MICROSCOPICAL STUDY OF POLY(ETHYLENE-ADIPATE)/
CHOLESTERYL PALMITATE BLENDS*

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Optical microscopy in ordinary and polarized light and FT-IR spectroscopy was used to study morphology and crystalline transition of the poly(ethylene-adipate)/cholesteryl palmitate blends. A smectic 1 to smectic 2 transition of the liquid crystalline component was detected only in the blends, proving influence of the poly(ethylene-adipate) on the crystallization behavior of the cholesteryl palmitate.

Key word: poly(ethylene-adipate), cholesteryl palmitate, blends, liquid crystal, optical microscopy, FT-IR spectroscopy, morphology, crystalline transition.

1. INTRODUCTION

There are many techniques sensitive to evidence the phase separation and transitions of the polymer blends such as FT-IR spectroscopy and thermal analysis. Optical microscopy is an important tool to evaluate the polymer supermacromolecular organization. In the case of crystalline organization, spherulite size and spherulite size distribution can be investigated by this technique that may be the better way to evaluate the crystalline morphology of polymer blends constituted by two crystalline polymers [1]. The optical microscopy has the advantage to permit a large area of observation.

In our previous paper [2], FT-IR spectroscopy has been used to follow the thermal behaviour of the poly(ethylene-adipate) (PEA)/cholesteryl palmitate (CP) blends and compatibility of components. From the variation of


crystalline band with temperature, melting temperatures have been determined. It has been found that in the blends the melting temperatures of the components are shifted because of the interaction between components. This supposes also a change in the morphology of the blends constituted from two crystallizable components.

This paper deals with the study of the morphological changes of PEA/CP blends and their components.

In this work, optical microscopy and FT-IR spectroscopy were used to evaluate the morphology and the transitions of poly(ethylene adipate) / cholesteryl palmitate blends.

Semi-crystalline PEA/CP blends have been examined by optical microscopy in ordinary and polarized light in successive cycles of heating and cooling. Because of the liquid crystalline nature of one of the components and interactions between components, very interesting morphological forms are observed and, also phase transition temperatures in dependence on blends composition were determined. The obtained values are in accordance with those evaluated by previous FT-IR and DSC measurements [2, 3].

2. EXPERIMENTAL PART

2.1. MATERIALS

As semi-crystalline isotropic polymeric compound was used poly(ethylene adipate) (PEA) with endcapped hydroxyl groups which is a commercial product purchased from Fibrex SA Savinesti, Romania ($\bar{M}_n = 2000$ g/mol) with the following chemical formulae:

\[
\text{HO-C-} \underbrace{\text{CH}_2}_4 \text{C-O-} \underbrace{\text{CH}_2}_2 \text{O}_n \text{H}
\]

Cholesteryl palmitate (CP) was used as a low molecular additive. It is a product 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 phase are obtained out from isotropic melt (I) in agreement with DSC, (4°C/min) determinations [3]. The transitions between that phases are: (C→Ch) 74.5°C, (Ch→I) 80°C, (Ch→S) 73.5°C.

2.2 BLENDS PREPARATION

Semi-crystalline 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. In order 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.

2.3. INVESTIGATION METHOD

Semi-crystalline PEA/CP blends have been examined with IOR MC1 optical microscope in ordinary and polarized light at room temperature and in successive cycles of heating and cooling with a rate of 2°C/min. Magnification 130x and 260x.

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 constant of 3mg / 500 mg KBr. The behaviour 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 Corporation].
3. RESULTS AND DISCUSSION

The microscopical aspect of the PEA/CP blends in ordinary light are given in Figure 1.
Both components and blends have non-homogeneous aspects because of crystalline morphological units of each of them. These crystalline entities have bigger size in CP. The morphology of the blends is much complex because both phase separation and crystallization occur. Comparing the microscopical aspects of the same magnification, it can be remarked that the non-homogeneity increases with increasing CP content, the blend with 64 wt % CP and 80 wt % CP showing an evident phase separation.

The temperature of all samples have been raised at 80°C and crystallization has been followed during cooling. In melting state all blends are non-homogeneous having a morphology as islands in a continuous matrix.

Comparing the microscopical images in polarized light can be remarked different morphological entities, concentric spherulites (typical maltese cross pattern) for PEA (Figure 2) of big dimensions (150–160 µm) and with radial increase of specific crystalline forms in CP (Figure 3) (840 µm) which present a splendid irradiation of colors as is expected for a liquid crystalline component.

These crystalline forms were detected at 68°C for CP, 20–23°C for PEA. In the case of the blends (Figure 4) the form of the morphological entity is much closer that of CP, for the blends with prevalent content of this component but it is changed for blends in the middle composition range or for the blend with PEA prevalent content. In this later case the observed spherulites have smaller dimensions (100–110 µm).

For the blends, two crystalline transitions temperatures have been detected at 55–58°C and 45–50°C depending on blend composition.
Fig. 2 – Optical micrograph in polarised light of PEA (130x).

Fig. 3 – Optical micrograph in polarised light of CP (130x).
These transitions have been evidenced also by FT-IR spectroscopy, by analyzing the evolution with increasing/decreasing of temperature of the 1257 and 1275 cm$^{-1}$ (Figure 5a) bands corresponding to the PEA and the band at 1221 cm$^{-1}$ (Figure 5c) corresponding to CP, which are crystalline bands because they disappear by heating and re-appear by cooling (Figure 5).
To determine the transition temperature the integral absorbance of the 1221 cm\(^{-1}\) band was plotted in function of temperature (Figure 6). To determine the transition temperatures they are fitted with a Boltzman function.

![Graphs of integral absorbance vs temperature for CP and CP/68 PEA blends](image)

Fig. 6 – The variation of the integral absorbance as a function of temperature for 1221 cm\(^{-1}\) band evidencing the transition temperatures: CP(a), 32 CP/68 PEA (b).

It is very clear that CP exhibits a single transition at 68-70\(^\circ\)C while blends have two transitions at 58\(^\circ\)C and 47\(^\circ\)C which are shifted with ~4-5\(^\circ\)C in function of the blend composition.

This is in accordance with temperatures of morphological changes observed by microscopy. One can suppose that a new smectic form is developed in the blends.

**REFERENCES**