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Toughness of polypropylene

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The deformation and fracture mechanisms of polypropylene (PP) have been analysed on the basis of instability of plastic deformation in the region of preformed voids under dilatational stress. It was suggested by three-point bending tests of a round notched bar under plane-strain conditions that the toughness of PP depends on the strength of the fibrils of the craze, the density of voids or microcrazes and the yield stress. The high toughness revealed by high-molecular-weight PP is attributed to lower yield stress and improved strength of the fibrils of the craze. The relaxation of the strain constraint due to the great number of microcrazes is effective for the improvement of toughness in highly crystalline PP.

(Keywords: polypropylene; toughness; craze)

INTRODUCTION

It is now well established that the fine structure of semicrystalline polymers has a strong influence in determining the fracture behaviour. Crazing, well known in amorphous polymers, is also the precursor of fracture in semicrystalline polymers. Shultz[1] and Friedrich[2] have already examined the nucleation processes of the crazing of semicrystalline polymers. We[3] have also discussed the mechanism of craze nucleation of polymethylpentene (PTX) from the region of preformed voids on the basis of a finite-element analysis for an elastic–plastic material containing a two-dimensional array of cylindrical voids. It was recognized that the unstable dilatational expansion of cavities is dominated by both the yield condition and the void density.

The structure of an amorphous polymer is comparatively homogeneous, and generally the variation of its cohesive strength has a narrow distribution. Since the critical stress for the nucleation of a craze is high[4-6] and the strength of fibrils in the craze is close to the critical stress for craze formation, the crazing of an amorphous polymer easily leads to brittle fracture by the propagation of an unstable crack[7]. On the other hand, semicrystalline polymers are organized into various microstructures such as spherulites consisting of lamella-type crystal and interlamellar amorphous region. These microstructures are widely distributed according to their cohesive strengths. Therefore, loading of a semicrystalline polymer easily results in the nucleation of porosity due to micro-rupture in a region with a weak molecular cohesive strength such as an amorphous layer connecting adjacent crystallites. As a result, crazes are initiated at a significantly lower stress level than the strength of fibrils (i.e. strength of craze) and, consequently, the propagation of a craze in the crystalline region is stable compared with that of the amorphous region. The criterion of craze nucleation of a crystalline polymer will be firmly influenced by the fine structure of the semicrystalline polymer.

The purposes of this paper are to analyse the process of deformation and brittle fracture of polypropylene (PP) and to elucidate the effects of both molecular weight and crystallinity on the toughness.

EXPERIMENTAL

The materials used in this study were six commercial grades of PP (Chisso Petrochemical Co. Ltd) supplied in the form of pellets. Their material characteristics together with codes are reported in *Table 1*. PP(F) has higher crystallinity and higher tacticity than PP(C), the melt flow rate of the latter corresponding to that of PP(F). It was suggested that their dissimilarity is caused by different polymerization methods.

Specimens for the tensile tests were prepared by compression moulding at 473 K into a 0.5 mm thick sheet. Tests were carried out at a strain rate of 0.2 min^{-1} at 296 K. The strengths of fibrillar bundles in the craze were estimated from the strength of the oriented region formed by necking in the uniaxial tensile test. Rectangular bars with width of 12.4 mm and thickness of 6 mm for a three-point bending test were prepared on an injection moulding machine (Dynamelter, MEIKI). The cylinder temperature is 493 K at a mould temperature of 303 K for PP (A–D), and is 525 K at a mould temperature of 323 K for high-molecular-weight PP (E). The moulded specimens were isotropic except for the surface. A round notch with radius of 0.5 mm was shaped by

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Table 1 Molecular weight and *MFR* of PP used

	M_n ($\times 10^4$)	M_w ($\times 10^5$)	M_w/M_n	*MFR*
A	3.63	1.67	4.59	23.0
B	3.83	1.74	4.54	10.8
C	4.86	2.15	4.43	5.2
D	5.82	2.25	4.49	3.8
E	7.86	3.61	4.60	0.7
F	3.21	2.06	6.41	5.2

machining with a convex milling cutter. The ligament thickness was 4.0 mm. The specimens were loaded at a bending rate of 2 mm min^{-1} with a span length of 40 mm in an Instron-type testing machine (Auto Graph, Shimadzu DSS-5000). The effects of bending rate on the toughness were examined at bending rates of 0.125–125 mm s^{-1} with an Instron Servodrulic testing unit (Servo Pulsar, Shimadzu EHF-EB5-10L).

To discuss the deformation processes of U-notched bars in three-point bending tests under plane strain, thin sections of about 25 μm were cut perpendicular to the plane of the initial notch using a microtome. The morphologies of crazes and plastic deformations were studied with an optical microscope for the microtomed sections. The changes in microstructure of plastic deformation zone were observed with a scanning electron microscope for the surfaces of cryogenically fractured samples. Samples subjected to the bending test were first immersed in a liquid-nitrogen bath for 5 min, and broken normal to the plane of the notch immediately after removal. Because strain recovery on unloading significantly influences the morphology of the deformation zone, the deformation by three-point bending was fixed by casting in epoxy resin, which consisted of 100 parts per hundred of resin (phr) of Epon 828 and 60 phr of Ankamide 506. Specimens were treated by ion sputtering to give an adhesiveness to the interfaces[3].

The crystallinity was determined by differential scanning calorimetry (d.s.c., Mac Science DSC3100). The crystallinity index (X_c) was calculated from:

$$X_c = \frac{\Delta H^*}{\Delta H^\circ}$$

where ΔH^* is the apparent enthalpy of fusion per gram of PP, and ΔH° is the heat of fusion per gram of 100% crystalline PP. The samples (5 mg) were collected at the centre of moulded specimens and were heated to 488 K at a rate of 20 K min^{-1}.

RESULTS

Figure 1a shows the effect of molecular weight on the stress–strain curves of the PP used. Both elastic modulus and yield stress decrease with increasing molecular weight. The values of crystallinity, elastic modulus, yield stress and strength of fibrillar bundles for each sample are indicated in *Table 2*. Increasing the molecular weight of PP seems to be correlated with the decrement of crystallinity and causes a drop in both elastic modulus and yield stress. *Figure 1b* shows the bending moment–displacement curves for U-notched bars of PP (A–D). The deformation mode of the higher-molecular-weight PP is ductile, similar to the case of uniaxial tensile test. On the other hand, the lower-molecular-weight PP fractures in a brittle manner before general yielding. It is suggested that toughness is obviously improved as the molecular weight increases. *Figure 2* shows the deformation processes of the lower-molecular-weight PP(B). As the external load increases, microscopic crazes, so-called microcrazes, are formed together with the development of a local plastic region at the tip of the notch. This microcraze zone spreads out with increasing load. When the size of the plastic zone reaches a critical extent and fulfils the unstable condition of deformation, a macrocraze, which is a local concentration of strain between the microcrazes, is developed. Brittle fracture occurs from this macrocraze by rupture of fibrillar bundles extending in the direction of principal stress. *Figure 3* shows scanning electron micrographs of a craze of the lower-molecular-weight PP(B) at a displacement of 1 mm. It is shown that a stable microcraze involving voids and fibrils, which are similar to those observed in polyethylene (PE)[8] or PTX[3], is produced in the initial deformation stage, and then a macrocraze is formed owing to the concentration of plastic strain at the tip of the local plastic deformation region as the external load is increased. The deformation processes of higher-molecular-weight PP(E) are shown in *Figure 4*. The size of microcraze formed in the initial deformation stage is larger than that of lower-molecular-weight PP(B) shown

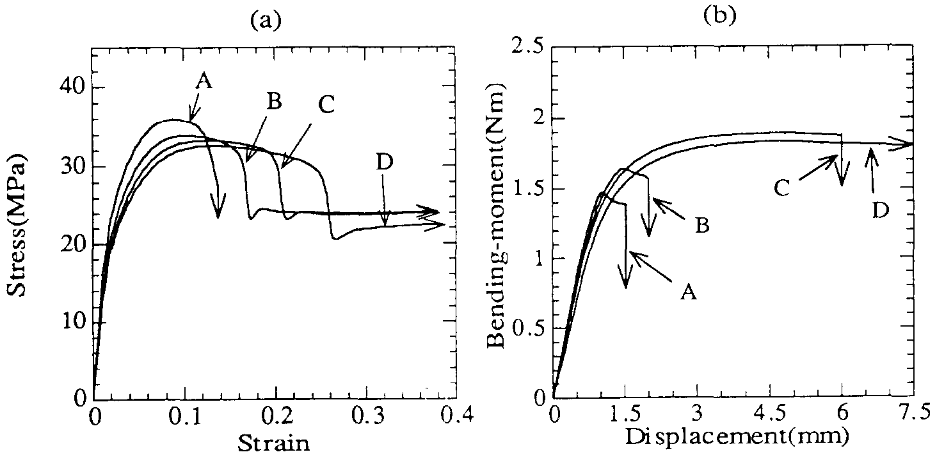

Figure 1 Effect of molecular weight on the stress–strain curves (a) and the bending moment–displacement curves (b) of PP

Table 2 Mechanical properties and crystallinity of PP used

Sample	Elastic modulus (GPa)	Yield stress (MPa)	Strength of fibril (MPa)	Crystallinity X_c (%)
A	1.46	35.2	40.0	41.4
B	1.30	33.1	41.7	36.1
C	1.21	32.7	42.2	36.8
D	1.21	32.4	43.4	35.9
E	1.02	28.9	–	49.9
F	1.51	37.8	41.5	41.5

in *Figure 2* because of larger spherulite size due to higher mould temperature in the injection moulding. In the higher-molecular-weight PP, the enlargement of the plastic deformation zone containing a great many microcrazes is stable compared to that of lower-molecular-weight PP in which an unstable macrocraze is developed. It can be observed to deform stably after general yielding, which describes the plastic deformation over the cross-section at the tip of the notch. The morphology of the plastic deformation zone containing numerous stable microcrazes in the higher-molecular-weight PP is similar to that of stable plastic deformation of semicrystalline polymers at high temperature[9], and to that of polymer blends containing a large number of

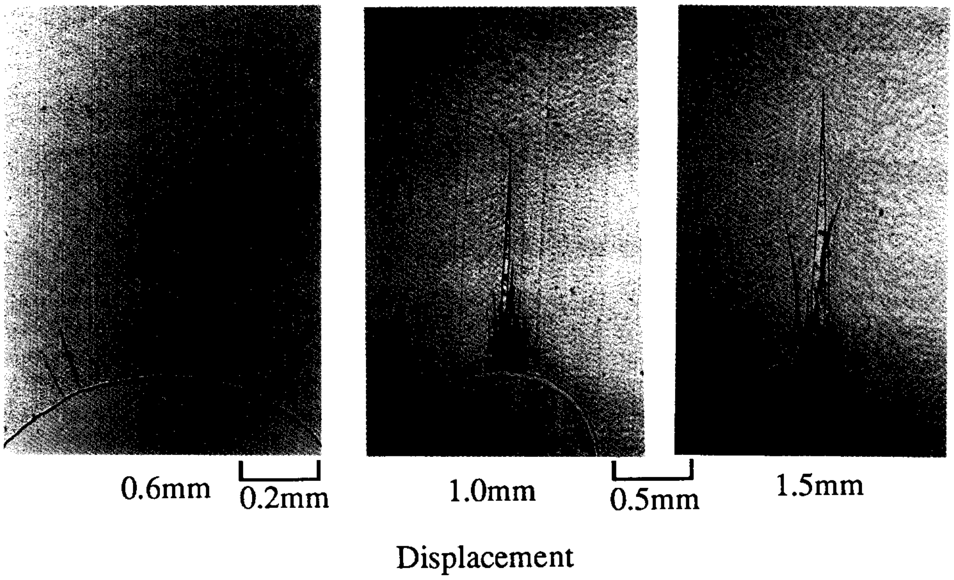

Figure 2 Deformation process of U-notched PP(B) bar of lower molecular weight

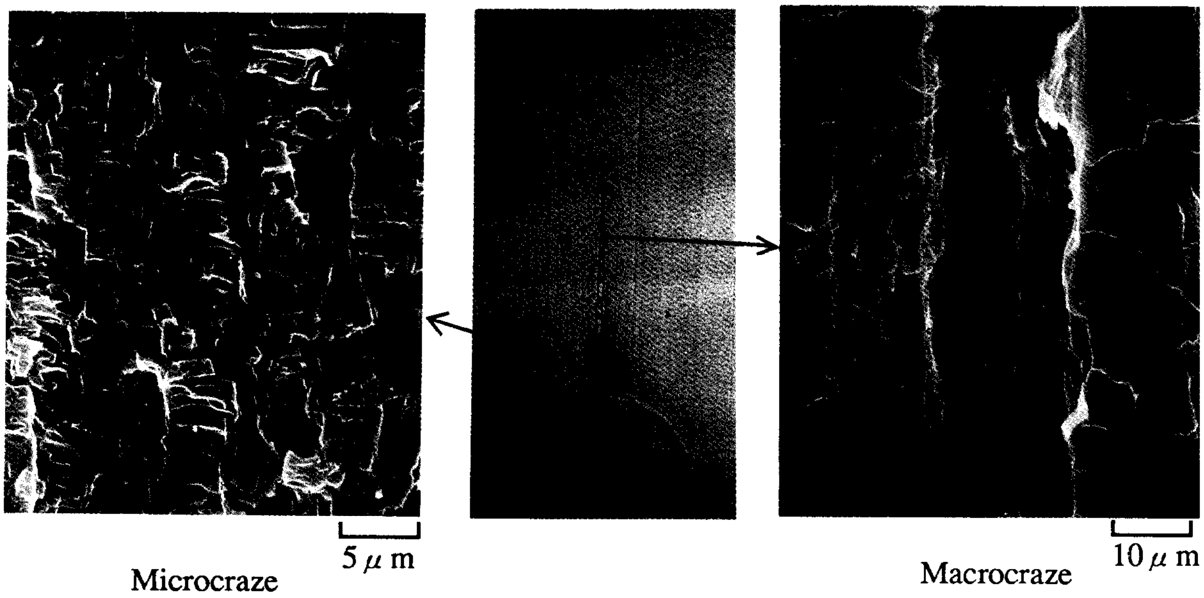

Figure 3 Scanning electron micrographs of the deformation zone of PP(B) of lower molecular weight

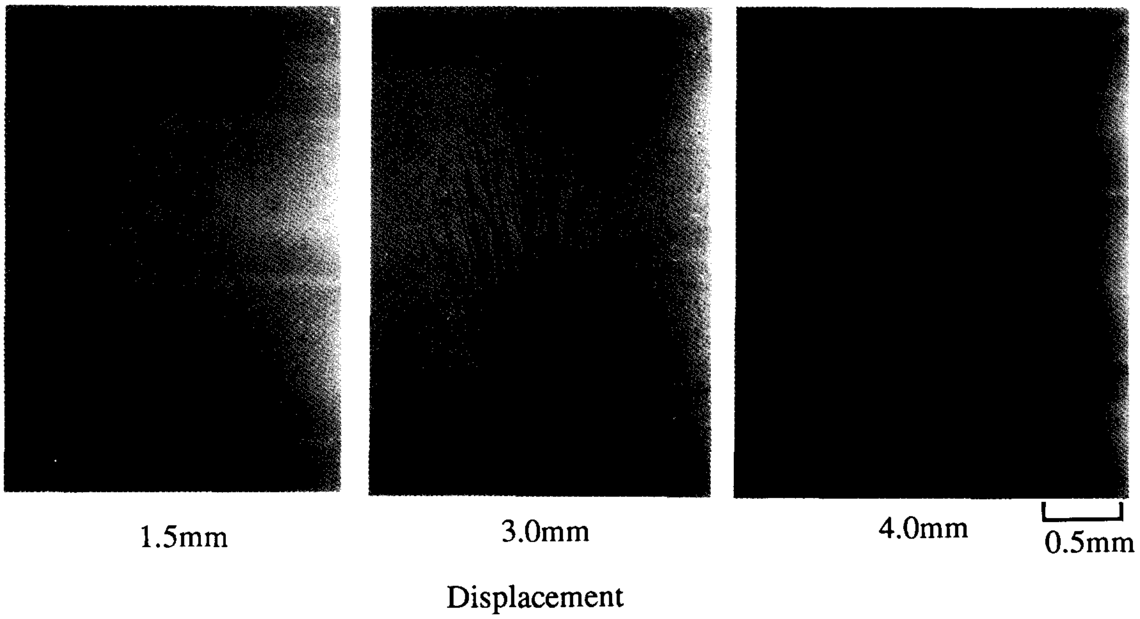

Figure 4 Deformation process of U-notched PP(E) bar of higher molecular weight

dispersion particles sufficient to demonstrate high toughness in the blends[10,11]. *Figure 5* shows the scanning electron micrographs of the surface of cryogenically fractured samples for the higher-molecular-weight PP. The tilting angle is 45°. It is suggested that the increase of molecular weight induces fine voids and homogeneously distributed fibrils in the structure of the microcraze in contrast to those of lower-molecular-weight PP.

The fracture mode of PP changes to brittle fracture with high impact loading. *Figure 6a* shows the variations of bending moment–displacement curves with the bending rate of the three-point bending test for U-notched bars of comparatively higher-molecular-weight PP(D). The fracture mode varies from ductile general yielding at lower bending rate to brittle fracture on increasing the bending rate. *Figure 6b* shows the variation of elastic modulus and yield stress of PP(D) estimated from three-point bending tests as a function of bending rate. Marked increases of both elastic modulus and yield stress with increasing bending rate are observed. The ductile–brittle transition derived from the increase of bending rate also depends on the molecular weight. In short, the critical bending rate of ductile–brittle transition reduced with decreasing molecular weight. *Figure 7* shows the effect of molecular weight on the toughness under a high bending rate of 125 mm s^{-1}. It is recognized that high-molecular-weight PP reveals higher toughness on impact loading. A photomicrograph of a thin section obtained from the specimen of high-molecular-weight PP(E), taken under polarized light, is shown in *Figure 8*, which was loaded to a displacement of 2 mm at a rate of bending of 125 mm s^{-1} and then fixed at the same displacement. It is revealed that the unstable macrocrazes are nucleated at the tip of the local plastic zone,

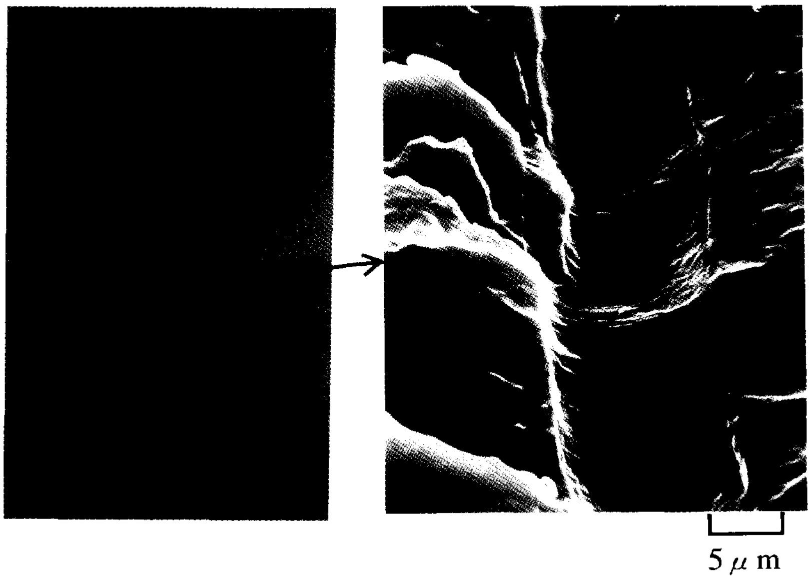

Figure 5 Scanning electron micrographs of the deformation zone of PP(E) of higher molecular weight

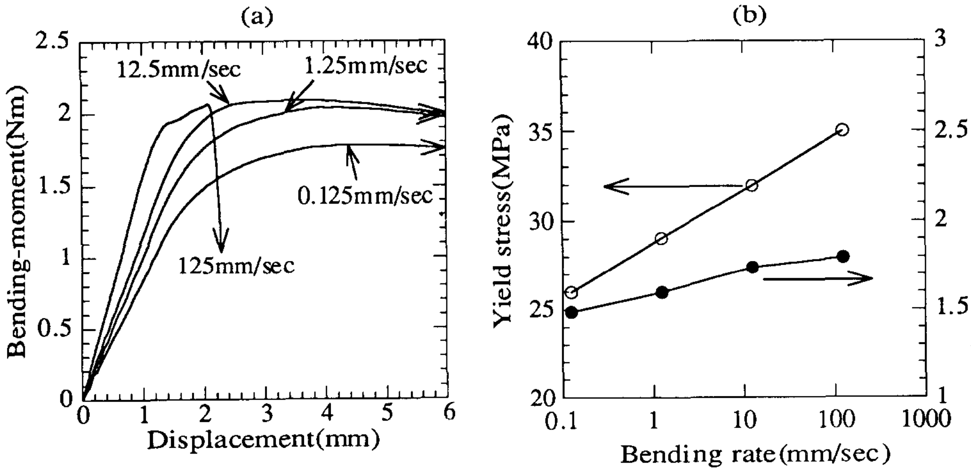

Figure 6 Variation of the bending moment–displacement curves of U-notched PP(D) bar (a) and the yield stress (b) as a function of the bending rate

which includes a lot of microcrazes dispersed homogeneously.

The yielding stress of PP, which influences the magnitude of stress concentration at the tip of a notch, also depends on the degree of crystallinity. The more highly crystalline PP reveals a higher yield stress owing to notably high modulus in crystalline layers. As is well known, the crystallinity increases with heat treatment after moulding. In *Figure 9*, the toughness of lower-molecular-weight PP(A) is compared with that of annealed PP(C) in which the yield stress was adjusted to coincide with that of PP(A) by heating at 373 K for 3 h in a forced convection oven. It is shown that the toughness of annealed PP(C) with higher molecular weight is higher than that of lower-molecular-weight PP(A) in spite of the same value of yield stress, though the toughness of annealed PP(C) is naturally reduced in comparison with the neat sample. The strengths of fibrils estimated in *Table 2* hardly vary by this thermal treatment. Therefore this difference in the bending moment–displacement curves gives rise to the assumption that variation of the toughness of PP originates from

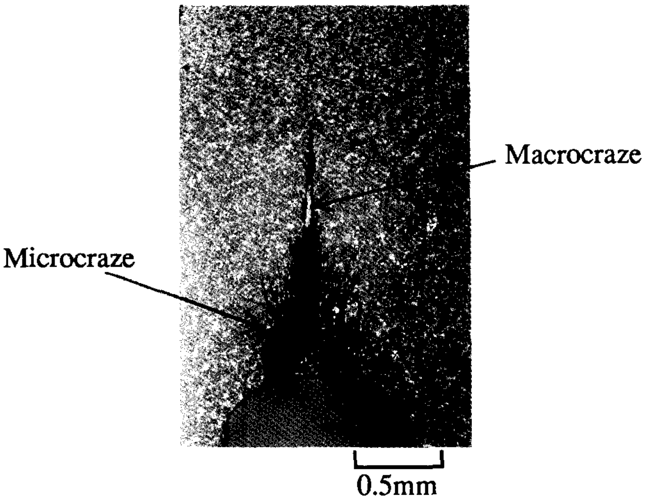

Figure 8 Deformation zone of U-notched PP(E) bar of higher molecular weight deformed at a bending rate of 125 mm s^{-1}

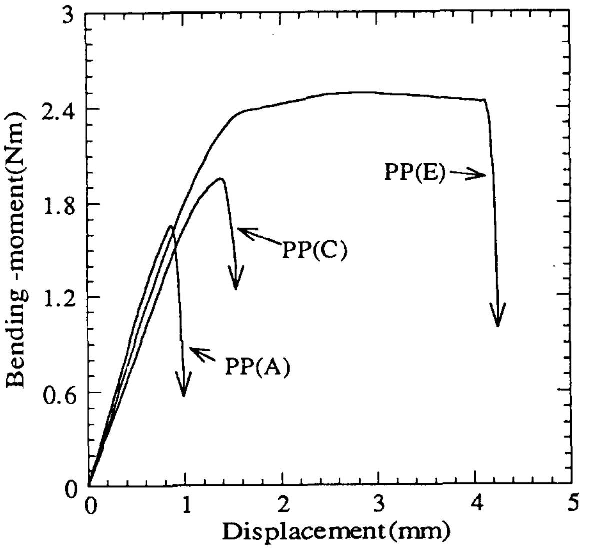

Figure 7 Effect of the molecular weight on the bending moment–displacement curves of U-notched PP bar at a bending rate of 125 mm s^{-1}

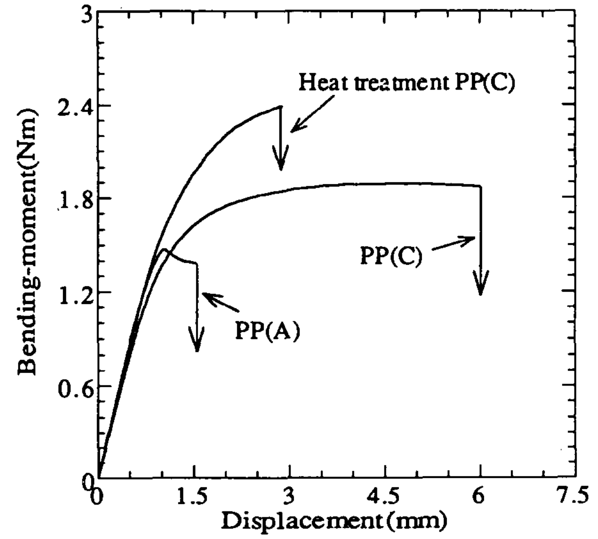

Figure 9 Bending moment–displacement of lower-molecular-weight PP(A) and medium-molecular-weight PP(C) annealed at a temperature of 373 K for 30 min

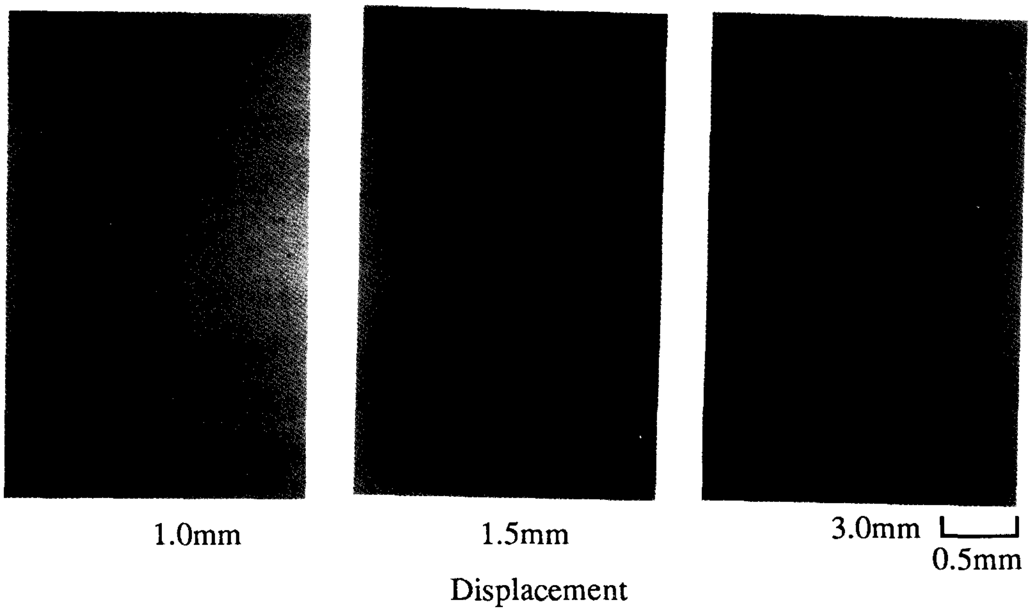

Figure 10 Deformation process of the U-notched PP(C) bar of medium molecular weight annealed at a temperature of 373 K for 30 min

the strength of fibrils. *Figure 10* shows photomicrographs of the deformation processes of annealed PP(C). The deformation process compared with the untreated sample approaches the unstable deformation mode of lower-molecular-weight PP as shown in *Figure 2*. Needless to say, the extent of the stress-whitened region ahead of a notch before final brittle fracture of the material depends on the magnitude of toughness.

The molecular characteristics of more highly crystalline PP are controlled by adjusting the type of polymerization system used in its production. *Figure 11* shows the toughness of high-crystallinity and high-tacticity PP(F). The number-average molecular weight of PP(F) is lower than that of conventional PP(C) with nearly equivalent melt flow index to high-crystalline PP(F). Despite the fact that the yield stress of PP(F) is higher than the value of annealed PP(C), it can be seen that the toughness of PP(F) is improved in comparison with treated PP(C) with high crystallinity index by heating after moulding because of the increase of the displacement of final fracture. *Figure 12* shows photomicrographs of the deformation process of PP(F), taken under parallel polars. The mode of plastic deformation of high-tacticity PP(F) is stable in comparison with-annealed PP(C). It must be pointed out that the density of the microcrazes of PP(F) is very high and the structure of microcrazes seems fine. This suggests that high tacticity is effective in the improvement of the toughness of PP.

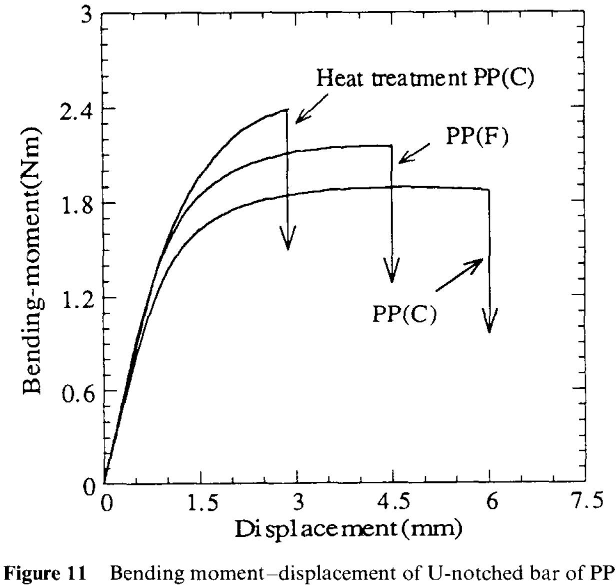

Figure 11 Bending moment–displacement of U-notched bar of PP(C) of medium molecular weight annealed at a temperature of 373 K for 30 min and highly crystalline PP(F)

DISCUSSION

A spherulite in semicrystalline polymers is made up of fine lamellar-type crystals oriented in the radial direction. Then Poisson's contraction results in compressing the lamellar crystals in the equatorial plane perpendicular to the direction of the maximum principal stress. Since this stress reduces the intermolecular distance in the lamellar crystals, the resistivity against the deformation compressing spherulites is large. Consequently the constraint of strain gives rise to high dilatational stress on equatorial planes of spherulites. Therefore, it is difficult for the volume of such a region to remain constant during plastic deformation. It seems reasonable to expect that the development of voids is initiated easily on the equatorial planes of spherulites together with yielding. Cavitation in PP occurs in comparatively low stress nearly equal to the yield stress at room temperature as shown in *Figure 2* or *4* because of the lower glass transition temperature around 260 K. If the average dilatational stress on a macroscopic area such as a region with scores of spherulites is low and near to the stress state of uniaxial tension, the deformation of a ligament between microcrazes is stable. It is the initial

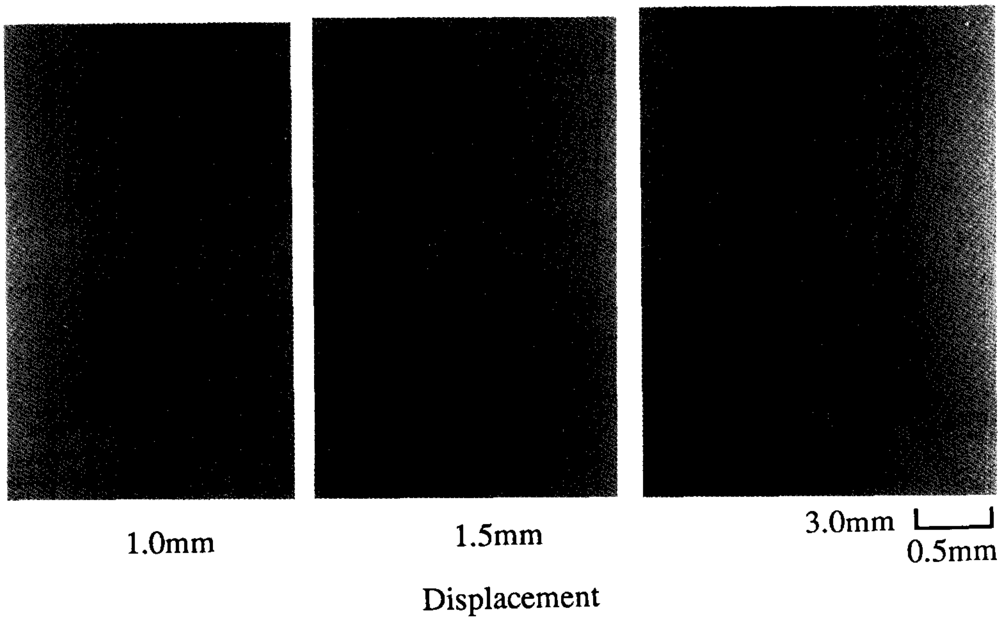

Figure 12 Deformation process of U-notched PP(F) bar of high crystallinity

deformation stage shown in *Figure 2*. This region containing numerous microcrazes can be stably deformed by the shear stress. It is already known that there is a maximum stress at the tip of the local plastic zone which spreads across the ligament thickness ahead of a round notch under plane strain[4]. In the notched bar of PP, the stress concentration depends on both yield stress and density of microcraze because the constraint of strain can be released by the microcraze. When the stress ahead of the plastic zone reaches a critical stress by extending the plastic zone, the development of a macroscopic craze, in which the plastic strain was locally concentrated between neighbouring microcrazes shown in *Figure 3*, occurs at the tip of the local plastic zone.

The mode of deformation of PP in a low dilatational stress is unstable in comparison with that of PE, PTX and nylon[9,12], although, in mechanical features, the microcraze is characterized as a void rather than a craze which leads to catastrophic cracking. The instability of the plastic deformation between voids is strictly governed by the compliance, i.e. ratio of shear yield stress (τ) to shear elastic modulus (G)[11,13]. This ratio τ/G is influenced by the temperature, strain rate and the structure of the polymer, and the decrease of the ratio introduces stable plastic deformation such as plastic deformation at high temperature. The ratio τ/G of PP estimated from *Table 2* is larger than that of other crystalline polymers, for example that of PE[8]. It could be understood from this result that the mode of deformation of PP in the low plastic constraint (i.e. microcraze) is unstable in comparison with that of PE, PTX and nylon.

The micro-rupture of the fibrils of a craze leads to catastrophic brittle fracture. Since the craze is formed by the unstable concentration of plastic strain in the same manner as necking in the uniaxial tensile test[9], it is reasonable to evaluate the breaking stress of the fibrils of the craze from the strength of the highly stretched necking region found in many polymeric materials[14]. It is found that increasing the molecular weight exhibits a tendency to enhance the strength of a fibril and to decrease the yield stress shown in *Table 2*. Therefore we might suggest that the toughness of PP is mainly governed by the strength of fibril and also yield stress. The stress distribution of the locally formed plastic zone of annealed PP(C) is equal to that of lower-molecular-weight PP(A) because the yield stresses of both samples are almost the same. Therefore comparison of bending moment–displacement curves for both PP(A) and annealed PP(C) indicates that the strength of fibrils is an essential factor for the improvement of toughness. It can be concluded from the above discussion that the toughness of high-molecular-weight PP is achieved by both the improvement of strength of fibrils which can sustain stress and relaxation of stress concentration caused by a decline of yield stress.

It is already represented for the toughening of polymer blends that the relaxation of stress concentration due to the formation of numerous voids from the dispersion particles is the basic mechanism[10,11]. In the case of semicrystalline polymers, it might be suspected that the cohesive strength is distributed widely depending on their inhomogeneous structure composed of radially arranged lamellae and intercrystalline layers. On account of lower cohesive strength, such as the strength of interlamellar molecules and the strength of boundaries between adjacent spherulites, the nucleation of voids may be liable to occur in such regions. The fine structure of semicrystalline polymers strongly depends on various factors such as polymerization methods, thermal history and the moulding conditions, not to mention chemical structure. It is suggested that the high stiffness of high-tacticity PP(F) is attributed to high crystallinity and a large number of effective interlamellar molecules by adjusting polymerization methods. As a result, the elastic modulus and yield stress increase. In this case, it will be assumed that the toughness of the highly crystalline polymer PP(F) compared with conventional PP(C) having similar melt flow rate to PP(F) reduces owing to high yield stress and lower number-average molecular weight (M_n), because the strength of fibrils relates closely to M_n (ref. 15). However, it can be suggested to improve the toughness of PP(F) compared with annealed PP(C) because of the increase of the displacement of final fracture. As shown in *Figure 11*, the slope of bending moment–displacement curves of PP(F) was reduced earlier than annealed PP(C), which results from considerably more voids and microcrazes. It is suggested from these results that the decrease of plastic constraint due to the high density of microcrazes in PP(F) leads to the relaxation of stress concentration. This result means that the toughness of semicrystalline polymers might be improved by the same mechanism as the release of strain constraint due to cavitation from the dispersed particles in polymer blends.

CONCLUSIONS

It is concluded that the toughness of PP depends on the strength of the fibrils of the craze, the yield stress and the density of voids or microcrazes. High toughness revealed in higher-molecular-weight PP is attributed to the lower yield stress and the improved strength of the fibrils of the craze, which can sustain external load until reaching the critical value. The relaxation of strain constraint due to a large number of voids and microcrazes is effective for improvement of toughness in highly crystalline PP.

REFERENCES

1 Schultz, J. M. *Polym. Eng. Sci* 1983, **24**, 770

2 Friedrich, K. 'Crazing in Polymers', Springer-Verlag, New York, 1983

3 Ishikawa, M. and Takahashi, H. *J. Mater. Sci.* 1991, **26**, 1295

4 Ishikawa, M., Narisawa, I. and Ogawa, H. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 1977

5 Ishikawa, M., Ogawa, H. and Narisawa, I. *J. Macromol. Sci., Phys. (B)* 1981, **19**, 421

6 Kramer, E.J., 'Crazing in Polymers', Springer-Verlag, New York, 1983

7 Ishikawa, M. *Kobunshi Ronbunshu* 1990, **47**, 83

8 Usui, K. and Ishikwa, M. *Polym. Prep. Jpn* 1994, **43**, 1326

9 Ishikawa, M. and Kobayashi, Y. *Kobunshi Ronbunshu* 1995, **52**, 141

10 Ishikawa, M. and Chiba, I. *Polymer* 1982, **23**, 291

11 Ishikawa, M. *Polymer* 1995, **36**, 2203

12 Ishikawa, M. and Narisawa, I. *Proc. 25th Jpn Congr. Mater. Res.* 1982, **20**, 282

13 Argon, A. S., 'The Solid State of Polymers', Marcel Dekker, New York, 1974, p. 573

14 Williamson, C. R., Wright, B. and Haward, R. N. *J. Appl. Chem.* 1964, **14**, 131

15 Ishikawa, M. and Sugimoto, M. *Kobunshi Ronbunshu* 1995, **52**, 149