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Morphology and mechanical properties of transcrystalline isotactic polypropylene

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Abstract: We examined mechanical and morphological properties of fully transcrystalline polypropylene grown from the surface of poly(tetrafluoroethylene) sheets. Comparison of mechanical properties between transcrystalline and spherulitic polypropylenes demonstrated that Young's modulus is dependent on the crystallinity and independent of the supermolecular structure. On the other hand, the mechanical yielding process was predominantly affected by the supermolecular structure, and the mechanical energy required for yielding of transcrystalline sheets was greater than that of the spherulitic morphology. In addition, it was found that mechanical necking is required for the alignment of lamellae in the stretching direction. This means that the unfolding process of lamellae orienting in the stretching direction is associated with necking and ductility.

Introduction

In filler-reinforced polymer composites, when a high modulus fibre is embedded into semicrystalline polymers such as polyethylene and polypropylene, a highly oriented layer, known as transcrystallinity (TC), is developed at the fibre/matrix interface. The formation of TC is associated with the consequence of a high heterogeneous nucleating ability of the fillers compared to that of the bulk matrix. The TC zone in the composites plays an important role in the improvement of the adhesion at the fibre-matrix interface as well as of the elastic modulus in the interphase zone [1]. Transcrystallization of crystalline polymers on various inorganic or organic fillers such as glass fibre, carbon, poly(tetrafluoroethylene) (PTFE) calcium carbonate, talc, and mica has been extensively investigated from a practical and scientific point of view [2-9]. However, the morphological and mechanical properties in the TC region, and its contribution to the mechanical performance of composite materials, have not yet been fully explained. Most of the published work has been qualitative in nature and for composites, and little has been done in the direction of morphology-property relationships of TC itself. Thus, the fundamental knowledge necessary to allow optimization of these composite systems is still missing. The reason is that it was very difficult to prepare full TC sheets so far. Kwei et al. [10] investigated mechanical properties of multi-layered sheets of polyethylene composed of TC and the spherulitic structure and indirectly estimated mechanical properties of single-layered sheets of TC using a simple composite rule.

Recently Hata et al. [11] and Folkes et al. [12] have found that entirely transcrystalline isotactic polypropylene (iPP) sheets can be obtained by sandwiching an iPP sheet between sheets of a nucleating material such as PTFE, poly(ethylene terephtalate) (PET), and poly(tetrafluoroethylene-*co*-fluoropropylene) (PEF). On the basis of these results, we have established an experimental method for preparing full TC sheets of PP controlling a wide range of microstructure.

Experimental part

Materials

Isotactic homo-polypropylene (h-iPP) of weight-average molecular weight M_w = 260 000 and M_w/M_n = 5.7 and random block type isotactic polypropylene (r-iPP) (M_w = 250 000 and M_w/M_n = 6.0) with 5.4 mol-% ethylene comonomer were mainly used throughout of this work.

TC sheets of PP were prepared according to a procedure proposed by Hata et al. [11]. The PP samples were interposed between PTFE sheets, pressed and molten at 503 K under a pressure of 28 kPa, followed by keeping the crystallization temperature after releasing the pressure. The TC grew simultaneously from nucleating PTFE surfaces to meet in the centre of the sheet, producing a fully transcrystalline morphology throughout the PP sheet. For comparison, spherulitic PP (PP-sphr) sheets were prepared using aluminium substrates under similar conditions. The thickness of the PP sheets was approximately 200 µm. The samples used in this work are summarized in Tab. 1.

Measurements

The crystalline morphology was observed directly using a transmission optical microscope (Olympus BX-50). The optical character, i.e., the sign of birefringence of the TC lamellar crystals, was determined by means of a primary red filter (λ-plate) (500 nm) located diagonally between crossed polarizers. The value of birefringence was determined using a Berek compensator (Olympus, U-CBE).

Wide-angle X-ray diffraction (WAXD) measurements were carried out with a Rigaku RU-200 diffractometer with Ni-filtered Cu-K_α radiation (40 kV, 100 mA, λ = 0.154 nm) under a sample-camera distance of 90 mm or 100 mm. The edge view diffraction patterns were taken on sections a few mm thick, cut out from the central parts of comp-molded sheets perpendicular to the surface, and the patterns of through view were taken on the section in the direction of original thickness.

Density for all samples was measured using a floating method. A binary medium prepared from various ratios of distilled water and ethyl alcohol was used. The degree of crystallinity in volume fraction χ_v was estimated using the density data:

$$\chi_v = \frac{\rho - \rho_c}{\rho - \rho_a} \tag{1}$$

where ρ is the density of the sample; ρ_a and ρ_c are the densities of amorphous and crystal regions, which are taken to be 854 and 936 (a-form) kg/m^3 [13,14].

Stress-strain behaviour under uniaxial tension was investigated using a Shimadzu AGS-5kN. The sample specimens were cut in dumbbell shape from PP sheets of 200 µm thickness in which the gauge length was 10 mm. Tensile strain was determined from the ratio of the increment of the length between clamps to the gauge length. Tensile stress was determined by dividing the tensile load by the initial cross section. Stress-strain curves were measured at a constant cross-head speed of 1 mm/min and in the temperature range from 23 to 100°C.

Dynamic mechanical properties were investigated using a Rheology DVE-V4 on sample specimens of the following dimensions: length 20 mm, width 3 mm, and thickness about 200 µm. The temperature dependence of storage modulus *E*' and loss modulus *E*" were measured between 200 and 450 K at a constant frequency of 10 Hz and a heating rate of 2 K/min.

Results and discussion

Fig. 1 shows polarized light micrographs of cross sections through transcrystalline and spherulitic PP sheets. A piece of the cross-sectioned sheets was placed on a microscope stage with an angle of 45° by right-handed rotation between the axes of polarizer and analyzer. In order to examine the optical character, the primary red filter (λ plate) was located diagonally between crossed polarizers. As suggested from these pictures, there are many nucleation sites on the PTFE sheet and then the resulting spherulite growth is restricted to the lateral direction. Consequently, a columnar layer as a transcrystalline structure develops from the substrates. On the pictures, the TC crystal of h-iPP crystallized at 395 K (h-iPP-TC395) is blue, indicating negative birefringence, whilst that of r-iPP crystallized at 395 K (r-iPP-TC) is yellow, indicating positive birefringence. According to the structural feature of typical PP lamellar crystals, the molecular chains folded into lamellae are nearly perpendicular to the lamellar axis. As the refractive index is higher in the chain direction than the indices perpendicular to the chain direction, the primary lamellae have a negative optical character. The structure with positive character is interpreted by the formation of a crosshatched texture owing to the addition of tangential lamellae (T-lamellae). This is because the T-lamellae nucleate and grow epitaxially on primary lamellae with a crossing angle of about 80˚ [15]. Therefore, the h-iPP-TC405 sheet crystallized at a relatively high temperature shows mixed birefringence, indicating the existing of T-lamellae.

In order to examine the lamellar morphology of TC, we monitored the melting process of TC *in situ* by using the polarized microscope. h-iPP-TC was prepared at 413 K by putting a thin section of the PTFE sheet in a small amount of h-iPP sample on a hot stage FP82 (Mettler Toledo). Fig. 2 shows the melting process of the TC sample at a heating rate of 1 K/min. The yellow portions in TC-lamellae disappeared at 440.5 K and the blue ones completely disappeared at 443 K, i.e., the meting temperature of T-lamellae is 2.5 K lower than that of primary lamellae. This means that T-lamellae are thinner than primary lamellae because the melting temperature is positively dependent on the lamellar thickness. According to the Thompson-Gibbs equation, the lamellar thickness of T-lamellae, $L_c{}^T$, can be related with the thickness of primary lamellae, L_c, as follows:

$$L_c^T = L_c \frac{T_m^0 - T_m}{T_m^0 - T_m^T} \qquad (2)$$

where T_m and T_m^T are melting temperatures of primary and T-lamellae, respectively, and T_m^0 is the equilibrium melting temperature (459.3 K) [16]. As a result, the thickness of T-lamellae becomes about 0.87 times that of primary lamellar thickness.

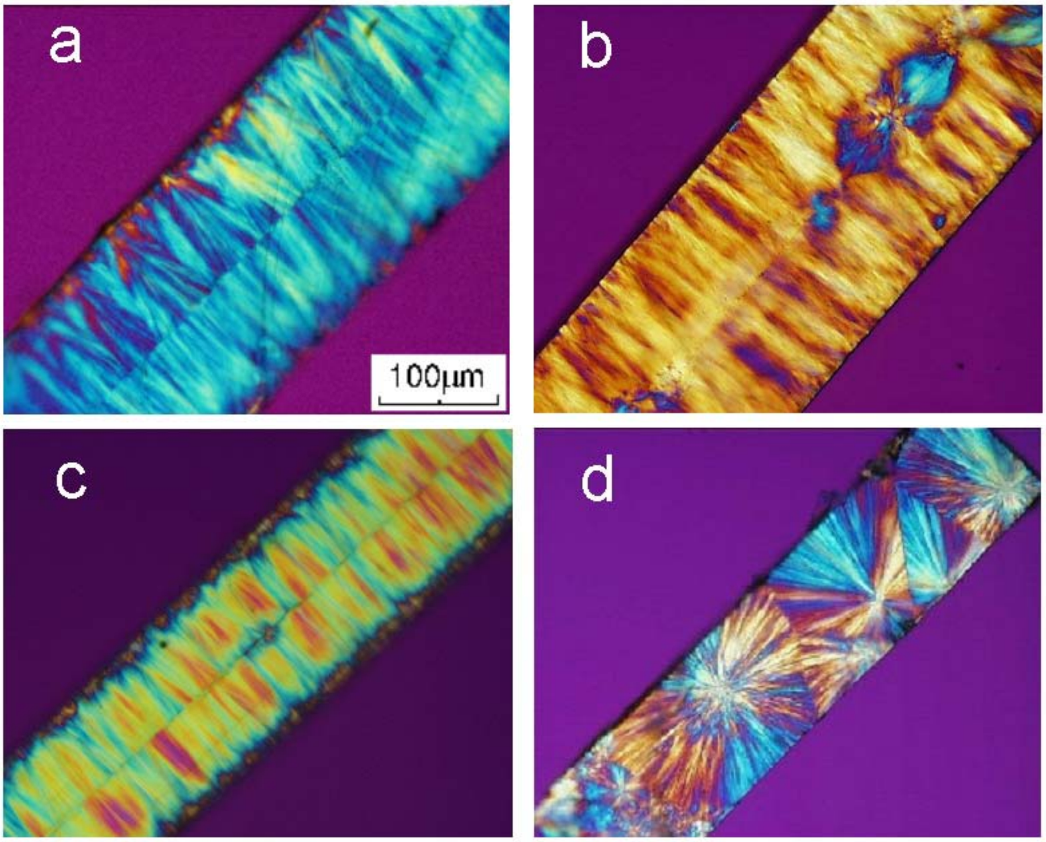

Fig. 1. Polarized optical micrographs of cross-sections of iPP sheets: (a) h-iPP-TC395, (b) r-iPP-TC395, (c) h-iPP-TC405, and (d) h-iPP-sphr. Polarizer and analyzer are in horizontal and vertical directions, respectively

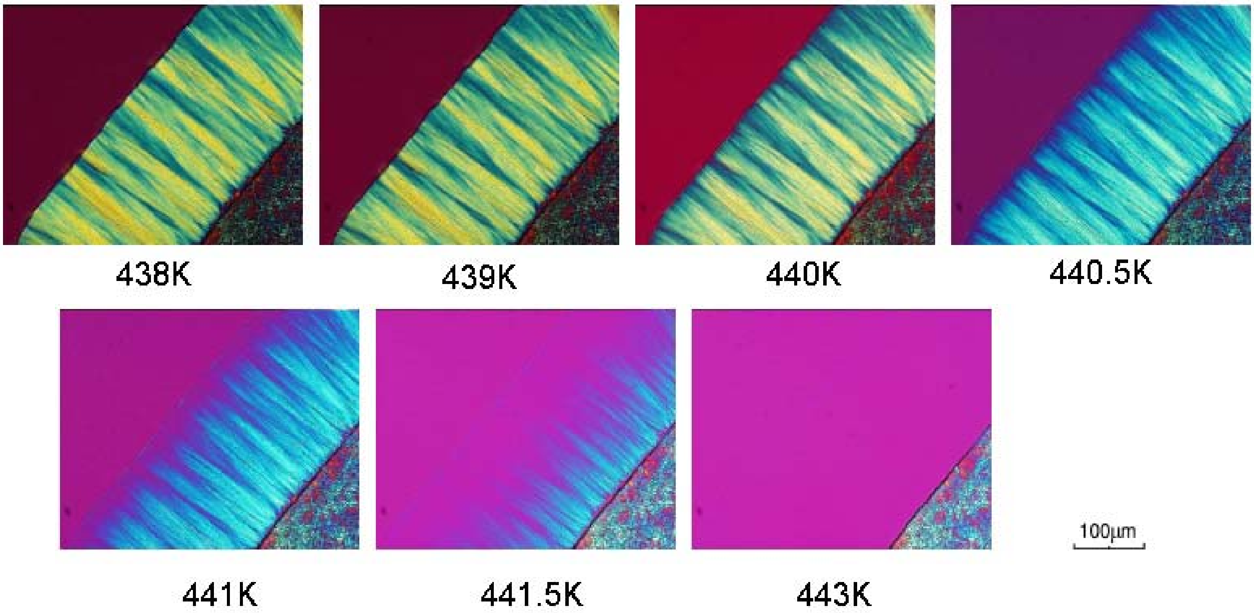

Fig. 2. Polarized optical micrographs of h-iPP transcrystals during elevating temperature. The polarizer and analyzer are in the horizontal and vertical directions

According to Awaya's procedure [17], the fraction $\Delta\phi_t$ of T-lamellae can be roughly estimated from the birefringence values Δn:

$$\phi_t = \frac{2\Delta n - 2n_a^* + n_b + n_c}{3\left(n_c - n_a^*\right)} \qquad (3)$$

where n_a^* (= 1.5067), n_b (= 1.5070), and n_c (= 1.5419) are the principal refractive indices of the α-form (monoclinic) along the reciprocal axis a^*, the b axis and the c axis, respectively. In Tab. 1, the values of T-lamellar content are listed. The formation of α-crystals is confirmed in all the sheets prepared in this work by WAXD measurements (see Fig. 3).

Tab. 1. Characteristics of samples (χ_V: volume fraction of crystallinity)

Sample	Substrate	Crystallization temp. in K	Cryst. time in min	χ_V in %	T-lamellae content in %
h-iPP-TC395	PTFE	395	30	75.9	6.0
h-iPP-TC405	PTFE	405	120	79.5	22.0
h-iPP-sphr395	Al	395	30	75.1	8.5
r-iPP-TC395	PTFE	395	150	65.2	42.0

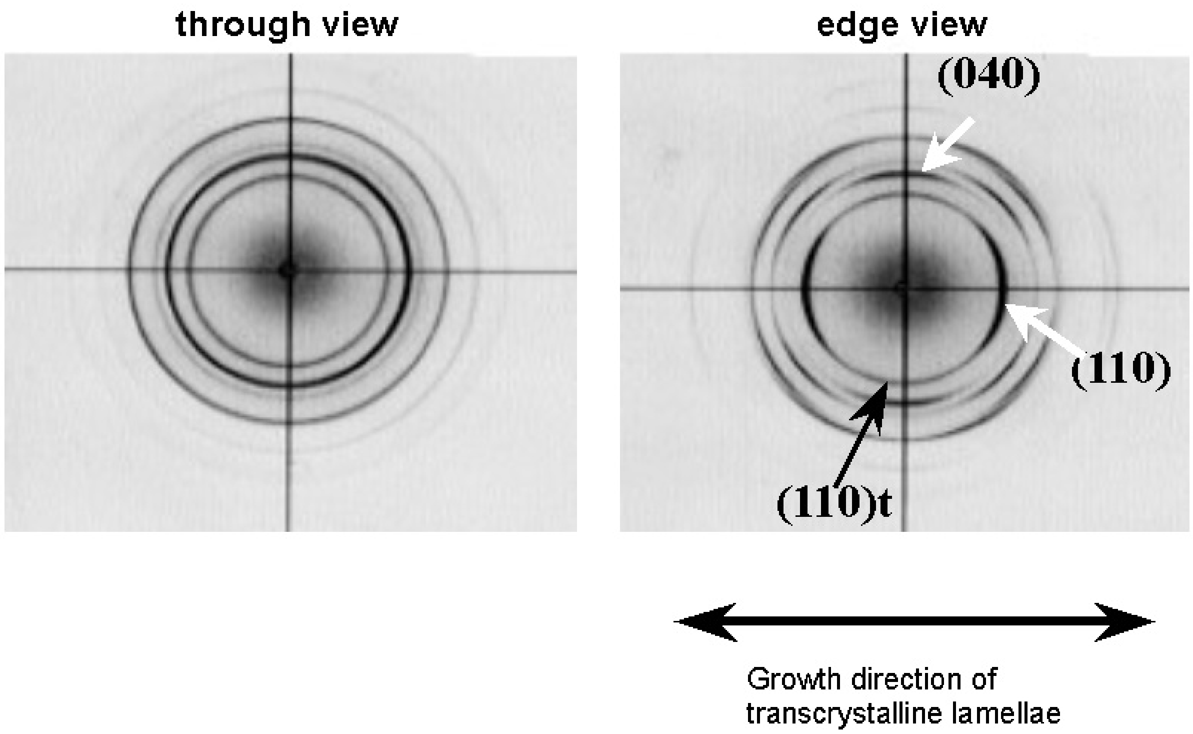

Fig. 3. X-ray diffraction patterns of a transcrystalline h-iPP sheet

In this work, WAXD patterns were taken from two different directions of through and edge views. The WAXD patterns of a TC-sheet are exemplified in Fig. 3. The growth direction is horizontal. All reflections show rings in through view whereas for edge view the (110) plane is strongly concentrated in the horizontal direction and (040) is concentrated in the vertical direction. These results indicate that the *a*-axis is oriented in crystal growth direction and the *b*- and *c*-axes are randomly oriented in the sheet surface. In addition, (110) and (040) are weakly concentrated around the vertical and horizontal directions, respectively. This is due to the T-lamellae with the *a*-axis in the growing direction. Other TC-sheets prepared from different crystallization temperatures, but not presented here, showed similar patterns as shown in Fig. 3.

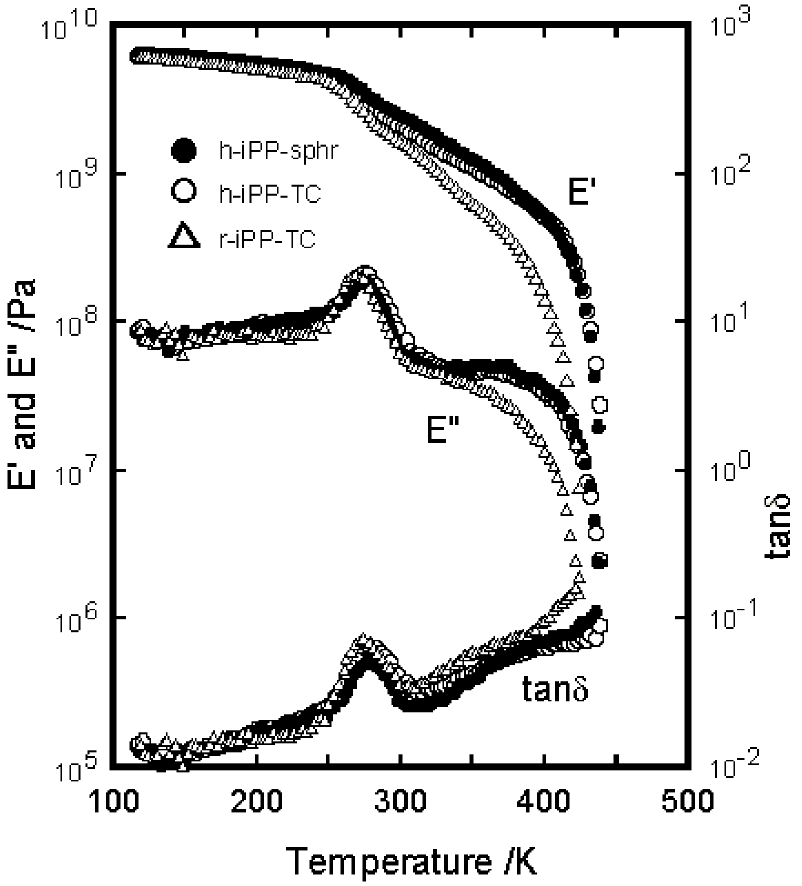

Fig. 4. Dynamic mechanical properties measured at 10 Hz of transcrystalline h-iPP-TC and r-iPP-TC sheets and a spherulitic h-iPP-sphr sheet

Fig. 4 compares the dynamic mechanical spectra of h-iPP-TC395, r-iPP-TC395 and h-iPP-sphr395 sheets. There are no differences in dynamic moduli between h-iPP-TC and h-iPP-sphr sheets, reflecting the same crystallinity in h-iPP-TC and h-iPP-sphr. This indicates that the dominant factor for dynamic mechanical properties is not the supermolecular structure but the microstructure. The dynamic moduli in the α-process region (above 300 K), which is ascribed to the molecular mobility in crystalline lamellae, of r-iPP-TC sheets are considerably lower than those of two h-iPP sheets and shifted to lower temperatures. It seems that softening of r-iPP lamellae is caused by additional defects owing to the comonomer (ethylene) units and is a reflection of continuous local melting. Kwei et al. [10] estimated the dynamic moduli of the TC zone or surface layer in spherulitic materials of iPP and polyethylene by changing the fraction of the transcrystalline zone to the bulk spherulitic region. By thinning of the film, they were able to vary the fraction of the TC zone, and the moduli of the TC zone were estimated by a model in which the surface TC region and the bulk region respond in parallel combination to an applied stress. They found that the moduli of the transcrystalline zone are greater than those of the spherulitic region. Their results are inconsistent with our data. This might be due to the fact that their TC films were very thin (less than a few μm). Thus, the deformation mode and morphological features of very thin TC films might be different from those of our TC sheets.

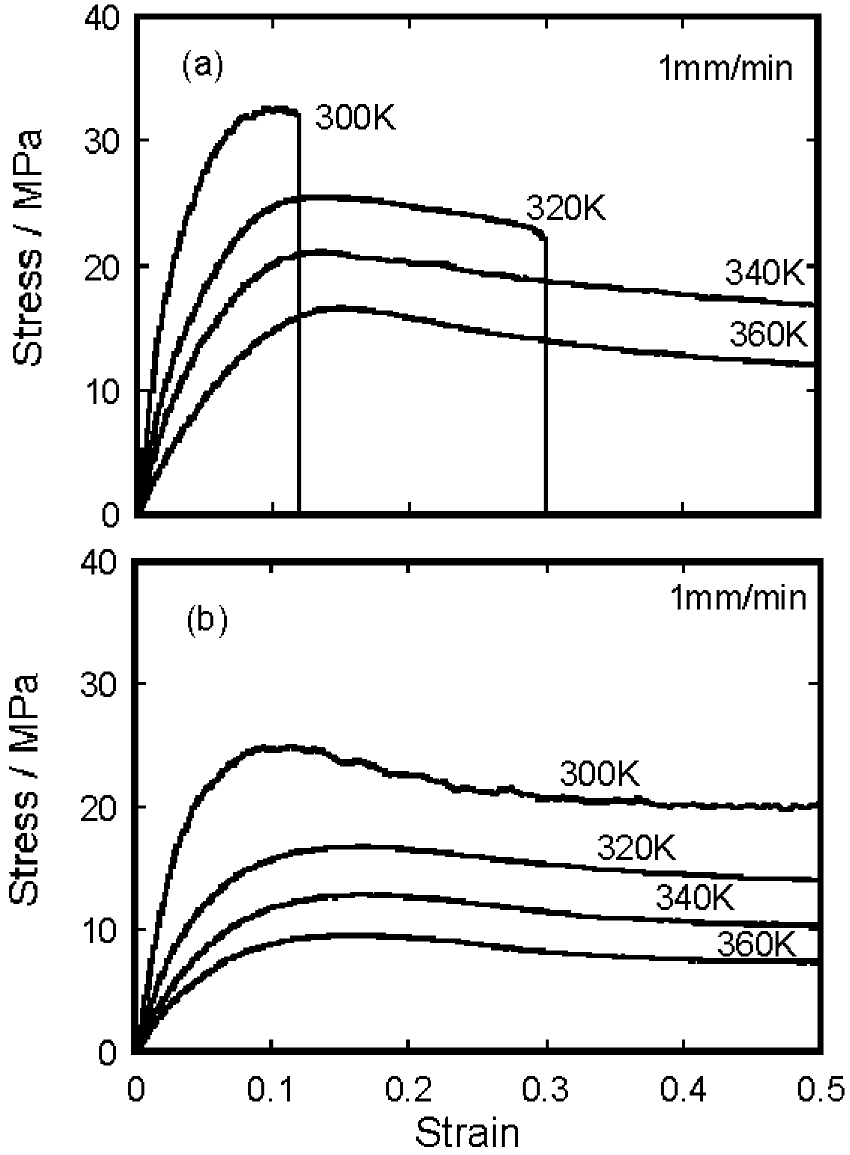

Fig. 5. Stress-strain curves measured at the crosshatch speed of 1 mm/min of (a) h-iPP-TC395 and (b) r-iPP-TC395

The tensile behaviour of all PP sheets was investigated at a crosshead speed of 1 mm/min in the temperature range from 300 to 360 K. The nominal stress-strain curves of h-iPP-TC and r-iPP-TC sheets are exemplified in Fig. 5. This work focused on mechanical parameters such as elastic modulus and yield energy, which is defined as the energy dissipated for yielding to take place [18]. The yield energy was estimated from the area under the stress-strain plot from the origin to the yield maximum point. The values of Young's modulus and yield energy are plotted against the inverse of the testing temperature in Fig. 6 and Fig. 7. The values of Young's modulus show a simple dependence on the testing temperature in an approximately linear manner with respect to $1/T$ and increase with increasing crystallinity of the samples. It is interesting to note that Young's moduli of h-iPP-TC395 and h-iPP-sphr395, having a similar crystallinity, are almost the same over the range of temperature employed, irrespective of their different gross morphology, suggesting that the elastic modulus is essentially independent of the supermolecular structure such as spherulitic and transcrystalline morphologies. These results are consistent with that of dynamic mechanical tests. Fig. 6 shows all the TC sheets to require similar energy for yielding and to be tougher in the yield process in comparison with the spherulitic sheet. As shown in Fig. 1, since the size of spherulites of h-iPP sheets prepared here is so large and is comparable with the thickness of the sheets, the external load concentrates on the boundary between the spherulites, leading to brittle fracture aiding the propagation of cracks across the sheet.

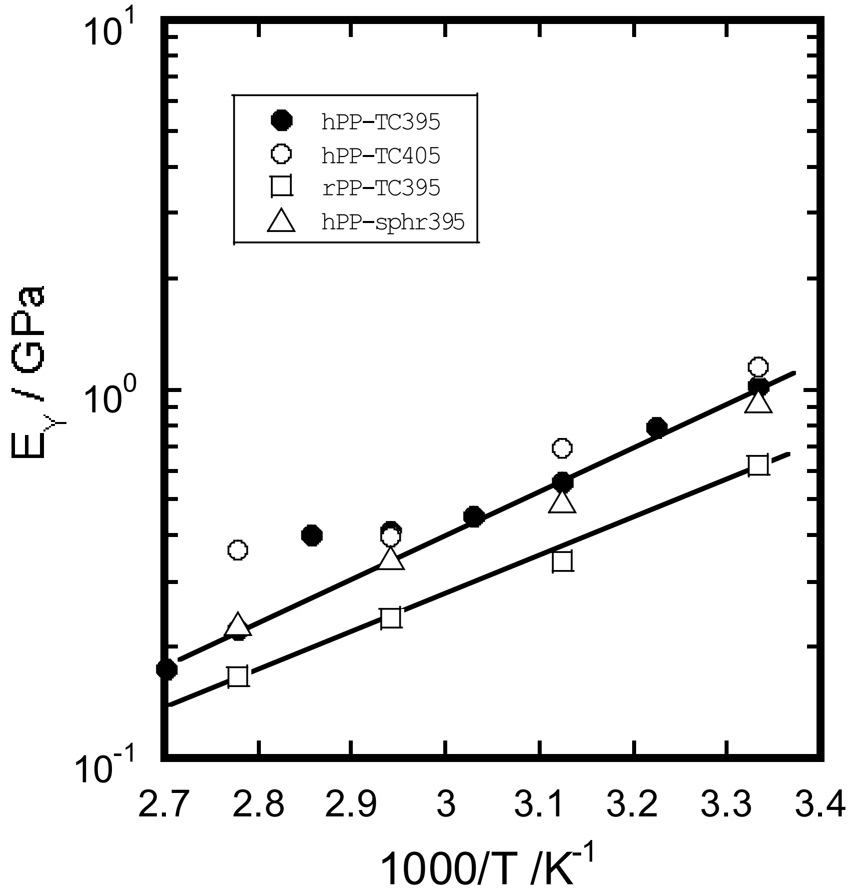

Fig. 6. Temperature dependence of Young's modulus for transcrystalline h-iPP-TC395, h-iPP-TC405, r-iPP-TC395 sheets and spherulitic h-iPP-spher sheet

This was also supported by direct observation of the h-iPP-TC sheet as shown in Fig. 8; visible crazes clearly did not occur, and it fractured on a plane exactly perpendicular to the stress direction just after yield point. Stress whitening occurred before the yield point, accompanied by a number of shear bands, and the necking process started after the yield point. h-iPP-TC shows highly crystalline, well-developed lamellae, compared with r-iPP-TC, and little interconnecting T-lamellae, which orient in the stress direction. As a result, h-iPP-TC sheets have a low strain to failure and this may explain why h-iPP-TC showed little evidence of necking. On the other hand, as seen in Fig. 8, r-iPP-TC sheets showed necking after the yield point, and stress whitening was localized to the neck area. This is well known behaviour as seen in typical spherulitic materials. These results led us to conclude that T-lamellae may link the TC lamellae, which prevents breaking between adjacent TC lamellae, and necking of PP under uniaxial deformation is required for *a*-axis lamellar orientation in the stretching direction, which is observed in spherulitic and transcrystalline PP with a large amount of T-lamellae. The plastic resistance leading to necking will be associated with the unfolding process of crystalline chains caused by uniaxial stretching of lamellae in the *a*-axis direction.

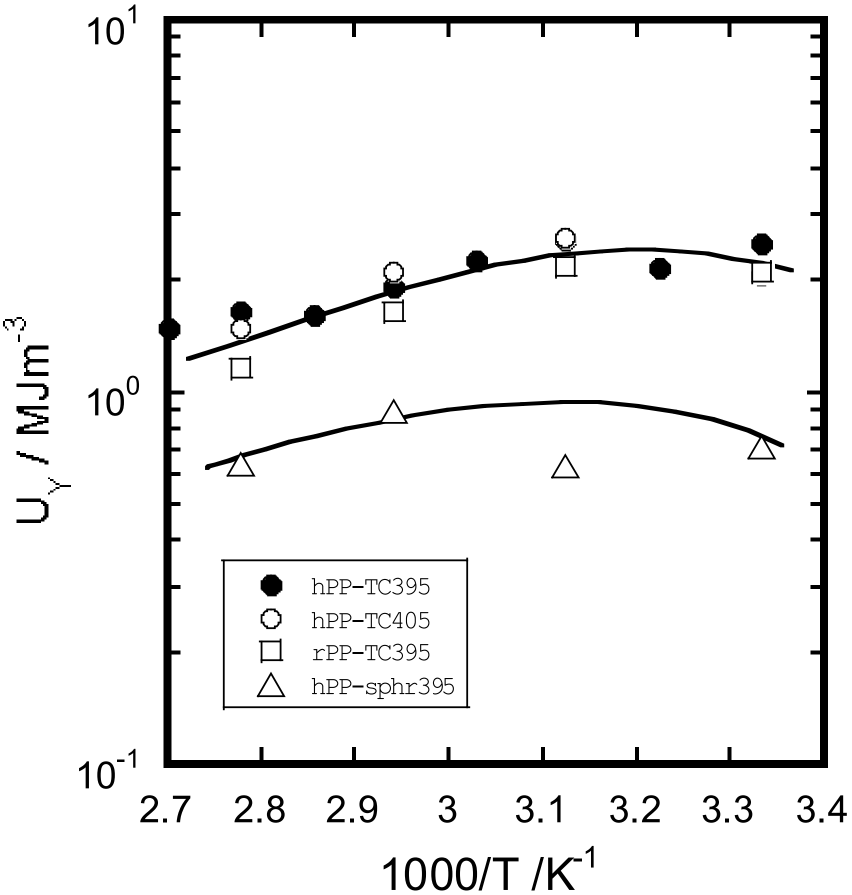

Fig. 7. Temperature dependence of yield energy for transcrystalline h-iPP-TC395, h-iPP-TC405, r-iPP-TC395 sheets and spherulitic h-iPP-spher sheet

Conclusions

In this work, we succeeded to obtain experimental data of mechanical and morphological properties of completely transcrystalline materials. Most previous studies have concentrated on the mechanical properties of spherulitic PP materials, and little effort has been made to investigate the mechanical behaviour of transcrystalline PP. Comparison of the mechanical behaviour of transcrystalline and spherulitic PP materials provided important information for a structural understanding of the mechanical behaviour of typical PP materials.

It was shown that the mechanical response in the initial strain region is governed not by the superstructure but by the degree of crystallinity, and the yielding process is essentially governed not by the degree of crystallinity but by the superstructure. Transcrystalline random block PP sheets having a large amount of tangential lamellae exhibited a more ductile behaviour and showed necking after the yield peak.

Such ductile behaviour is suggested to be associated with the plastic deformation of lamellae orienting in the tensile direction. As a result, transcrystalline PP sheets with few tangential lamellae showed a brittle behaviour. The results presented in this work have important implications in composites such as fibre-filled PP materials, which have a transcrystalline zone growing on the fibers, because the presence of the transcrystallinity zone makes it possible to modify the plastic deformation of the PP materials.

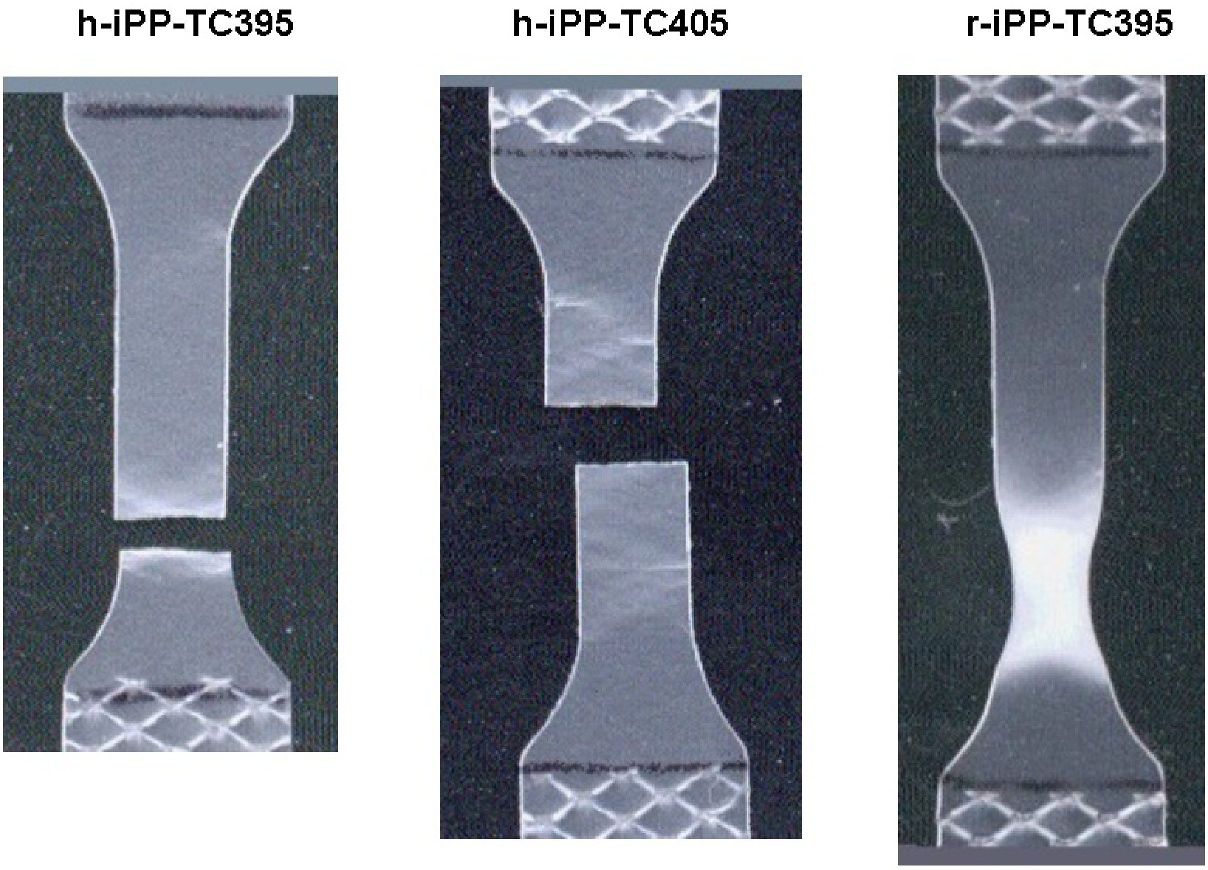
h-iPP-TC395 **h-iPP-TC405** **r-iPP-TC395**

Fig. 8. Test pieces of transcrystalline iPP sheets just after breaking

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