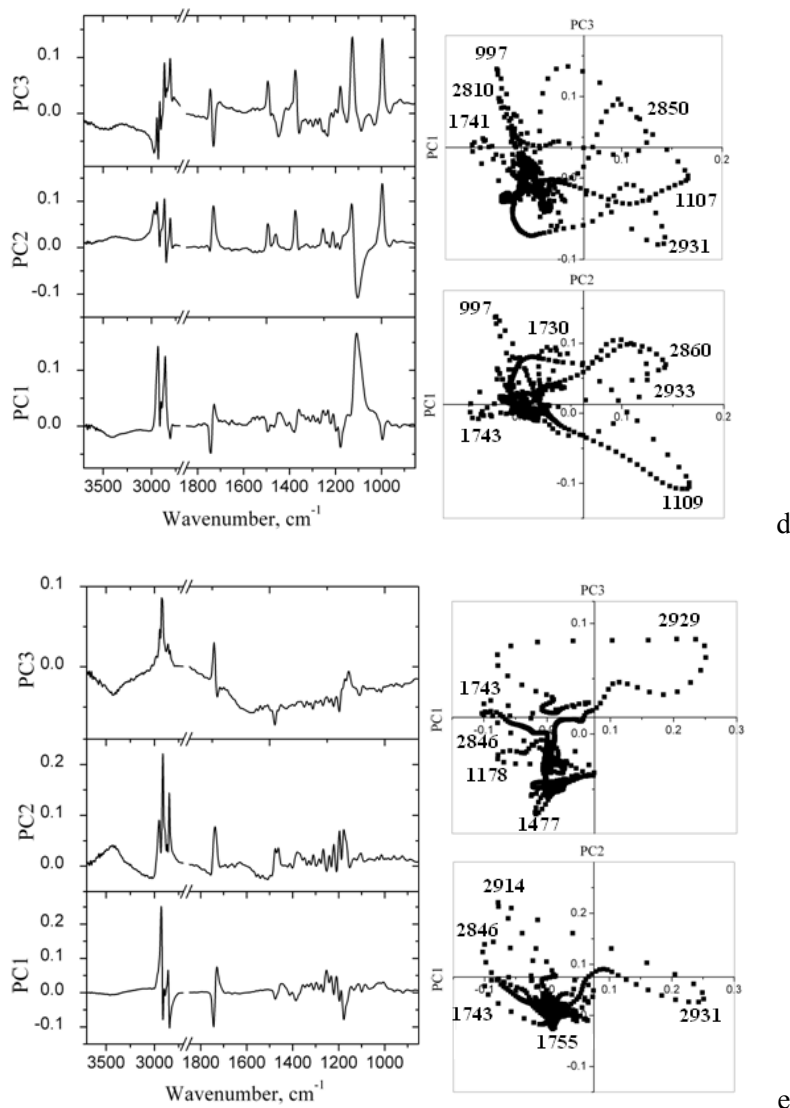


Fig. 2 – Loading plots of PC1, PC2 and PC3 versus temperature and PC1 versus PC2 and PC3 loadings of the temperature-dependent FTIR spectra of the PTHF (a), 84PTHF/16CP (b), 36PTHF/64CP (c), 20PTHF/80CP (d) and CP (e).

The PCA loading plot can be used to condense the data contained in many spectra into information which fully describes the system. Thus, based on the distance from the origin, the relative variation in absorbance at a specific wavenumber can be used to describe the system, while the width and symmetry of a loop describes the change in band heights and shapes between samples, and the wavenumber sequence in loop describes the direction of bands shift relative to wavenumber.²² The loading plots also allow a better understanding of the molecular origin of the transitions. A large value of the loading indicates that the implied bands have a higher effect on the PC score as compared to other spectral regions.

The important wavenumbers from loop apexes of the loading plots are equally divided in

importance between PC1 and PC2 and/or PC3. The loading plots of PTHF (Fig. 2a) show that the bands located at 2943, 2914, 2880, 2866 and 2846 cm^{-1} , assigned to stretching vibrations of aliphatic groups, 1130 cm^{-1} assigned to symmetric stretching vibrations of C-O-C groups, 1097 cm^{-1} assigned to asymmetric stretching vibration of C-O-C and 997 cm^{-1} assigned to deformation vibrations of aliphatic groups are sensitive to temperature variation evidenced in PC1 and PC2 score plots. In addition, the variation of the band located at 1375 cm^{-1} assigned to the symmetric bending vibration of CH_3 groups is observed in PC1 versus PC3 loading plots. This band contributes, together with the previous ones, to the temperature variation observed in PC3 score plot.

In the case of CP (Fig. 2e), significant changes in PC1 and PC2 loading plots present the bands located at 2931, 2914 and 2846 cm^{-1} , assigned to stretching vibration of CH groups, and the bands located at 1743 and 1755 cm^{-1} , assigned to stretching vibrations of C=O groups. These groups contribute significantly to the transitions evidenced in the first two score plots. In the PC1 *versus* PC3 loading plot significant changes show the bands assigned to stretching and bending vibrations of CH groups and the band assigned to stretching vibrations of C=C, C=O and C-O groups. These groups can be assigned to the crystalline structure of CP and the change in band position and shape evidences the conformational/structural changes of the CP molecules at the C→Ch→I transitions.

The loading plots of the blends indicate changes of the spectral bands located at 2940, 2867, 1743, 1105 and 997 cm^{-1} , assigned to stretching vibrations of aliphatic groups, stretching vibration of C=O groups and deformation vibration of CH groups, in both PC1 *versus* PC2 and PC1 *versus* PC3 loading plots. In the case of the blends with low CP content, the PC1 *versus* PC2 loading plots also evidence changes of the bands located at 2846, 2808, 1126 and 989 cm^{-1} , assigned to the stretching vibrations of CH groups and to symmetric stretching vibrations of C-O-C groups from PTHF and to bending vibrations of CH groups from CP. In the PC1 *versus* PC3 loading plots additional bands were evidenced at 2976, 2929 and 1120 cm^{-1} , bands assigned to stretching vibrations of CH groups of CP and to stretching vibrations of C-O-C groups from PTHF. In this case the transition temperatures are influenced especially by PTHF content.

For the 36PTHF/64CP blend, in the PC1 *versus* PC3 loading plots are evidenced additional bands at 2960, 2929, 1743 and 1124 cm^{-1} , assigned to stretching vibrations of CH and C=O groups from CP and to stretching vibrations of C-O-C groups from PTHF, respectively.

In the last case (20PTHF/80CP), new bands are evidenced in the PC1 *versus* PC2 loading plot at 1730 cm^{-1} , assigned to stretching vibrations of C=O groups from amorphous CP, and in the PC1 *versus* PC3 loading plots at 2931, 2810 and 1741 cm^{-1} , bands assigned to stretching vibrations of CH and C=O groups from crystalline CP.

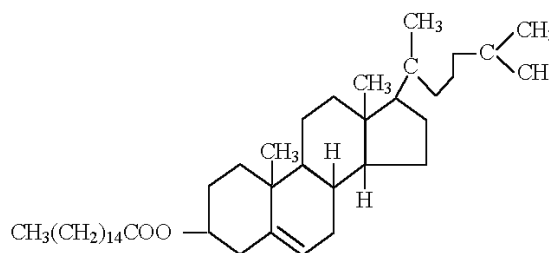
It can be concluded that the first transition temperature decreases due to the incorporation of CP in PTHF, while the second one increases due to the incorporation of PTHF in CP.

MATERIALS AND METHODS

Materials

The used PTHF $\{-[\text{O}-(\text{CH}_2)_4]_n-\}$ was a commercial product purchased from BASF, $\bar{M}_n=2000\text{ g/mol}$, with the melting temperature $T=36.4\text{ }^\circ\text{C}$.^{22,23}

CP is a compound with liquid crystalline properties characterized by two mesophases, *i.e.* a cholesteric (Ch) and a smectic (S) one, and was purchased from Nopris SRL, Cluj-Napoca, Roumania.



According to DSC data (4° C/min), the monotropic phases were obtained from the isotropic melt (I).²³ The transitions between these phases are:

(C→Ch) 74.5 $^\circ\text{C}$, (Ch→I) 80 $^\circ\text{C}$, (Ch→S) 73.5 $^\circ\text{C}$.

For blend preparation, semi-crystalline PTHF and CP were separately dissolved in 1,2-dichloroethane (DCE) to form 0.8 g/dL solutions. The solutions were then mixed in different PTHF/CP ratios and stirred for 5 h. The solvent was evaporated at room temperature and in order to remove the residual solvent and moisture the samples were dried in a vacuum oven at 50 $^\circ\text{C}$ for 2–6 days. The total removal of the solvent was checked by IR spectroscopy.

Investigation methods

FT-IR Spectroscopy. 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^{-1} . The concentration of the sample in the tablets was kept constant at 3 mg/500 mg KBr. The behaviour of the samples was followed both on heating and on cooling using a heating/cooling rate of 1 $^\circ\text{C/min}$.

PCA analysis. The original variables are reduced to a number of significant PCs, each of which is orthogonal to each other. By plotting the principal components, one can view interrelation-

ships between different variables, and detect and interpret sample patterns, groupings, similarities or differences. Spectral data can be expressed and visualized in a low dimensional space with new orthogonal bases. It is much easier to predict chemical properties and determine chemical constituents from a few PC scores than from the raw spectral data. A change in the direction (from negative value to positive one or reverse) of a PC score at the same temperature implies that some chemical properties change at that point. The transition temperature represents the temperature at which the highest band occurs in the absolute PC score plot, *i.e.*, the point at which the most significant change occurs in terms of magnitude and direction. Loading plots are calculated per PC and indicate which variables (wavenumbers) contribute to the variance explained by that particular PC. The absolute value of the loading for a given variable (wavenumber) is directly related to the contribution of that variable to the explained/modeled variance. PCA analysis was performed by use of the Excel program and processing of the spectra was performed by means of Grams 9.1 program (Thermo Fisher Scientific).

CONCLUSIONS

The PCA method was used to evidence the transition temperatures of PTHF, CP and PTHF/CP blends. The scores plots of PCA illustrate a transition at around 38 °C for PTHF, at 77 °C for CP and two transition temperatures between 34-37 °C and 67-73 °C for PTHF/CP blends. The dependence of the melting temperatures on the composition evidenced a partial miscibility between the components. The loading plots suggest that the aliphatic and C-O groups from both components and the C=O groups from CP are implied in the structural changes which affect the thermal properties of the blends.

Correlating these data with those obtained by IR spectroscopy and DSC, one can 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 PCA method. This study also evidences the usefulness of the PCA method in the

characterization of the thermal properties of polymers and polymer blends for determination of the transition temperatures and to establish the structural changes implied in this transitions.

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