

Blends of Thermoplastic Polyurethane and Polypropylene.

II. Thermal and Morphological Behavior

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Received 15 May 2008; accepted 28 November 2009

DOI 10.1002/app.31997

Published online 29 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Neat thermoplastic polyurethane (TPU), polypropylene (PP), and TPU/PP blends with different weight ratios that were prepared in a twin-screw extruder were investigated with differential scanning calorimetry and light and scanning electron microscopy. The results confirmed PP matrix to TPU matrix phase inversion in the concentration region between 60/40 and 80/20 TPU/PP blends. The total degree of crystallinity of the blends and the crystallization temperature of PP decreased with

increasing TPU content. On the other hand, the addition of elastomeric TPU to PP significantly increased the spherulite size of PP. The TPU melt islands in the PP matrix prolonged the crystallization of PP during solidification, and this enhanced the growth of spherulites. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1378–1384, 2010

Key words: blends; morphology; poly(propylene) (PP); polyurethanes; thermal properties

INTRODUCTION

Thermoplastic polyurethanes (TPUs) are an important class of elastomers used in many novel and specialized applications for which high mechanical and chemical performances are prerequisites. They are known for their good mechanical strengths, wear and tear resistance, and low-temperature elasticity.^{1,2} TPUs are linear segmented copolymers composed of microphase-separated hard and soft segments. The hard-segment domains, consisting of a diisocyanate extended with a short-chain diol or diamine, are distributed in the soft-segment matrix, which contains either polyesters or poly(ether glycol)s. The hard segments are held together by hydrogen bonds, which form physical crosslinks. These physical crosslinks are thermally labile at melting temperatures. The blending of polymers has been the subject of intensive research in both academic and industrial laboratories. The main goals of blending are the modification of the mechanical properties, the improvement of the impact strength at low temperatures and particularly the abrasion resistance, and, last but not least, the improvement of processability.³ Polymer blends are intimate mixtures of different commercially available polymers with no covalent bonds between individual component polymers that are mostly immiscible.^{4,5} The properties of the

resulting materials may be tailored to meet the requirements of customers or the expectations of specific new applications with a satisfactory balance of a wide range of material properties and costs.⁶ The tailoring of the properties of the final polymer blends, which are combinations of the useful properties of the components that are superior to the properties of the single polymers, can be achieved through the control of the blend phase structure/morphology in processing. It is well known that the morphologies of uncompatibilized polymer blends (the shape, size, and spatial distribution of the dispersed phase and the structure of the polymer matrix) depend on the composition, component properties (viscosity, elasticity, and interfacial tension), and preparation conditions.⁵

Polyolefins can be blended with TPUs to reduce the TPU cost and improve the TPU thermal stability, mechanical properties, and processing performance.⁷ On the other hand, TPUs are blended with polyolefins to improve the polyolefin properties. Polypropylene (PP) belongs to the family of polyolefins; it is a vinyl polymer with a hydrogen atom substituted by a methyl group ($-\text{H}_2\text{C}-\text{CRH}-$)_n. The idea of selecting PP as the second component is mainly due to its ease of processing, chemical resistance, high melting point (T_m), which provides high temperature stiffness, good rigidity, and heat resistance, and relatively low cost.^{8–10} PP as a dispersed phase in a TPU/PP blend can improve the physical properties of the blend.

To complete investigations of the structure–property relationships of TPU/PP blends, in this work, the thermal and morphological behavior of pure

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TPU, pure PP, and their blends was studied as a continuation of previous work dealing with their mechanical and phase behavior.¹¹

EXPERIMENTAL

Materials and preparation

The TPU used (Desmopan 300) was a commercial product of Bayer (Leverkusen, Germany). It was a polyester-type TPU with a number-average molecular weight of 106,951 g/mol and a hard segment formed by the addition of butanediol to diphenyl methane-4,4'-diisocyanate. Isotactic polypropylene (iPP; melt flow index = 12 g/10 min; Moplen HP 500N) was supplied by Basell. Five compositions were prepared with TPU/PP weight ratios of 80/20, 60/40, 50/50, 40/60, and 20/80. The neat polymers (TPU and PP) and their blends (TPU/PP blends) were prepared in a Haake Record 90 twin-screw extruder. Mixing took place with a temperature profile of 170, 170, 180, and 200°C and a screw speed of 60 rpm. Then, the specimens were compression-molded in a hydraulic press at 220°C.

Differential scanning calorimetry (DSC)

DSC measurements were made on a DSC 2910 differential scanning calorimeter (TA Instruments, New Castle, DE) under a nitrogen atmosphere. Calibration was performed with pure indium. The samples were heated from 25 to 200°C at a heating rate of 10°C, melted at 200°C for 10 min, and then cooled to -100°C at a cooling rate of 10°C/min; this was followed by reheating to 200°C for the second heating run. The crystallization and melting parameters were recorded from the cooling and reheating scans.

The crystallinity percentage ($w_{c,h}$) of iPP and the blends was calculated through a comparison of the heat of fusion of the blend sample to the heat of fusion of the completely crystalline polymer as an external standard¹²:

$$w_{c,h} = \frac{\Delta h}{\Delta h_{pp}^0} \times 100 \quad (1)$$

where Δh is the enthalpy of fusion per gram of the sample recalculated for the iPP mass and Δh_{pp}^0 is the enthalpy of fusion per gram of 100% crystalline iPP. For Δh_{pp}^0 , we used 165 J/g as the average heat of fusion of the five data points.¹³

The glass-transition temperature (T_g) was taken as the midpoint of the specific heat increment.

Scanning electron microscopy (SEM)

A JEOL JSM-5800 scanning electron microscope (Tokyo, Japan) was used to study the morphology.

Samples were fractured in liquid nitrogen and covered with gold before being examined with the microscope at an acceleration voltage of 10 kV. All SEM micrographs were secondary electron images.

Optical microscopy

A Leica model DMLS light microscope (Wetzlar, Germany) with a digital camera (Olympus) was used for the observation of thin, crossed, microtomed sections. Because of the anisotropic spherulite forms that arose, the maximal anisotropic diameter of the spherulites was measured with several polarization micrographs of each sample and was quantified as the number-average spherulite diameter (d_{sph}) as follows:

$$d_{sph} = \frac{\sum N_i d_{i,max}}{\sum N_i} \quad (2)$$

where N_i is the number of measured spherulites with maximal diameter $d_{i,max}$.

RESULTS AND DISCUSSION

Thermal properties

DSC measurements were performed to characterize the glass-transition, crystallization, and melting behavior of the neat components and TPU/PP blends. The DSC heating curve of the neat TPU revealed two phase transitions; that is, T_g of the soft segment of TPU was observed at -41.1°C, and T_m of the hard-segment crystallites with a long-range order was observed at 135.7°C. The DSC cooling curve exhibited one exothermic peak at about 70°C corresponding to the crystallization of TPU. Slight melting and crystallization peaks indicated the low degree of crystallinity of the neat TPU.^{14,15} The DSC heating curve of the neat PP exhibited a melting endotherm (T_m) at 162.2°C, whereas the DSC cooling curve revealed an exothermic crystallization peak [i.e., the crystallization temperature (T_c)] at 118.4°C. T_g of the PP phase could not be determined by DSC because PP usually exhibits a negligible glass transition at -10°C.

The miscibility between any two polymers in the amorphous state can be discussed in terms of T_g . DSC scans of TPU/PP blends showed a single T_g , which was attributed to the glass transition of the soft phase of the TPU. The soft-segment T_g increased slightly from -41.1°C for the neat TPU to higher temperatures with increasing PP content (to -35.7°C for the 20/80 TPU/PP blend), and this suggested the presence of the PP phase dissolved in the soft segments, which decreased the mobility of the soft segments (Table I). A slight shift of T_g of the TPU to

TABLE I
Physical Properties of the Neat Components and TPU/PP Blends

TPU/PP blend (wt %)	$T_{g,TPU}$ (°C)	T_m^* (°C)	ΔH_m (J/g)	$T_{c,TPU}$ (°C)	$\Delta H_{c,TPU}$ (J/g)	$T_{c,PP}$ (°C)	$\Delta H_{c,PP}$ (J/g)	$w_{c,h,PP}$ (%)
100/0	-41.1	135.7	7.4	72.6	3.9	—	—	—
80/20	-40.8	157.9	34.4	71.5	3.2	111.3	24.9	20.8
60/40	-38.9	159.1	36.4	70.7	2.8	112.4	26.7	22.1
50/50	-40.2	159.2	48.0	70.1	1.9	112.0	41.1	29.1
40/60	-39.1	159.1	52.2	70.0	0.9	112.3	47.1	31.6
20/80	-35.7	160.8	75.8	69.9	0.4	112.4	75.3	46.0
0/100	—	162.5	103.2	—	—	118.4	96.9	62.5

T_m^* melting temperature of TPU and PP. H_c is the enthalpy of crystallization of TPU, PP.

higher temperatures may indicate a low degree of partial miscibility between the TPU and PP components in amorphous regions.

The DSC heating scans of the TPU/PP blends exhibited one melting peak over the entire composition range, as shown in Figure 1. The melting endotherm of the neat PP widened, and its peak at $T_m = 162.5^\circ\text{C}$ slightly shifted to lower temperatures with the addition of the TPU (Fig. 1 and Table I). The T_m values of crystalline polymers can be related to the size and perfection of their crystal units. Melting of the TPU/PP blends began before T_m of the TPU (onset $T_m < 135.7^\circ\text{C}$) and occurred continuously, so the slight endotherm of the TPU merged into the endotherm (T_m) of PP. An early start of melting and a broadened endotherm indicated the growth of smaller, imperfect crystallites with a widened size distribution.

In Figure 2, two separate T_c peaks can be observed for the TPU/PP blends corresponding to the T_c values of the TPU ($\sim 70^\circ\text{C}$) and PP ($\sim 118^\circ\text{C}$).

The apparent T_c of PP (118.4°C) decreased even with the smallest addition of TPU (20 wt %; $T_c = 112.4^\circ\text{C}$). Further addition of the TPU caused a negli-

gible decrease in T_c up to 111.3°C for the 80/20 TPU/PP blend. The decrease in T_c implied an increase in the supercooling effect (supercooling level = $T_m - T_c$) caused by the addition of the TPU elastomer. The delay of crystallization, observed in some polymer blends,¹⁶ could be the result of decreased mobility and slowed diffusion of the PP chains from a partially miscible amorphous TPU/PP melt.

Figure 3 presents the heat of fusion (ΔH_m) and $w_{c,h}$ versus the TPU content. $w_{c,h}$ and ΔH_m of the TPU/PP blends decreased with an increase in the TPU content. The aforementioned thermal analysis data are in agreement with the results obtained from wide-angle X-ray diffraction.¹¹

Morphological observations

Two-phase morphology

SEM micrographs of the cryogenically fractured samples as well as optical micrographs revealed dispersed particles of the minor phase (TPU or PP) in the polymer matrix of the major phase (PP or TPU), and this thus indicated a two-phase morphology. Spherical and coalesced TPU particles and smaller

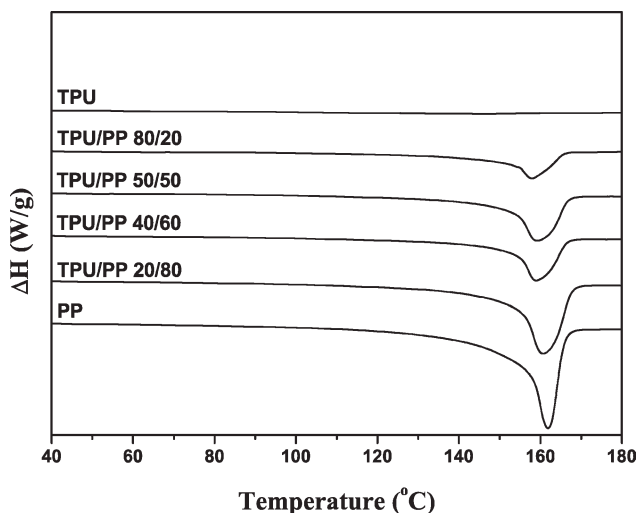


Figure 1 Melting behavior of the neat components and TPU/PP blends. ΔH , Heat flow W/g.

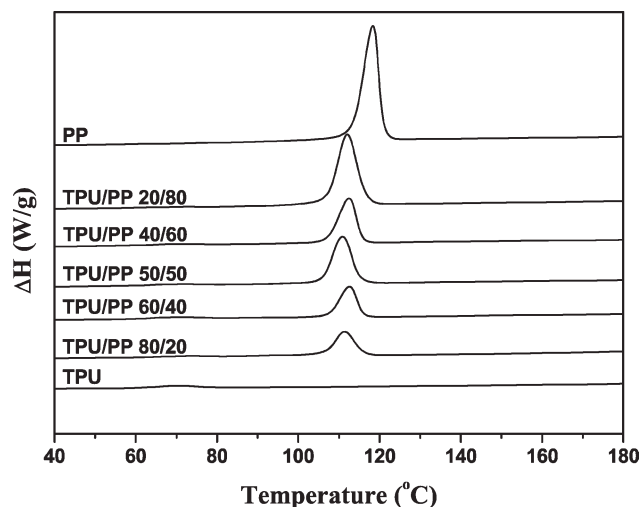


Figure 2 Crystallization behavior of the neat components and TPU/PP blends. ΔH , Heat flow W/g.

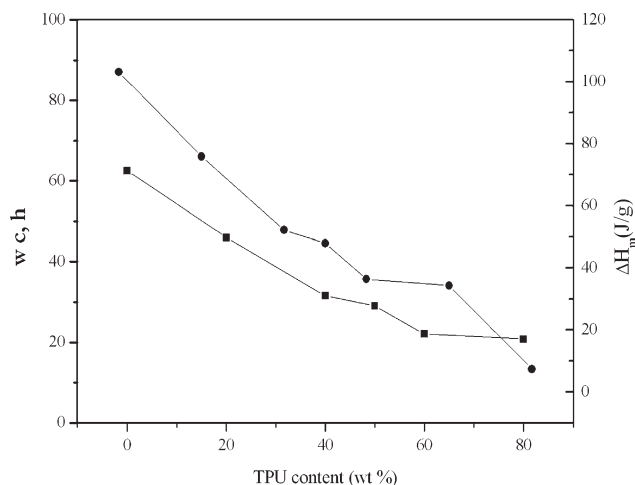


Figure 3 Composition dependence of (●) $w_{c,h}$ and (■) ΔH_m for the TPU/PP blends.

hollows, which arose when these particles were pulled from the surface, can be observed in the SEM micrograph of the 20/80 TPU/PP blend (Fig. 4). In the SEM micrograph of the blend with the TPU matrix phase (80/20 TPU/PP blend; not presented), more black hollows were shown to have arisen from dispersed PP particles that were pulled out. Obviously, stiff PP particles could be pulled out more easily from the fractured surface of the softer elastomeric TPU. The observed two-phase morphology of the TPU/PP blends indicated the immiscibility and low compatibility of the components.

Optical micrographs of the TPU/PP blends, presented in Figure 5, show the region of the PP matrix to TPU matrix phase inversion. An increase in the added amount of the TPU resulted in an enlargement of the dispersed TPU particles by coalescence up to the 60/40 TPU/PP blend [Fig. 5(a)]. The micrograph of this sample revealed large, spherical, and elongated TPU particles because the completion of the cocontinuous phase morphology still did not appear in this blend. Within coarse TPU particles, the dispersed droplets were observed [Fig. 5(b)].

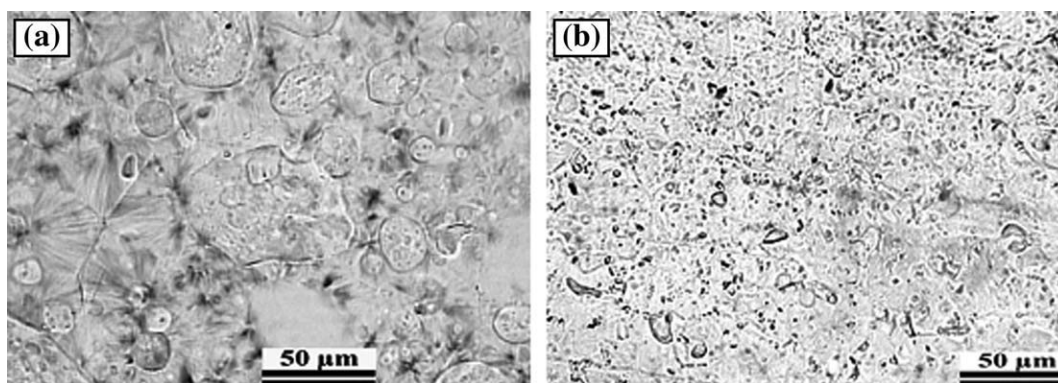


Figure 5 Optical micrographs of TPU/PP blends with (a) 60/40 and (b) 80/20 weight ratios (bar = 50 μm).

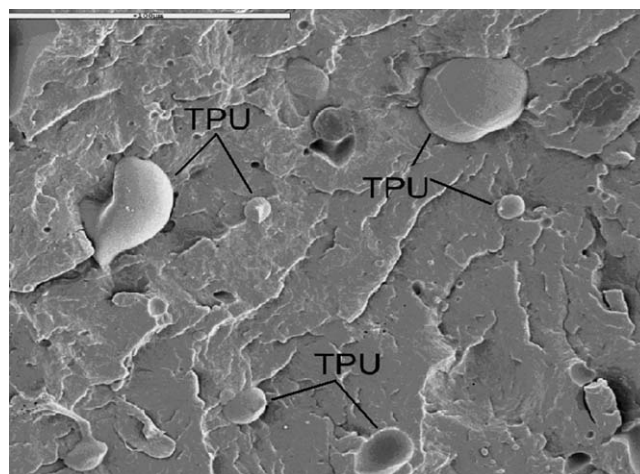


Figure 4 SEM micrograph of the blend (bar = 100 μm).

Favis and Chalifoux¹⁷ proposed the term *composite droplet type* for such a phase morphology observed in PP/polycarbonate blends. In contrast to the 60/40 TPU/PP blend, the optical micrograph of the 80/20 TPU/PP blend revealed small, obviously PP particles dispersed in the TPU matrix [Fig. 5(b)]. Obviously, the completion of the cocontinuous phase morphology could be expected between the 60/40 TPU/PP and 80/20 TPU/PP blends. These results, as well as the stepwise change in the ductility and Young's modulus,¹¹ locate the PP matrix to TPU matrix inversion, in the concentration region between the 60/40 and 80/20 TPU/PP blends. This is in accordance with some morphological models predicting the occurrence of a cocontinuous (bicontinuous) phase morphology on the basis of the viscosity ratio of the components (the empirical Jordhamo law).¹⁸

Structure of the TPU and PP matrices

Thin, microtomed slices of all the samples exhibited (under a light microscope with crossed polars) a spherulitic morphology (characteristic for semicrystalline polymers) that changed with the TPU/PP

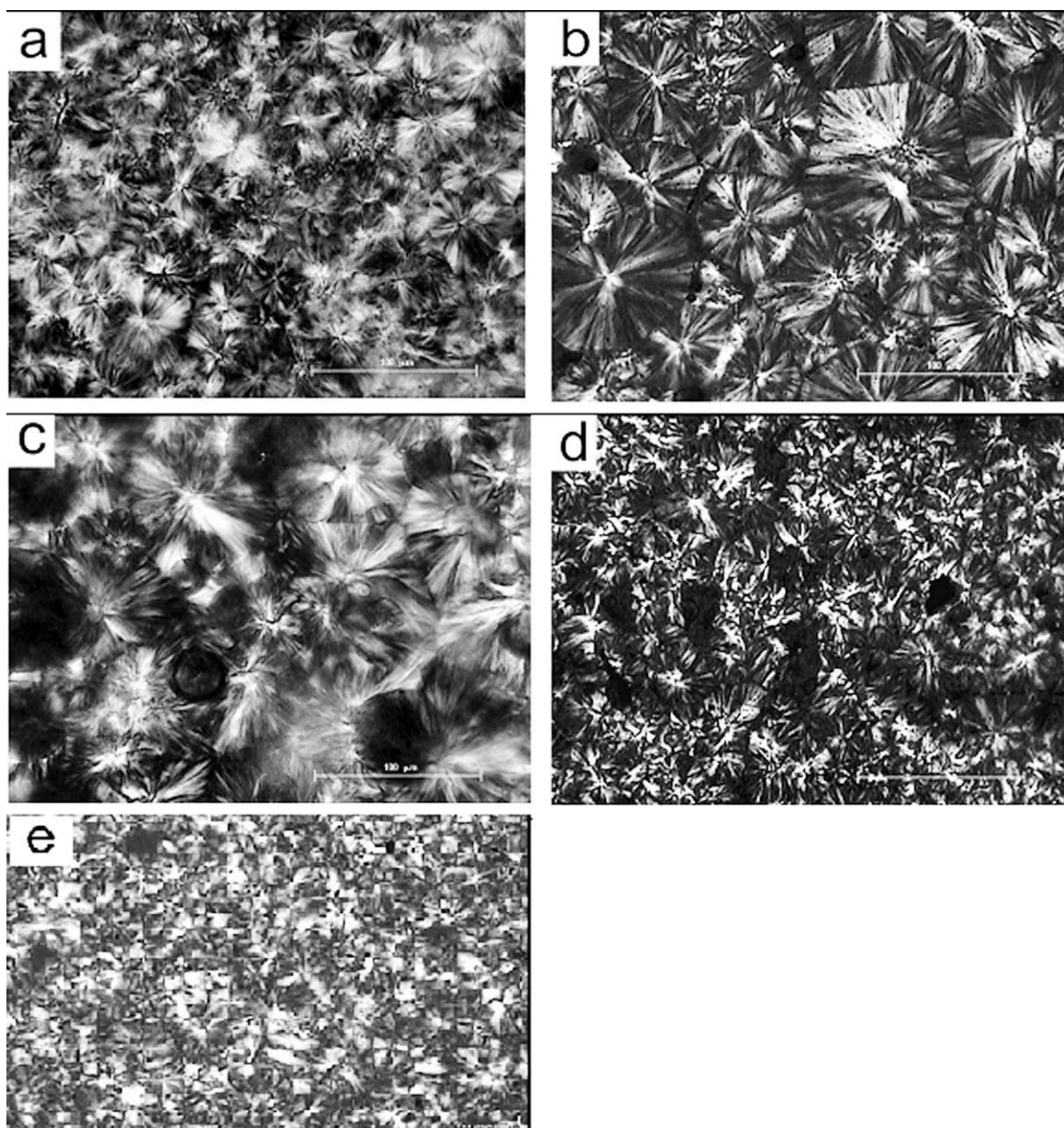


Figure 6 Polarization micrographs of (a) the neat PP, (b) the 40/60 TPU/PP blend, (c) the 60/40 TPU/PP blend, (d) the 80/20 TPU/PP blend, and (e) the plain TPU (bar = 100 µm).

content ratio. Polarization micrographs of plain PP and TPU as well as the 40/60, 60/40, and 80/20 TPU/PP blends [Fig. 6(a–e)] presented characteristic points in the concentration range within which the change in the spherulitic morphology occurred. The polarization micrograph of the neat PP revealed a uniform, spherulitic morphology with irregular or flowerlike spherulites [Fig. 6(a)]. The addition of the TPU elastomer to the PP matrix enhanced spherulitic growth to such an extent that radially growing PP lamellae of adjacent spherulites impinged on one another at clear boundaries and formed polygonal spherulites, as shown in the micrograph of the 40/60 TPU/PP [Fig. 6(b)]. The appearance of well-developed spherulites with the addition of more TPU is

in good agreement with the enlargement of spherulites in PP blends with ethylene–propylene–diene monomer and poly(styrene-*b*-ethylene-*co*-propylene) (SEP) elastomer.^{19,20}

It is well known that the addition of a small amount of low-molecular-weight or polymer components, such as various elastomers, increases the heterogeneous nucleus density and thus decreases the spherulite size.¹⁹ However, it has been proven that the addition of larger amounts of elastomers to a semicrystalline PP matrix leads to the growth of spherulites.^{19,20} This enlargement of the spherulites observed in the TPU/PP blends seems to have been caused by different factors in the solidification process. The addition of the TPU elastomer prolonged

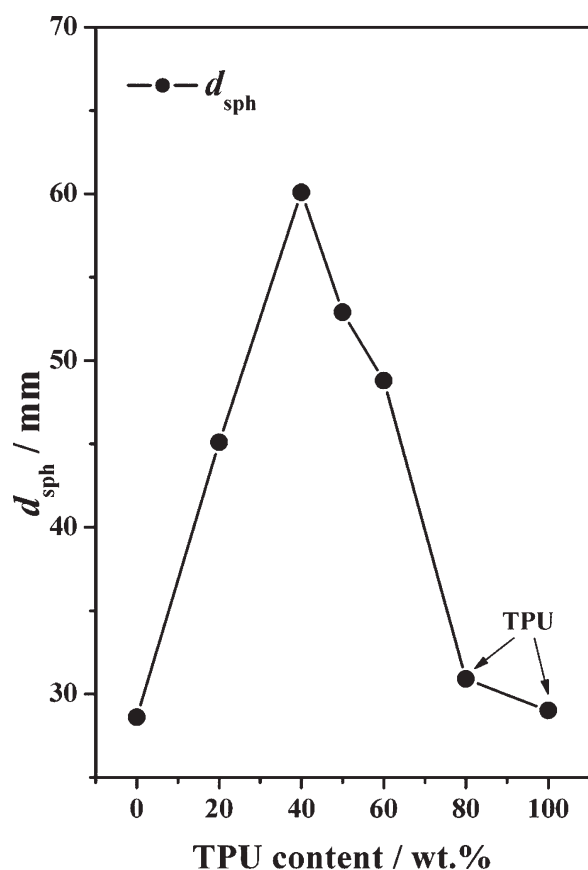


Figure 7 d_{sph} versus the TPU weight content.

the solidification of the TPU/PP blend to a lower T_c ($\sim 70^\circ\text{C}$ for TPU vs $\sim 118^\circ\text{C}$ for PP) and thus prolonged the crystallization of the PP matrix. The TPU melt that remained during the solidification of the blend enabled the easier migration of PP chains from the melt into growing lamellar crystals and spherulites. It is possible that the PP chains remaining in the TPU melt islands and/or the TPU chains, as a transport medium, that were partially included in the amorphous intraspherulitic and interspherulitic regions of the PP matrix led to the apparent partial miscibility in amorphous regions. This partial miscibility of trapped TPU or PP chains in the amorphous regions could be due to the lack of interfacial interactions between the polar, amorphous TPU and nonpolar, crystalline PP phases. The mixing of the PP and TPU chains in the soft, amorphous phases reduced the mobility of macromolecular chains, and this led to the stiffer TPU/PP blends when PP was the matrix phase.¹¹ This explanation may reconcile the structural changes of both the TPU and PP amorphous phases and the TPU T_g during crystallization by partial miscibility on the one hand and by immiscibility on the supermolecular or macrophase level deduced from the two-phase morphology revealed by SEM and optical microscopy on the other hand. The values of d_{sph} calculated with eq. (2), increased

with the TPU elastomer up to 40 wt % (Fig. 7) as a result of the solidification effect of the TPU elastomer. On the other hand, the addition of the TPU elastomer to the PP matrix caused the coalescence of the melt TPU regions and the growth of the dispersed TPU particles. Enlarged, dispersed TPU particles, presenting steric hindrance, may have hindered regular growth of the spherulites, and thus the effect of solidification in the blend with higher TPU contents prevailed. This could be the most effective factor for decreasing the spherulite size from the 40/60 TPU/PP blend to the 60/40 TPU/PP blend [Figs. 6(b,c) and 7]. The polarization micrograph of the 60/40 TPU/PP blend in Figure 6(c) reveals still well-developed and somewhat more diffuse spherulites belonging to PP as the matrix phase. The spherulite size decreased stepwise from the 60/40 TPU/PP blend to the 80/20 TPU/PP blend [Figs. 6(c,d) and 7], and this indicated the PP matrix to TPU matrix phase inversion in the concentration region between these blends. In this way, the spherulitic morphology of the 80/20 TPU/PP blend belonged to the matrix TPU phase, which included dispersed PP particles [Fig. 6(d)]. The neat TPU [Fig. 6(e)] and 80/20 TPU/PP blend [Fig. 6(d)] had a similar irregular spherulitic morphology with a similar spherulite size (Fig. 7).

CONCLUSIONS

The completion of the investigation of the structure-property relationships of TPU/PP blends through examinations of their thermal and morphological behaviors confirmed some conclusions presented in a previous article¹¹ and emphasized new conclusions:

- The two-phase morphology, finally proved by SEM and optical micrographs, indicated the immiscibility of the components in the TPU/PP blends on the supermolecular macrophase level.
- The slight shift of the TPU T_g observed on DSC curves and the crystallization behavior of the blends (as well as the analysis of dynamic mechanical analysis curves in the previous article¹¹) indicated apparent partial miscibility in amorphous regions. It seems that the PP chains remaining in the TPU melt islands and/or TPU chains partially included in the amorphous PP regions partly modified these amorphous regions.
- The growth of the PP spherulites seemed to be caused by different factors in the solidification process: prolonged crystallization of the PP matrix enabled easier diffusion of the PP chains from the melt islands, and steric

hindrance was caused by enlarged TPU particles. Enlargement of the PP spherulites achieved a maximum in the 40/60 TPU/PP blend as a result of the first two effects. At higher TPU contents, enlarged, dispersed TPU particles could hinder the spherulite growth, thus, the first two effects in the solidification process prevailed.

- The stepwise decrease in the dispersed particle and spherulite size (as well as the stepwise change in the ductility and Young's modulus in the previous article¹¹) from the 60/40 TPU/PP blend to the 80/20 TPU/PP blend indicated the PP matrix to TPU matrix phase inversion in the concentration region between these blends.

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