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Effect of tie molecules on the craze strength of polypropylene

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The fracture mechanism of crazing in polypropylene (PP), the molecular weight of which was controlled by several different methods, was examined. The craze strength was improved with increasing number-average molecular weight in all specimens regardless of the weight-average molecular weight. Examination of the number of tie molecules between neighbouring lamellae suggested that craze fracture was caused by the failure of tie molecules. It may be expected from these results that PP of high fluidity can be produced without a drop in strength if the weight-average molecular weight approaches the number-average molecular weight under the retention of the number-average molecular weight. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polypropylene; craze strength; tie molecules)

INTRODUCTION

In a recent study the authors demonstrated that brittle fracture of polypropylene (PP) occurs when the stress ahead of the local plastic zone developed from a notch reaches the strength of fibrils within the craze due to stress concentration caused by the plastic constraint[1]. It is known from elastic–plastic analysis around the notch that the stress concentration at the tip of this local plastic zone is strongly affected by both the yield stress of the material and the density of crazes[2]. The yield stress of PP produced by injection moulding decreases with increasing molecular weight because the yield stress of PP depends on the degree of crystallinity, which decreases with the increase of molecular weight at a constant mould temperature[1]. On the other hand, the density of crazes increases with increasing tacticity of PP. Numerous crazes relax the stress concentration due to the release of strain constraint[3]. Our studies on toughness of PP have led us to suggest that the craze strength depends on the number-average molecular weight rather than on the weight-average molecular weight[1,3,4]. It is well known that the viscosity of polymeric materials depends on the weight-average molecular weight[5]. Therefore if the craze strength (which is a dominant factor for the toughness of PP) depends on the number-average molecular weight, then it is expected to develop PP with low melt viscosity, excellent processability and high toughness.

The purpose of this paper is to examine the fracture mechanism of crazing in PP, the molecular weight of which is controlled by several different methods.

EXPERIMENTAL

Preparation of specimens

The materials used in this study were three grades of PP (Chisso Petrochemical Co. Ltd) in which the molecular weight was controlled by the following methods.

1) conventional PP with tacticity of about 0.93–0.94;
2) high tacticity PP of about 0.94–0.96; and
3) PP decomposed with a peroxide.

Craze strength was estimated by tensile testing of 0.5 mm thick sheets, prepared by compression moulding. The PP pellets were melted at 473 K for 30 min and then cooled to 293 K. The test specimens, which were 6 mm wide and 60 mm long, were shaped mechanically.

Measurement of craze strength

The toughness of polymeric materials depends on both stress concentration and craze strength[2,6]. The yield stress strongly affects the stress concentration at the tip of a notch due to plastic constraint[7]. The craze strength for amorphous polymers can be estimated from the stress for the nucleation of crazing because their strength is close to the stress of craze nucleation[2,6]. On the other hand, the nucleation of voids for crystalline polymers occurs at low stress compared with that of amorphous polymers because of the inhomogeneity of the structure. Hence the craze strength of a crystalline polymer is considerably higher than the stress for craze nucleation[1,8,9]. We have pointed out that the stress of fracture, evaluated from the strength of the oriented region formed by necking during uniaxial extension, is adequate for estimation of the craze strength of PP[1]. The craze

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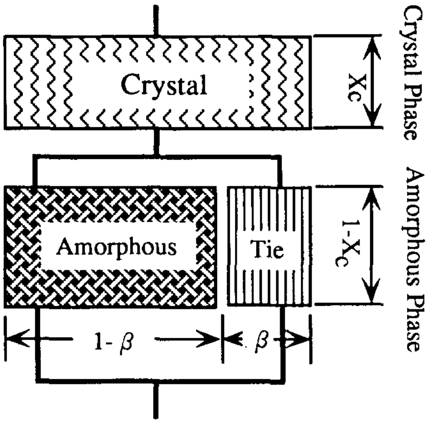

Figure 1 Mechanical model of oriented crystalline polymer

accompanying the nucleation of voids is developed under the constraint of strain in the direction perpendicular to the maximum principal stress. Therefore, it is expected that if the density of crazing is sufficiently large and, as a result, Poisson contraction occurs between the neighbouring voids, the stress state of the fibrils is equivalent to that during uniaxial extension with the reduction of cross-section.

The craze strengths were estimated from the strength of the oriented region formed by necking in a uniaxial tensile test. The latter was calculated from the force of fracture divided by the cross-sectional area before deformation, because a craze is a local plastic deformation without the contraction of cross-section. The strain rate was 0.33 min^{-1}. The fibril strength, which reveals the true strength of the oriented polymer, was calculated by dividing by the true area of cross-section after deformation. At room temperature, uniaxial extension leads to the ready development of voids with an increase of volume of about 10%. Hence, in this case, the fibril strength is underestimated. The increase of volume with tensile deformation was not detected at the temperature of 393 K. Therefore, in order to estimate the strength of craze and fibril, the oriented sample was prepared at this temperature. The extension ratio, i.e. the strain immediately before fracture, was about 7–8; this ratio increased with increasing molecular weight and tacticity.

Evaluation of crystalline structure of undeformed PP

For the undeformed PP, the long period, thickness of crystalline lamellae and thickness of amorphous layers were estimated by small-angle X-ray scattering (SAXS). The number of regular folds of a chain between two intercrystalline tie molecules was calculated from the variation of elastic modulus of the undeformed PP with temperature; using the Krigbaum model[10,11]. The elastic modulus was estimated from dynamic mechanical measurements by use of a Rheonograph (Toyo Seiki). The samples used were compression sheets of 0.2 mm thickness.

Estimation of volume fraction of tie molecules of oriented PP

It was pointed out that the number of tie molecules of amorphous phase between neighbouring crystalline lamellae strongly affects the strength and elastic modulus of an oriented crystalline polymer[12]. Although the number of tie molecules cannot be estimated directly, it is useful to estimate their number by use of the mechanical model of an oriented crystalline polymer proposed by Takayanagi *et al.*[13,14]. Referring to the mechanical model shown in *Figure 1*, the elastic modulus (E) of the oriented sample is given by

$$\frac{1}{E} = \frac{X_c}{E_c} + \frac{(1 - X_c)}{(1 - \beta)E_a + \beta E_t} \tag{1}$$

where E_c (41 GPa[15]) is the elastic modulus of the crystalline lamellae, E_a is the elastic modulus of the amorphous region, E_t is the elastic modulus of tie molecules, X_c is the crystallinity of the oriented sample and β is the volume fraction of tie molecules within the amorphous phase. β is approximately calculated by

$$\beta = \frac{(1 - X_c)E}{E_c - X_c E} \tag{2}$$

It was assumed that the elastic modulus of the tie molecules, which connect the neighbouring crystalline lamellae and transfer an applied load efficiently, is nearly equal to the elastic modulus of the crystalline lamellae, and the contribution of the amorphous region to overall modulus was negligible. It is known from *Figure 1* that β corresponds to the fraction of cross-section occupied by the tie molecules within the amorphous phase. The crystallinity was determined by differential scanning calorimetry (d.s.c.: Mac Science DSC3100). The crystallinity index (X_c) was calculated from

$$X_c = \frac{\Delta H^*}{\Delta H^\circ} \tag{3}$$

where ΔH^* is the apparent enthalpy of fusion per g of PP; ΔH° (209 J g^{-1})[16] is the heat of fusion of per g of 100% crystalline PP. The samples (5 mg) were collected from the compression moulded sheets and heated to 488 K at a rate of 20 K min^{-1}.

RESULTS

Effect of molecular weight on craze strength

Figure 2 shows the craze strength and yield stress as a function of the number-average molecular weight. The craze strength increases with increasing number-average molecular weight in all specimens. Of the specimens examined, the high tacticity PP has the highest craze strength and the PP decomposed with peroxide has the lowest. The yield stress decreases with increasing number-average molecular weight. The difference of yield stress among the three kinds of PP is negligibly small.

Figure 3 shows the craze strength and yield stress for PP of two levels of tacticity which have the same weight-average molecular weight, although the number-average molecular weight varies. Despite the constant weight-average molecular weight, it is found that the craze strength increases and the yield stress decreases with increasing number-average molecular weight.

Crystalline structure of undeformed PP

We have already examined the effect of tacticity on the crystalline structure of undeformed PP[3]. *Table 1* shows structural characteristics such as thickness of

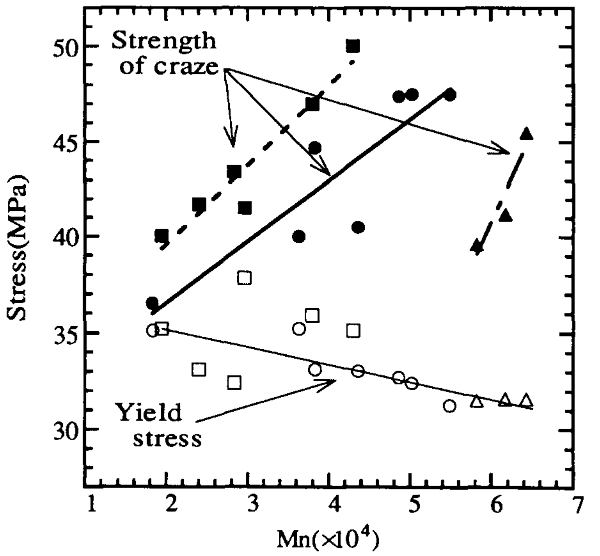

Figure 2 Craze strength and yield stress as a function of number-average molecular weight: □,■, high tacticity PP; ○, ●, conventional PP; △, ▲, PP decomposed with peroxide

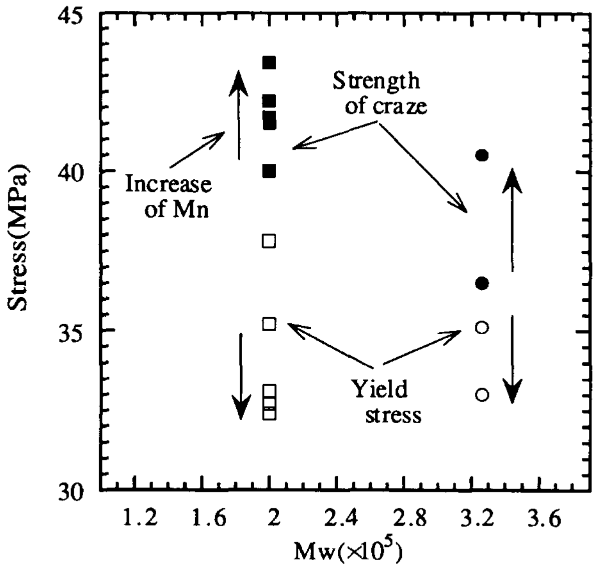

Figure 3 Craze strength and yield stress for PP of two levels of tacticity that have the same weight-average molecular weight and different number-average molecular weight: □, ■, high tacticity PP; ○, ●, conventional PP

Table 1 Characteristics of the crystalline structure of undeformed PP (C = conventional PP; H = high tacticity PP)

	M_n(×10^4)	Tacticity	X_c(%)	L_c(Å)	L_a(Å)	n
C	3.63	0.93–0.94	41.4	49.6	79.4	6.9
	3.83	0.93–0.94	36.1	39.3	78.7	6.9
	4.86	0.93–0.94	36.8	41.5	80.5	6.9
	5.02	0.93–0.94	35.9	39.1	78.9	6.9
H	4.30	0.94–0.95	42.3	50.8	78.2	7.8
	3.80	0.95–0.96	42.7	49.3	74.7	8.8

lamellae (L_c), thickness of amorphous layer (L_a) and number of regular folds (n) of a chain. It is found that the number of regular chain folds (n) increases with the increase of tacticity, although its number is independent of the number-average molecular weight.

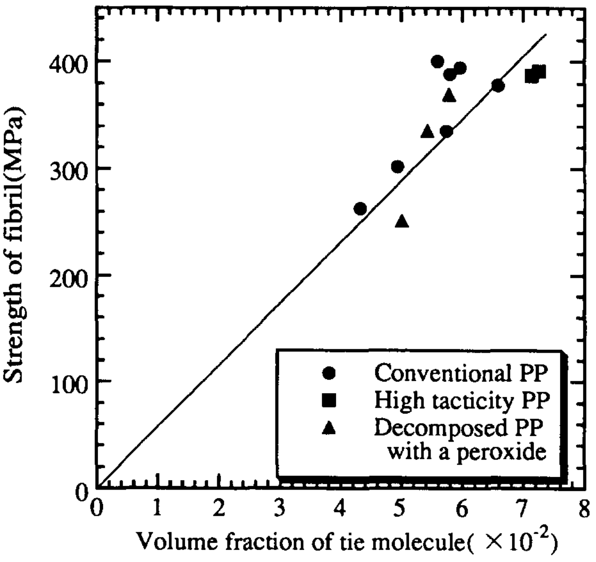

Figure 4 Fibril strength as a function of volume fraction of tie molecules estimated from the elastic modulus of the oriented specimen

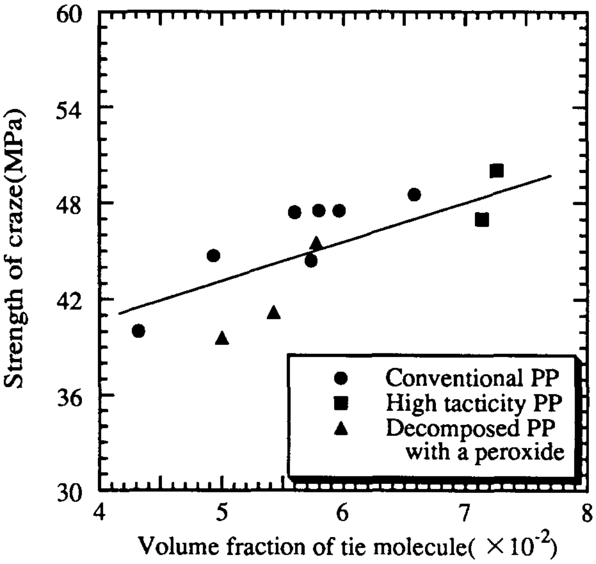

Figure 5 Craze strength as a function of volume fraction of tie molecules estimated from the elastic modulus of the oriented specimen

Volume fraction of tie molecules of oriented PP

Figure 4 shows the fibril strength as a function of the volume fraction of tie molecules estimated from the elastic modulus of the oriented specimen. The fibril strength is nearly proportional to the volume fraction of tie molecules and its linear line passes through the origin. Thus the fibril strength is determined by the number of tie molecules per unit area of amorphous phase between the neighbouring crystalline lamellae. A marked difference among the linear relationships between fibril strength and volume fraction of tie molecules was not detected for the three kinds of specimen. The fibril strength of the high tacticity PP has the largest value among the specimens examined because of the largest volume fraction of tie molecules. *Figure 5* shows the relationship between craze strength and volume fraction of tie molecules. The craze strength also was nearly proportional to the volume fraction of tie molecules. The variation of fibril strength

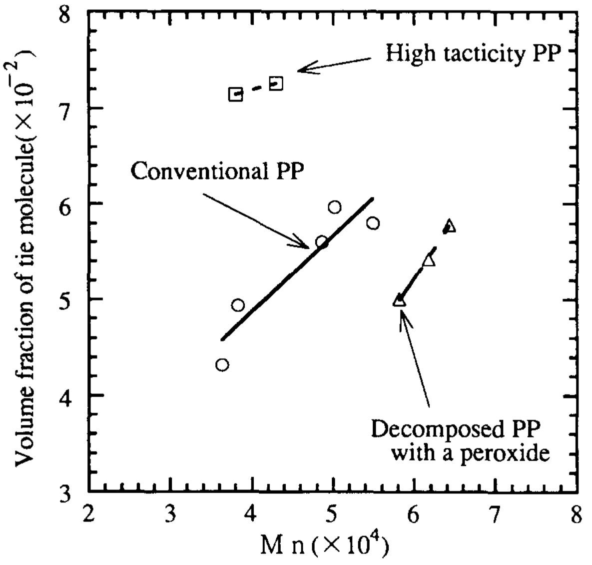

Figure 6 Volume fraction of tie molecules as a function of number-average molecular weight

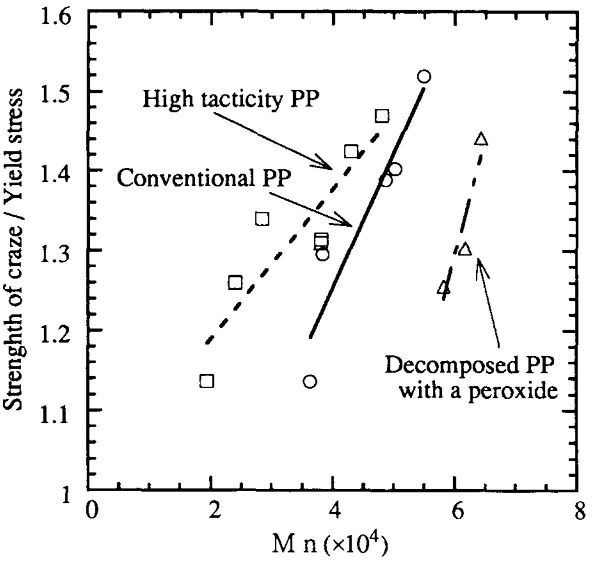

Figure 7 Ratio of craze strength to yield stress as a function of number-average molecular weight

with increasing volume fraction of tie molecules is larger than that of craze strength. The pronounced decrease of the cross-section of high-molecular-weight or high tacticity PP due to the high extension ratio is responsible for this discrepancy.

For oriented PP, the volume fraction of tie molecules (i.e. the number of tie molecules per unit area of amorphous phase) depends on both the method of preparation and the molecular weight. *Figure 6* shows the volume fraction of tie molecules as a function of the number-average molecular weight. The volume fraction of tie molecules is nearly proportional to the number-average molecular weight. For the same number-average molecular weight, the number of tie molecules is greatest for high tacticity PP and smallest for PP decomposed with peroxide.

DISCUSSION

Effect of molecular weight on toughness of PP

The dependence of craze strength on the number-average molecular weight is different for the specimens of different tacticity and the specimen decomposed by peroxide. On the other hand, because the increase of molecular weight reduces the crystallinity at constant moulding temperature, then the yield stress is decreased. If material containing a notch is plastically deformed without the development of voids, then the concentration of stress at the tip of this local plastic zone is proportional to the yield stress of the material[7]. Therefore, a large size of plastic zone is required to nucleate a crack in the specimen having a large ratio of craze strength to yield stress and, as a result, the toughness of such a material is large. *Figure 7* shows the ratio of craze strength to yield stress as a function of the number-average molecular weight. It is suggested that this ratio is increased with increasing number-average molecular weight. Therefore, the toughness of PP is improved with increasing number-average molecular weight because the development of a crack requires a large size of local plastic zone initiated from the notch[1]. Furthermore, this ratio is influenced by the method of preparation of the PP. In the case of PP with the same number-average molecular weight, high tacticity PP has a large toughness, and PP decomposed with peroxide has a low toughness[3]. In addition, it has been already suggested by the authors that the stress concentration at the tip of this local plastic zone depends on the constraint of strain[17]. If the density of voids is sufficiently large, the relaxation of stress concentration by Poisson's contraction between the neighbouring voids results in improved toughness. Since, in high tacticity PP, numerous microcrazes similar to voids were developed, this contributed to the improvement in toughness of PP[3].

Mechanism of craze fracture of PP

Since the distribution of a molecular chain in the melt state spreads with increasing molecular weight, the interaction between the molecular chains is strengthened and the melt viscosity is increased. It seems that the improvement of craze strength with increasing molecular weight is due to the interaction over the molecular length from which the mechanism of viscosity originates. On the other hand, it was shown that the number of tie molecules between the crystalline lamellae strongly affects the strength and modulus of an oriented crystalline polymer[12]. In this case, it seems that the craze strength depends on the number of tie molecules regardless of the length of the molecular chain.

It is suggested that both the fibril strength shown in *Figure 4* and the craze strength shown in *Figure 5* are influenced by the number of tie molecules per unit area of amorphous phase; furthermore, the number of tie molecules depends on the number-average molecular weight as shown in *Figure 6*. These results substantiate that the fracture of oriented PP occurs by the failure of tie molecules between crystalline lamellae, and it is concluded that the craze strength of PP depends on the number of tie molecules per unit area of amorphous phase. There is a probability of the presence of the end of a molecular chain within the amorphous region. Since a decrease of the number of molecular chain ends is expected as the length of the molecular chain increases, then the number of tie molecules increases. It is reasonable to assume that the increase of the number of tie molecules due to the decrease of molecular chain ends is one factor responsible for the improvement of craze strength with increasing number-average molecular weight, although a quantitative explanation based on this factor alone may be difficult.

The number of tie molecules depends on the method of preparation. For the oriented samples, the high tacticity PP has a larger number of tie molecules than conventional PP of the same number-average molecular weight. On the other hand, the number of regular chain folds between two intercrystalline tie molecules, estimated from the crystal model of the undeformed PP, increases with increasing tacticity regardless of molecular weight as shown in *Table 1*. This result means the decrease of the number of tie molecules per unit area of amorphous phase with the increase of tacticity in the undeformed PP. It is suggested from these examinations that the structure of the crystalline lamellae and tie molecules connecting the neighbouring lamellae change dramatically upon large-scale plastic deformation. The mechanism of plastic deformation of crazes for PP is basically identical to that of uniaxial extension, although the crazing process is accompanied by the development of voids and concentration of plastic strain. The plastic deformation of spherulites under uniaxial extension proceeds via the processes of lamella slip, orientation and separation, until the lamellae in all regions of the spherulite become aligned with their long spacing direction nearly parallel to the deformation direction[18]. When the extension ratio increases beyond a certain critical strain (about 7) which depends on both tacticity and molecular weight, the stress is increased up to fracture of the specimen by strain hardening. At the point of transition from yielding to strain hardening, the transition from a deformed spherulitic to a microfibrillar structure can be considered to be complete. This transition greatly alters the structure of the crystalline polymer as speculated from the large variation of long period between neighbouring lamellae, and it seems that the number of tie molecules per unit area of amorphous phase also changes. The mechanism of the variation of craze strength due to the preparation of PP, such as the tacticity or the decomposed PP, must be investigated by further examination.

Effect of molecular weight on craze strength and viscosity

The viscosity of polymeric materials depends on the weight-average molecular weight. It is well known that the viscosity of a molten polymer indicates the interaction between the neighbouring molecular chains over the chain length, and the viscosity follows a 3.4 power law for molecular weight. Therefore, the melt viscosity depends on the weight-average molecular weight, because chains of high molecular weight strongly affect the viscosity of a specimen that has a distribution of molecular weight. On the other hand, it was concluded in this study that the craze fracture occurs by the failure of tie molecules. Because the fraction of tie molecules within the amorphous phase is proportional to the number-average molecular weight, the improvement of craze strength is dependent on the number-average molecular weight. It is concluded from the above discussion that the mechanism of interaction between molecular chains in the process of craze fracture is different from that of melt viscosity. Therefore it may be expected that PP of high fluidity is produced without a drop in strength when the weight-average molecular weight approaches the number-average molecular weight under the retention of the number-average molecular weight ($M_w/M_n \rightarrow 1$).

CONCLUSION

Craze strength was improved with increasing number-average of molecular weight in all specimens, regardless of the weight-average of molecular weight. Examination of the number of tie molecules between the neighbouring lamellae suggests that craze fracture is caused by the failure of tie molecules. It may be expected from these results that PP of high fluidity can be produced without a drop in strength when the weight-average molecular weight approaches the number-average molecular weight under the retention of the number-average molecular weight.

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