

Blends of Thermoplastic Polyurethane and Polypropylene. I. Mechanical and Phase Behavior

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ABSTRACT: Pure thermoplastic polyurethane (TPU), polypropylene (PP), and TPU/PP blends with different weight ratios prepared in a twin-screw extruder were investigated by dynamic mechanical analysis (DMA), the universal tester for mechanical investigation, and by wide-angle X-ray diffraction (WAXD). The addition of PP above 20 wt % to the TPU stepwise changed the ductility and Young's modulus, i.e., apparently a kind of ductile → brittle transition occurred between TPU/PP 80/20 and TPU/PP 60/40 blends. This fact and the result of analysis of WAXD curves indicated matrix → dispersed phase inversion in this concentration region. TPU melt

enabled easier migration of the PP chains and prolonged crystallization of PP matrix during solidification process affecting thus crystallite size, orientation, and crystallinity. In accordance to this fact, DMA results indicated partial miscibility of PP with polyurethane in the TPU/PP blends due to the lack of interfacial interaction and adhesion between the nonpolar crystalline PP and polar TPU phases. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104, 3980–3985, 2007

Key words: blends; polyurethane; polypropylene; mechanical properties; phase structure

INTRODUCTION

Polymer blends are intimate mixtures of different commercially available polymers with no covalent bonds between individual component polymers.¹ Polymer blending has received increasing attention from both the scientific and industrial communities as it is widely accepted as an efficient method to offer an attractive low-cost substitute to the development of entirely new materials. The main goal of blending is modification of mechanical properties, improvement of impact strength at low temperatures, in particular abrasion resistance, and, last but not least, improvement of processability.² The properties of polymer blends are usually controlled by the properties of the components, morphology of the blends, and interaction between components in the blends. Thermoplastic polyurethane (TPU) continues to play an important role within the rapidly growing family of thermoplastic elastomers and its application can be found in almost all industrial branches such as engineering materials, coatings, adhesives as well as films. The TPUs are the systems with microphase-separated domains composed of relatively flexible soft segments (SSs) and stiff hard segments (HSs). The SS consists mainly of polyethers or polyesters, while the HS is composed of the diisocyanate

component and the so-called chain “extender,” a low-molecular-weight diol. The HSs are able to aggregate, forming separate microdomains with a regular crystallite-like structure consisting of chain segments paralleled aligned. The TPU domains are stabilized by hydrogen bonds between the NH group as donor and the carbonyl of another urethane group as acceptor.³ Glassy or crystalline HS domains act as physical crosslinks and reinforcing fillers, while the SS phase causes the flexibility. Increased interest for blending of TPU with other polymers has been caused by the necessity of handling the problems resulted from specific structures of TPU macromolecules, interphase interactions, and microphase transformations.

Polypropylene (PP), a semicrystalline polyolefin plastomer, is quite an outstanding polymer material with respect to its wide property spectrum performance, in particular its ease of processing, good chemical resistance, rigidity and heat resistance, and relatively low cost.⁴ To improve low PP impact toughness at low temperatures, the common practice is to incorporate elastomers into PP.

According to above-mentioned facts, the idea of selecting TPU/PP blends was to improve of lack properties of one TPU or PP polymer in a complementary way by blending with other PP or TPU components. The aim of this work was to study the effects of different TPU/PP blending ratios on the dynamic mechanical properties, mechanical properties, and phase structure characteristics.

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TABLE I
Compositions of TPU/PP Blends and Molding Temperatures

TPU/PP blends (wt %)	Molding temperature (°C)
100/0	160
80/20	160
60/40	180
50/50	180
40/60	180
20/80	220
0/100	220

EXPERIMENTAL

Materials and methods

TPU (Desmopan 300) obtained from Bayer (Germany) and PP, a commercial product Moplen HP 500N, obtained from Basell were used in this study. It is a polyester-type TPU with HS formed by the addition of butanediol to diphenyl methane-4-4'-diisocyanate (MDI). The molecular weight of TPU was reported to be 221,378 g/mol (M_w) based on gel permeation chromatography (GPC) and its T_g is -24.6°C . The pure polymers and TPU/PP blends (of 80/20, 60/40, 50/50, 40/60 and 20/80 wt % compositions) were prepared in a Hake Record 90 twin-screw extruder. The samples used for the measurements were prepared by pressing the extruded granules in a hydraulic press. Table I summarizes the blend compositions used in this study.

Dynamical mechanical properties

The viscoelastic properties of the pure TPU, PP, and TPU/PP blends were carried out with a Dynamic Mechanical Analyser DMA 983, TA Instruments, at a frequency of 1 Hz. The changes of storage (E'), loss (E''), and damping ($\tan \delta$) moduli were measured over the temperature range of -100 to 250°C at a heating rate of $5^\circ\text{C}/\text{min}$. The sample length between the clamps was approximately 25 mm. All the samples were cooled to -100°C using liquid nitrogen. The miscibility of the TPU/PP blends is characterized also by employing DMA technique.

Mechanical testing

Mechanical properties of pure TPU, PP, and TPU/PP blends were measured on a Zwick (Model 1445) tensile machine. Tests were performed at ambient temperature (23°C) and a crosshead speed of 50.00 mm/min. At least five test specimens of 30.00 mm \times 13.0 mm \times 3.5 mm were tested for each blend and average values were calculated.

Wide-angle X-ray diffraction

The wide-angle X-ray diffractograms of the plates were obtained using a Philips diffractometer PW1710, with monochromatized CuK_α radiation in the diffraction range $2\theta = 5\text{--}40^\circ$. Overall degree of crystallinity, $w_{c,x}$, was evaluated by the Ruland method⁵:

$$W_{c,x} = \frac{I_c}{I_c + KI_a} \tag{1}$$

where I_c and I_a are integrated diffraction intensity from crystalline (PP + TPU) and amorphous (PP + TPU) phases, respectively. The value of correction factor was $K = 1.00$ in accordance to proposal of Bodor, Grell, and Kallo for PP⁴ as a component with significantly higher crystallinity in blends. Theoretical values of degree of crystallinity ($w_{c,\text{calc}}$) were calculated by the additivity rule⁶:

$$w_{c,\text{calc}} = w_{c,x,1}f_1 + w_{c,x,2}(1 - f_1) \tag{2}$$

where $w_{c,x,1}$ and $w_{c,x,2}$ are the crystallinities of polymers 1 and 2 in the blend and f_1 is the weight fraction of polymer 1.

The crystallite size L_{040} was calculated by Scherrer formula⁷ after the correction for instrumental broadening with a (111) germanium diffraction profile.

The orientation parameters A_{110} and C , used as measures for orientations of corresponding (110) and (040) α -iPP planes, were calculated using Zipper et al.'s⁸ formulae:

$$A_{110} = \frac{I_{110}}{I_{110} + I_{111} + I_{131+041}} \tag{3}$$

$$C = \frac{I_{040}}{I_{110} + I_{040} + I_{130}} \tag{4}$$

where I_{hkl} represents the intensities of the reflections from corresponding planes of α -form of the iPP phase.

RESULTS AND DISCUSSION

Dynamic mechanical analysis of the blends

The E'' , E' , and $\tan \delta$ curves obtained from a DMA technique for pure TPU and PP components and for TPU/PP blends are shown in Figures 1–3, and the values of dynamic mechanical properties are given in Table II.

The curves of loss modulus (E'') versus temperature (T) are shown in Figure 1. The E''/T curve of pure TPU exhibits one sharp intense peak at -24.6°C , which corresponds to the glass transition (T_g) of SS of the TPU.^{9,10} In the E''/T curve of pure PP three transitions can be distinguished. Wide relaxation region

TABLE II
Dynamic Mechanical Properties of Pure TPU, PP,
and TPU/PP Blends

TPU/PP blends (wt %)	T_g (TPU) (°C; E'')	T_g (PP) (°C; E'')	E' (GPa) at 25°C	α_c (°C)	γ (°C)
100/0	-24.6	-	0.033	-	-
80/20	-21.7	-	0.262	-	-
60/40	-21.6	18.7	0.810	82.7	-66.4
50/50	-22.0	21.3	1.281	81.8	-59.4
40/60	-20.8	23.0	1.667	79.4	-66.4
20/80	-18.6	24.7	3.000	83.9	-59.4
0/100	-	25.1	3.838	87.0	-49.5

(from -10 to 50°C) has a maximum at 25.1°C , which corresponds to glass transition (or β relaxation) of amorphous phase in semicrystalline iPP.¹¹ The γ relaxation of the PP appears at -49.5°C due to the motions of small-chain groups like methyl and methylene.¹² The α_c -transition maximum appears at higher temperatures (at $\sim 87.0^\circ\text{C}$). It corresponds to a more rigid chains with amorphous character related to the PP crystallites (tie molecules etc.). The TPU/PP blends show two relaxation transition peaks located in temperature region between -4.5 and $+25.1^\circ\text{C}$. These E'' peaks correspond to the T_g values of pure TPU and pure PP, respectively, indicating thus the existence of essentially pure amorphous TPU and PP phases in blends. The T_g s maxima of the TPU and PP phases slightly broaden and shift towards to each other. Such shift of T_g s suggests partial miscibility of the TPU and PP chains.¹³

Figure 2 shows the variation of the storage modulus (E') as a function of the temperature for the pure TPU, PP, and TPU/PP blends.

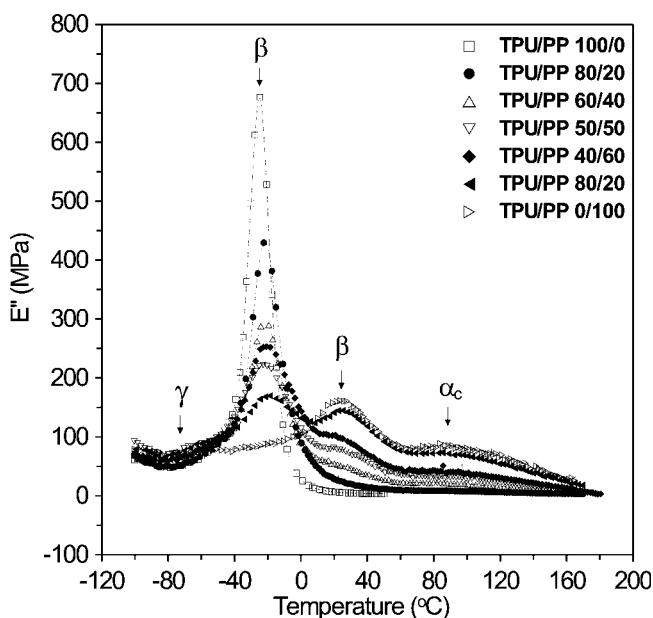


Figure 1 Variation of the loss modulus (E'') as a function of the temperature for the pure TPU, PP and TPU/PP blends.

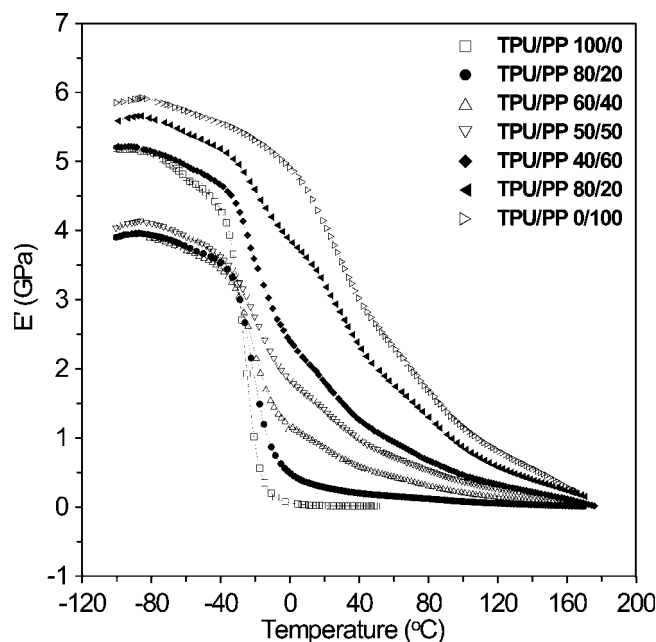


Figure 2 Variation of the storage modulus (E') as a function of the temperature for the pure TPU, PP, and TPU/PP blends.

TPU and PP, as well as for the TPU/PP blends. The values of storage modulus decrease monotonically with increasing temperature. The E' curve of TPU shows a typical behavior of an elastomer. At low temperatures the curves of storage modulus of the blends with 20, 40, and 50 wt % of PP are beneath the E' curve for pure TPU. This effect may be due to less interaction between SSs and HSs in pure TPU in low temperature range. This effect seems to prevail over

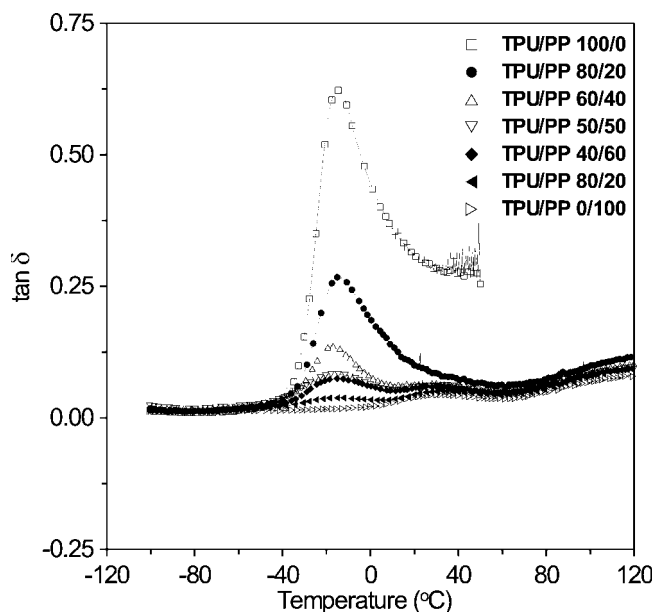


Figure 3 $\tan \delta$ curves as function of the temperature for the pure TPU, PP, and TPU/PP blends.

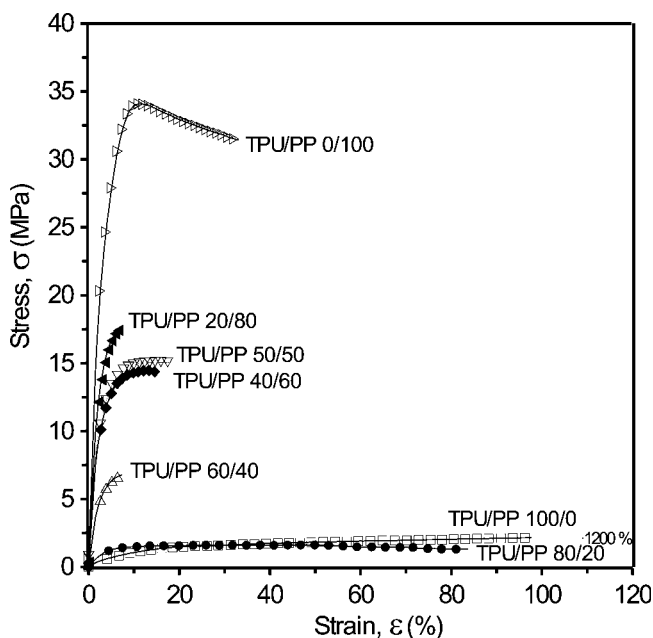


Figure 4 Stress-strain curves for pure TPU, PP and TPU/PP blends.

the increase of rigidity by addition of rigid PP.¹⁴ The storage modulus curves of the blends around the glass transition zone are intermediate between the E'/T curves of the pure TPU and PP. The value of storage modulus of blends steady increases with increasing PP content in blends (Fig. 2, Table II).

The damping factor, $\tan \delta$, of the pure TPU, PP, and TPU/PP blends are shown in Figure 3. The $\tan \delta$ peaks of the TPU and PP phases in the TPU/PP blends broaden asymmetrically causing thus apparent approach (even partial overlapping) their temperature ranges. The variation of $\tan \delta$ with temperature shows the same trend as the loss modulus indicating thus partial miscibility of the blends.

Mechanical properties

The mechanical properties of pure TPU, PP, and TPU/PP blends were measured by stress-strain tests and obtained results are shown in Figure 4 and Table III.

Pure TPU is ductile elastomer, while pure PP is a rigid material. Simultaneously, the TPU has low tensile strength (3.0 MPa) in comparison to pure PP (31.4 MPa). The addition of 20 wt % of the PP to TPU somewhat decreases the tensile strength (from 3.0 to 1.3 MPa; Table III). It is generally expected that an increase in the amount of stiff material in elastomeric material results in an increase in tensile strength of blends. The opposite effect can be attributed to the immiscibility and incompatibility between TPU and PP at this content ratio that lead to the inhomogeneities with weak interfaces in this blend. Incorporated PP may cause disruptions of the

TPU interchange hydrogen bonding, make easier crack propagation at weak phase interfaces lowering thus of tensile strength.¹⁵ However, the tensile strength of blends expectable increases with further PP addition (higher than 20 wt %). In this way, tensile strength minimum at TPU/PP 80/20 blend looks like a breaking point in strength versus composition curve. The addition of the PP, as a stiffer component, to elastomeric TPU decreases the elongation at break as shown Table III. Stepwise decrease of the elongation at break occurs between the TPU/PP 80/20 and 60/40 blends. Simultaneously, Young's modulus stepwise increases between these two blend. Irregular variation of low values of elongation at break with further PP addition (>20 wt %) is reasonable behavior characteristic for brittle fracture of polymer materials.

Zhang et al.¹⁶ have shown how the point of phase inversion could be indicated on the basis breaking point in curves of tensile or flexural behavior of blends. According to this, break in tensile strength curve indicated as a minimum for TPU/PP 80/20 blend, as well as the stepwise change in Young's modulus and elongation at break between the TPU/PP 80/20 and 60/40 blends, indicate substantial structural or morphological change in between the TPU/PP 80/20 and 60/40 blends caused by phase inversion.

Wide-angle X-ray diffraction

Diffraction curves of pure TPU and PP components and blends are presented in Figure 5. Diffractograms of PP and TPU/PP samples reveal mainly reflections characteristically for stable monoclinic α -phase of semicrystalline isotactic PP.¹⁷ Weak reflections (signed with arrows) superimposed on amorphous diffraction halo of pure TPU and TPU/PP 80/20 blend indicate low degree of crystallinity of TPU. The addition of TPU to PP does not affect the nucleation β - or γ -PP phase. The intensity of α -PP peaks decreases from pure PP till TPU/PP 60/40 gradually because TPU build in blend as an amorphous component. The co-existence of crystalline PP and TPU peaks exists only

TABLE III
Mechanical properties of pure TPU, PP and TPU/PP blends.

TPU/PP blends (wt %)	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
100/0	3.0 ± 0.2	2500.0 ± 33.5	19.75 ± 0.8
80/20	1.3 ± 0.1	84.0 ± 2.5	37.70 ± 1.6
60/40	7.1 ± 0.3	8.0 ± 1.0	243.2 ± 8.3
50/50	14.6 ± 0.7	17.0 ± 3.0	446.3 ± 33.7
40/60	15.1 ± 0.2	19.1 ± 2.0	480.3 ± 35.3
20/80	17.4 ± 0.6	7.0 ± 0.8	645.3 ± 37.1
0/100	31.4 ± 0.4	33.0 ± 2.1	933.8 ± 41.3

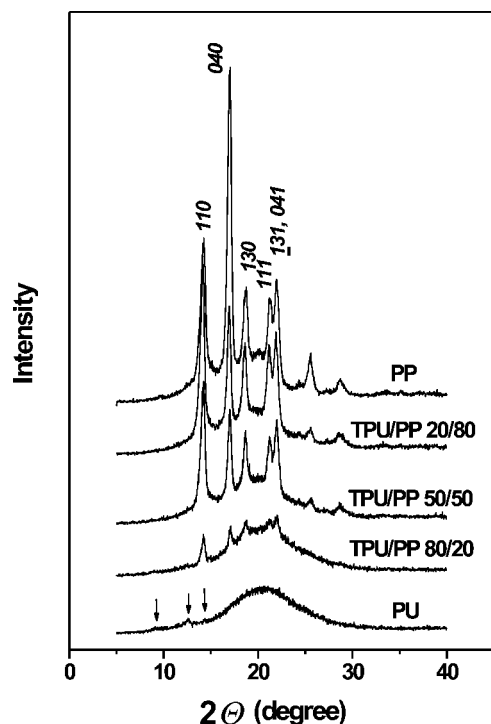


Figure 5 Diffractograms of pure PP and TPU components and TPU/PP blends.

in diffractogram of TPU/PP 80/20 blend indicating thus the cocrystallization of both crystalline phases TPU and PP (Fig. 5). Obviously, scarce crystallization of TPU ($\sim 70^\circ\text{C}$)¹⁸ follows the crystallization of α -phase of PP ($\sim 120^\circ\text{C}$)¹⁸ dispersed in TPU in matrix during the solidification of the TPU/PP 80/20 melt. The crystalline TPU peaks are too weak already in TPU/PP 80/20 blend to notice them in blends with higher PP contents.

Somewhat stronger decrease of α -PP peaks intensities between TPU/PP 60/40 and TPU/PP 80/20 blends and the coexistence of slight TPU and PP peaks in diffractogram of the TPU/PP 80/20 blend coincide with apparently ductile \rightarrow brittle transition of blends in this concentration region revealed by stress-strain curves (Fig. 4). These facts may indicate substantial morphological change due to presumable matrix \rightarrow dispersed phase inversion in this concentration region.

The overall degree of crystallinity, $w_{c,x}$ (the sum of crystalline PP + TPU phases) and the crystallite size, L_{040} , are shown in Figure 6. The experimental values of crystallinity decrease with the addition of TPU polymer almost accordingly to the additivity rule (eq. (2)), i.e., they are close to the calculated crystallinity values. Somewhat exceeding of the experimental values in comparison to the calculated crystallinity values in the region between TPU/PP 20/80 and 80/20 is in agreement with the behavior of crystallite L_{040} size of α -iPP (Fig. 6). Steady increase of the crys-

tallite L_{040} size of the α -PP (dotted fitting curve shows general increase) might be ascribed to the solidification effect that prevail possible nucleation ability of TPU at higher amounts (20 wt % and more of added TPU). During solidification of TPU/PP blend melt the crystallization of the α -phase of isotactic PP occurs firstly ($\sim 120^\circ\text{C}$).¹⁸ Remaining TPU melt enables easier migration and transferring of PP chains to growing PP lamellae and prolongs the crystallization of the PP matrix. As a consequence (of prolonged and enhanced crystallization) the crystallite size and overall crystallinity increase although low crystalline TPU remains in these blends amorphous. The PP chains trapped in dispersed TPU particles, as well as the TPU chains built in amorphous intra- and interspherulitic PP regions, form amorphous TPU or PP regions with partial miscible TPU and PP chains indicated by DMA curves. On the other side, the inhomogeneity of these region and weak interfaces between matrix and dispersed phases cause brittle fracture behavior in wide blend composition range.

Diffractograms in Figure 5 exhibit the change of α -PP reflections intensity indicating thus the influence of TPU on (re)orientation α -PP crystallites during crystallization process, while the addition of TPU to PP slightly change A_{110} index, even small content of TPU significantly decreases the values of C parameter to steady low C values (Fig. 7). According to Zipper et al.,⁸ $C = 1$ corresponds to pure a^* -axis orienta-

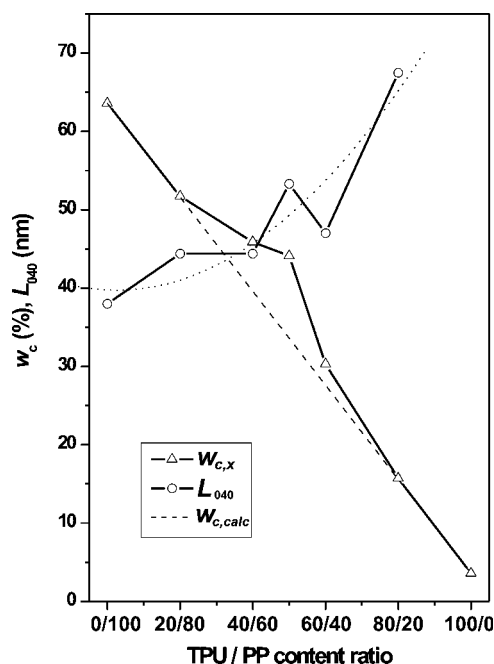


Figure 6 The experimental ($w_{c,x}$) and calculated ($w_{c,calc}$) degree of crystallinity, and crystallite size, L_{040} , as a function of the TPU/PP content ratio. Dotted curve represents best fitting experimental crystallite size values.

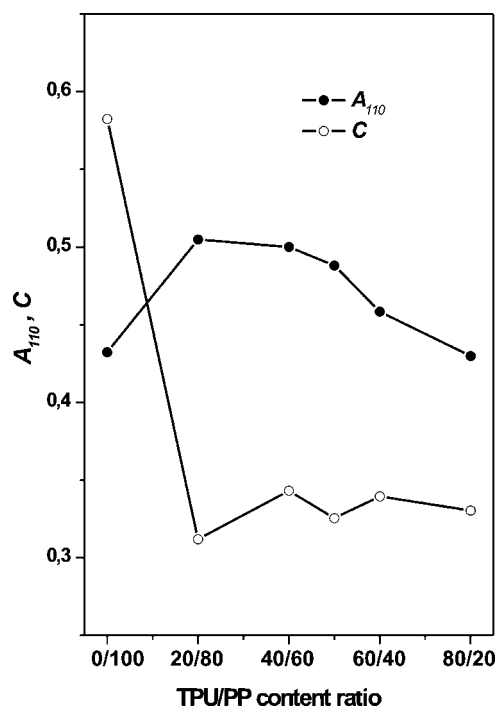


Figure 7 Dependence of orientation A_{110} and C parameters on TPU/PP content ratio.

tion, whereas low C values might be explained by maintaining either c -axial orientation or isotropic iPP matrix ($0 < C \ll 1$ for pure c -axis orientation or for isotropic material). The decrease of C value with addition of TPU indicates the decrease of a^* -axis-oriented lamellae or the direction of lamellar and radial growth of spherulites of PP in plane parallel to the sample surface. According to Fujiyama et al.¹⁹ c -axis-oriented lamellae imply orientation of macromolecular c -axes in planes parallel to the sample surface in machine direction. Isotropic or c -axis (re)orientation influence of TPU proves significant role TPU melt in crystallization process of PP matrix.

CONCLUSIONS

The results from the DMA measurements show that in TPU/PP blends, the loss modulus, and $\tan \delta$ curves demonstrate two T_g peaks which were slightly broaden and shift towards to each other, this suggests partial miscibility of the TPU and PP chains. The storage modulus for the blends is between the E'/T curves of the pure TPU and PP, which also suggested

that the TPU and PP are partially miscible. The addition of PP above 20 wt % to the TPU stepwise changed the ductility of blends. Break point in tensile strength values at TPU/PP 80/20, as well as the stepwise change of the elongation at break, Young's modulus, and reflections intensities in WAXD diffractograms, between the TPU/PP 80/20 and 60/40 blends indicated substantial structural or morphological change caused by phase inversion. The PP chains trapped in dispersed TPU particles, as well as the TPU chains built in amorphous intra- and interspherulitic PP regions, form amorphous TPU or PP regions with partial miscible TPU and PP chains indicated by DMA curves. On the other side, the inhomogeneity of these region and weak interfaces between matrix and dispersed phases cause brittle fracture behavior in wide blend composition range.

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