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

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## Introduction

Poly(ε-caprolactone) (PCL) is a highly crystalline polymer that is miscible with several amorphous polymers including chlorinated polyether, poly(vinylchloride), poly(hydroxyether) and Bisphenol A polycarbonate. The crystallization behavior of miscible blend of amorphous/crystalline polymers has widely been studied. Generally a depression of the crystallization ability has been found with addition of amorphous component because of the reduction of chain mobility, the change of free energy of nucleation as a result of a specific interaction, and so on [1]. In this work, for the first time, the blend of PCL and copolymer of polyurethane containing polycaprolactone as a soft segment is considered. The structural similarity of TPU soft segment with PCL affects on formation of the miscible component and crystallization behavior of PCL in the blend. This has been studied using differential scanning calorimetry (DSC) and Wide-angle X-ray Scattering (WAXS).

## Experimental

Polyurethane 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, density of 1.145 gr/cm$^3$ and melting point of 60 °C. All blends were prepared by melt blending in a Brabender internal mixer at 200 °C and a rotor speed of 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$_\alpha$ radiation in the diffraction range of 2θ = 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 [2] 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.
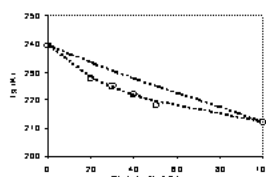


**Figure 1.** Glass transition temperatures versus composition for TPU/PCL blends: (—·—) Fox equation; (—·—) Gordon-Taylor equation; (⊙) data of this work.

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 [3], 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. $\Delta H_f^0$ is the perfect crystal heat of fusion per mole of repeat unit.
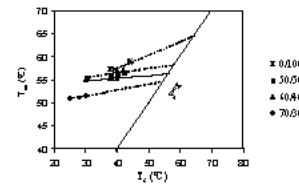


**Figure 2.** Plots of the observed T$_m$ vs T$_c$ for TPU/PCL blends

Subscripts 1 and 2 indicate the amorphous polymer (here TPU) and crystalline phase (here PCL), respectively. $V_{2u}$ the molar volume of repeat unit, $\Phi_1$ 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 [4] to calculate T$_m^0$s. Plot of T$_m$ versus T$_c$ are shown in figure 2.
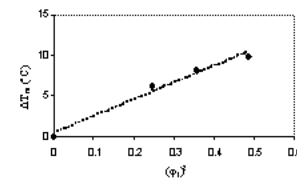


**Figure 3.** Melting point depression versus $\phi_1^2$

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 $\Delta T_m^0$ versus $\phi_1^2$ 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 blend is miscible.

### Crystallization and Melting Behavior of PCL

In the thermal analysis of TPU/PCL blend by DSC, T$_c$ of PCL in the blend decreased by about 3-40 degrees with blend composition compared to T$_c$ of pure PCL. Tm of the PCL in the blend, decreased by about 5-20 degrees with blend composition compared to T$_m$ of pure PCL. These results indicate that TPU retards or even inhibits the PCL crystallization in the blends.

### Wide-angle X-ray Scattering

Representative WAXS patterns of TPU, PCL and their blend are shown in Fig. 4. Two main diffractions for PCL and the blends, at 2θ around 21° and 23° attributed to the (110) and (200) planes in PCL [5], are detected.
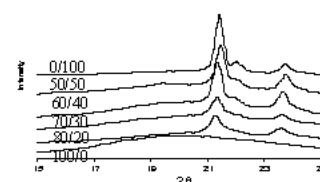


**Figure 4.** WAXS of TPU/PCL Blends

It is observed that the position of diffraction peak related to (110) planes 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.

## Conclusions

The analysis 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.

Thermal behavior and WAXS pattern of PCL in the blends show that the crystallization ability of PCL in the blends decreases compared to pure PCL. This is due to miscibility of the blend components and polymer-polymer interactions.

**References**

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