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Miscibility of TPU(*PCL diol*)/PCL Blend and Its Effect on PCL Crystallinity

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Summary: Poly(ε-caprolactone) (PCL) was melt blended with thermoplastic polyurethane based on polycaprolactone diol (TPU(*PCL diol*)). The amount of PCL was varied from 20% to 50% by weight. A single composition dependent glass transition temperature (from DSC) shows the miscibility of system. Also the negative value of polymer-polymer interaction density, obtained from the analysis of the equilibrium melting point depression, confirms the blends' miscibility. T_c and T_m of the PCL component in the blend decrease significantly with an increase in the TPU content, in comparison with that of pure PCL. The position of the diffraction peak related to (110) planes of PCL in the blends using WAXS has been shifted to lower value. This means the *b*-axis of orthorhombic unit cell of PCL is spread out in the blends. On the whole, increase of TPU content in the blend decreases crystallization ability of PCL compared to pure PCL.

Keywords: blend; crystallinity; miscibility; polycaprolactone; polyurethane

Introduction

Poly(ε-caprolactone) (PCL) is a highly crystalline polymer that is miscible with a wide variety of amorphous polymers.[1–3] Crystallization behavior of miscible blends of amorphous/crystalline polymers has widely been studied.[4–7] Generally, the change of crystallization behavior of the crystallizable component has been found with the addition of amorphous component because of the change in the chain mobility, the dilution of the crystallizable component at the growth front, the change in free energy of the nucleation as a result of a specific interaction, and the morphology of the amorphous/crystallization binary blend competition between the advancing spherulite front and diffusion of the amorphous component interlamellar and interfibrillar regions.[8] However, to our knowledge, there is not a detailed study on the blends of PCL with TPU based on PCL diol. In this work, the blends of PCL and copolymer of polyurethane containing polycaprolactone as a soft segment were prepared by melt mixing. It is believed that the blends of TPU(*PCL diol*) and PCL are miscible because of their micro-structural similarity and intermolecular interaction. In this paper, we have studied the miscibility behavior in TPU/PCL blends as fully miscible blends and its effect on crystallization of PCL in the blends using differential scanning calorimetry (DSC) and Wide-angle X-ray Scattering (WAXS).

Materials and Methods

Polyrurethane based on polycaprolactone-diol was delivered from Coim co. (Italy). This polyesterurethane is food grade with density of 1.16 gr/cm^3. Poly (ε-caprolactone) (PCL) was obtained from Sigma-Aldrich co. (Germany). It has a number-average molecular weight of 42500 and density of 1.145 gr/cm^3. All blends were prepared by melt blending in a Brabender internal mixer at 200 °C and a rotor speed of

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50 rpm for approximately 5 min. Four types of blends with PCL content of 20, 30, 40 and 50 wt% were prepared. The glass transition temperature (T_g), melting and crystallization behaviour of the polymer blends were studied by DSC with a Mettler Toledo DSC-822 instrument. WAXS of the samples were obtained on a Philips diffractometer using monochromatized Cu K_α radiation in the diffraction range of $2\theta = 10–40°$.

Results and Discussion

Miscibility, T_g and Melting Point Depression Analysis

Blend miscibility is often quantified by measuring the blend T_g and analyzing its dependence with composition. The dependence of the T_g on the composition of TPU/PCL blends is illustrated in Figure 1.

The T_g versus composition curve does not obey the Fox relationship, but it is fitted with Gordon-Taylor equation[9] which is valid in the case of miscibility in the amorphous phase. In the latter equation, fitting parameter of k is defined as $k = \Delta\alpha_{p2}/\Delta\alpha_{p1}$, which $\Delta\alpha_{pi}$ is the difference in the thermal expansion coefficient between the liquid and glassy states at T_{gi}. Subscripts 1 and 2 indicate PCL and TPU, respectively. In this work k is obtained as 0.37. Data fitting with Gordon-Taylor equation shows that the blend is miscible.

Thermodynamic considerations predict that chemical potential of a polymer will be decreased by adding a miscible diluent. If the polymer is crystalline, this decrease in chemical potential will result in a decreased equilibrium melting point. According to the Flory-Huggins theory,[10] the melting point depression is given by

$$T_m^0 - T_m^{0'} = \Delta T_m^0 = -B\frac{V_{2u}}{\Delta H_f^0}T_m^0\phi_1^2 \qquad (1)$$

where $T_m^{0'}$ and T_m^0 are the equilibrium melting points of the blend and pure crystallizable component, respectively. ΔH_f^0 is the perfect crystal heat of fusion per mole of repeat unit. Subscripts 1 and 2 indicate the amorphous polymer (here TPU) and crystalline phase (here PCL), respectively. V_{2u} is the molar volume of repeat unit, ϕ_1 is the volume fraction of the component in the blend and B is the interaction energy density of two polymers. The correct calculation of parameter B requires the adequate determination of the equilibrium melting temperatures, which here we used Hoffman and Weeks approach[11] to calculate T_m^0s. Plots of T_m versus T_c are shown in Figure 2.

The values of T_m^0 and $T_m^{0'}$ evaluated by extrapolating the least squares fit lines of experimental data to intersect the line of $T_m = T_c$. A plot of ΔT_m^0 versus φ_1^2

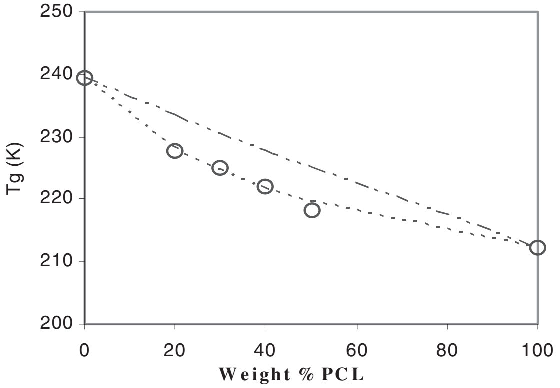

Figure 1.
Glass transition temperatures versus composition for TPU/PCL blends: (–···) Fox equation; (·····) Gordon-Taylor equation; (○) data of this work.

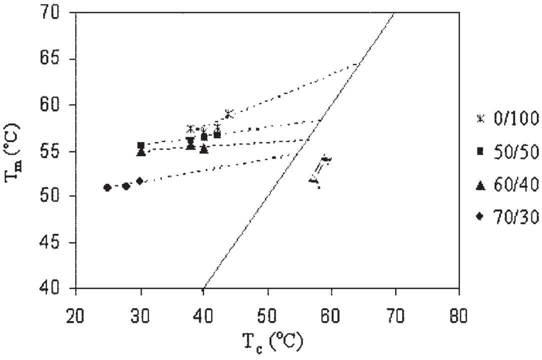

Figure 2.
Plots of the observed T_m vs T_c for TPU/PCL blends.

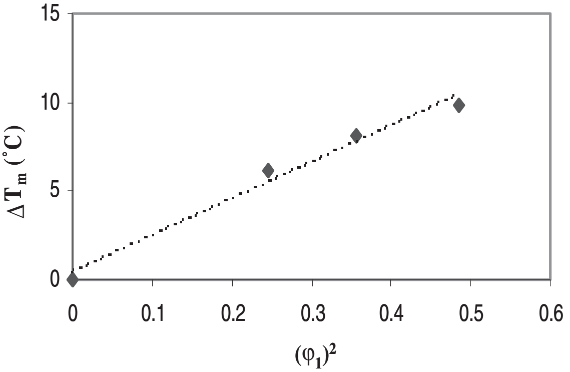

Figure 3.
Melting point depression versus φ_1^2.

according to equation 1 should yield a straight line with a slope which is proportional to B and a zero *y*-intercept. Figure 3 shows such a melting point depression.

The negative value of B (-1.8 cal/cm^3) shows that TPU/PCL blends are miscible.

Crystallization and Melting Behavior of PCL

As a single T_g was detected on the DSC thermograms and a negative value of the polymer-polymer interaction energy density obtained, it is supposed that TPU/PCL blend to be a miscible system. Therefore, it is expected that blend miscibility affects on crystallization behavior of PCL in the blends.

Figure 4 shows the DSC thermograms of pure PCL and various TPU/PCL blends at a cooling rate of -10 °C/min from 80 °C. As shown in this figure, T_c of the PCL in the blends, compared to pure PCL, decreases about 3–40 degrees with blend composition

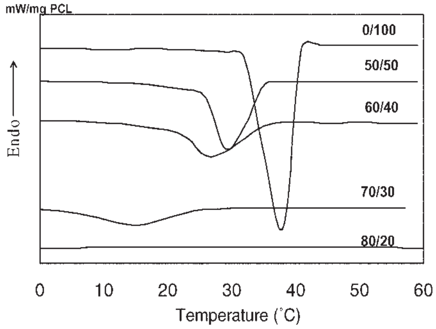

Figure 4.
DSC scans of TPU/PCL blends with different compositions at a cooling rate of -10 °C/min from 80 °C.

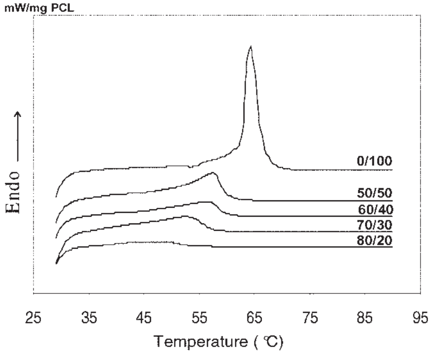

Figure 5.
DSC scans of TPU/PCL blends with different compositions at a heating rate of 10 °C/min from 80 °C.

and also becomes broader. This suppression of T_c indicates that TPU retards or even inhibits the PCL crystallization in the blends.

Furthermore, figure 5 shows the DSC heating thermograms of pure PCL and various TPU/PCL blends after cooling the samples under the same conditions. T_m of the PCL in the blends, decreases by about 5–20 degrees with blend composition compared to T_m of pure PCL.

These results indicate that the crystallization behavior of PCL in these blends is changed. It is reasoned[12] that the interactions that are often established between two constituents in miscible blends can contribute to slowing down of the rate of crystallizing species being drawn into (or diffusing to) the crystals.

Woo et al.[12] suggest that chain mobility in miscible blends is also a factor that affects the crystallization rate. Figure 6 allows comparison of the DSC curves of pure PCL and TPU/PCL(50/50) and TPU/PCL(60/40) blends in the case of isothermal crystallization ($T_c = 40\,°C$). As shown, with increasing TPU content in the blends the crystallization rate, corresponding to the reciprocal of the peak time of the exotherm, decreases. The presence of amorphous TPU with high T_g in the blends significantly decreases the rate of PCL crystallization.

In general there are three main factors affecting the crystallization rate, T_m and T_c depression in the miscible crystalline/amorphous polymers with higher T_g's than pure PCL: (1) the decrease in the segmental mobility of the crystalline polymer transporting across the liquid-solid interface due to the high T_g's of the blends, (2) the dilution effect of PCL in the blends which reduces the number of crystallizable segments on the front of the growth spherulite, and (3) the decrease in the supercooling due to melting point depression.

Wide-Angle X-Ray Scattering

Representative WAXS patterns of TPU, PCL and their blend are shown in Figure 7. Two main diffractions for PCL and the blends, at 2θ around 21° and 23° attributed

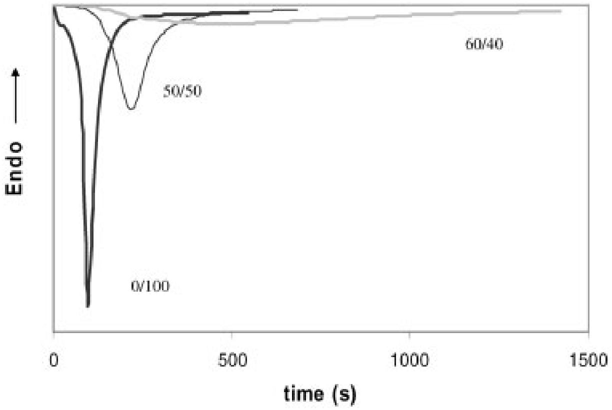

Figure 6.
DSC curves for the isothermal crystallization of TPU/PCL blends at 40 °C.

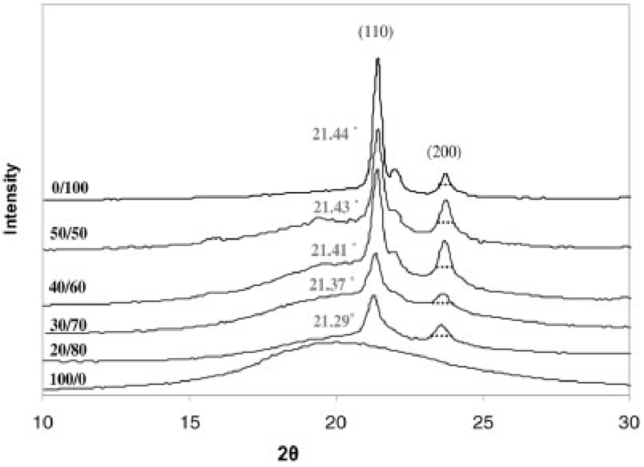

Figure 7.
WAXS of TPU/PCL Blends.

to the (110) and (200) planes in PCL,[13] are detected.

It is observed that the position of diffraction peak related to (110) planes of PCL shifted to lower values with increasing of TPU content in the blends. This shows that *b*-axis of orthorhombic unit cell of PCL being more spread out in the blends and interplanar spacing of (110) planes was increased with increasing of TPU content according to Bragg law. It can therefore be concluded that considerable interaction occurs between PCL and TPU in the blends. Moreover, the half width of both peaks was increased, indicating that the PCL crystal size decreased in the blends with increasing TPU content. These observations are because of various main factors of miscibility that contribute to crystal formation of PCL in the blends.

Conclusions

The analyses of glass transition temperature and melting point depression show that the TPU/PCL blend is miscible reflected to composition dependence of T_g and negative value of polymer-polymer interaction density.

Blending of TPU with PCL causes a depression in overall crystallization, T_c and T_m. Such thermal behavior and WAXS pattern of PCL in the blends show that the crystallization ability of PCL in the blends decreases compared to the pure PCL. These results are attributed to miscibility of the blend components and polymer-polymer interactions.

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