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Stability of plastic deformation in polyolefins

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The difference in the stability of plastic deformation between polypropylene (PP) and polyethylene (PE) was analysed by a theory of instability of plastic deformation around the preformed voids under a dilational stress. It could be concluded that the unstable plastic deformation of PP compared with that of PE is the result of a high ratio of shear yield stress to shear modulus related to the difference in the microstructural changes during deformation. Copyright © 1996 Elsevier Science Ltd.

(Keywords: stability; plastic deformation; polyolefins)

INTRODUCTION

It is found in polymers that plastic deformation is unstably concentrated into a narrow region. This concentrated unstable plastic deformation often reduces the fracture of specimens. Necking on uniaxial tension and craze on dilatational stress are well known examples. We[1-3] have already discussed the mechanism of plastic instability by a concept similar to the theory of Griffith[4] which is the role of crack transmission controlled by the balance of several energies. When the rate of change of the energy for plastic deformation with the progress of deformation is less rapid than the allowable decrease of the elastic strain energy, the plastic strain is spontaneously concentrated into a narrow region. It can be suggested from the elastic–plastic analysis that the instability of plastic deformation depends on both the constitutive equation and compliance of materials[3]. The stability of plastic deformation in a uniaxial tensile test was studied recently by the infinite element method[5]. On the other hand, it was suggested by the authors[3] that the instability of plastic deformation occurred between adjacent voids under dilatational stress, i.e. the criterion of craze nucleation is strictly governed by a compliance (i.e. ratio of shear yield stress (τ) to shear elastic modulus (μ)). This analysis indicated the decrease of the ratio (τ/μ) leading to suppression of craze nucleation. It is often pointed out that the difference of the glassy transition temperature of the polymer has a strong effect on the behaviour of plastic deformation. Since the dependence of τ and μ on temperature is influenced by the glassy transition temperature, this transition temperature is responsible for the stability of plastic deformation in such a sense. For example, craze nucleation in an amorphous polymer is suppressed by the decrease of τ/μ as the temperature is increased towards the glassy transition temperature. Since τ/μ sensitively depends on the microstructure of the polymer, the mechanism of craze nucleation in the crystalline polymer is considered to be complex. It was suggested that the unstable deformation of poly(butylene terephthalate) (PBT) at a temperature higher than the glassy transition temperature was due to the increase of τ/μ with temperature[3]. On the other hand, the plastic deformation of polyamide-66 (PA-66) above the glassy transition temperature became stable with increasing temperature[3]. The value of τ/μ of PA-66 was constant and independent of temperature, although both τ and μ decreased with increasing temperature. In this case, a general yielding between voids due to shear plastic deformation occurs before dilatational stress reaches the condition of plastic instability.

The values of τ and μ are generally estimated from the maximum value and initial gradient of stress–strain curves respectively. A large plastic strain occurs in the ductile crystalline polymers until unstable plastic deformation develops. Then the material constants of the mechanical properties will vary with the change of microstructure. As a result, τ/μ may be different from the initial value estimated by a conventional method.

The purpose of this paper is to examine the variation of the elastic modulus and yield stress at larger strain for two kinds of polyolefins and to discuss the stability of plastic deformation in connection with the theory of plastic instability.

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EXPERIMENTAL

Preparation of specimen

The materials used in this study were three commercial grades of polypropylene (PP) (Chisso Petrochemical Co. Ltd) and also three commercial grades of polyethylene (PE) (Showa Denko Co. Ltd). The grades A, B and C corresponded to high, medium and low molecular weight materials, respectively.

Sheets of 2 mm thickness were prepared for the tensile test by compression moulding. The pellets were melted at 473 K for 30 min and were then cooled to 293 K. The dumbbell test specimens, having a width of 10 mm in the parallel part and length of 60 mm, were shaped mechanically. Rectangular bars with width of 12.4 mm and thickness of 6 mm for a three-point bending test were prepared by an injection moulding machine (Dynamelter, MEIKI). The temperature of the cylinder was 493 K at a moulding temperature of 303 K. The moulded specimens were isotropic except for the surface regions. A round notch with radius of 0.5 mm was shaped by machining with a convex milling cutter. The ligament thickness was 4.0 mm. The specimens were cooled with water during machine processing in order to prevent a rise of temperature.

Mechanical testing

The initial longitudinal elastic modulus and upper yield stress were estimated from the stress–strain curves measured at room temperature (296 K) by the conventional method. Poisson's ratios were calculated from the change of both width and length during uniaxial tensile deformation. The contraction of width was measured by laser equipment (Keyence, LS-3100) and extensional strain was measured by an extension meter with strain gauge (Shimazu SG-50-100). Tests were carried out at a strain rate of 0.15 min^{-1} at 296 K in an Instron Servodraulic testing unit (Servo Pulsar, Shimadzu EHF-EB5-10L). It is expected that the material constants of a polymer at large strain, which depend on the microstructure, may differ from the initial values estimated by the conventional method. Above the yield strain, the yield stress was estimated from the true stress–strain curve and the longitudinal elastic modulus was estimated from the gradient of unloading curves at an arbitrary strain as shown in *Figure 1*. The strengths of fibrillar bundles in the craze were estimated from the strength of the oriented region formed by necking on the uniaxial tensile test. In this experiment, the strain rate was 0.33 min^{-1}.

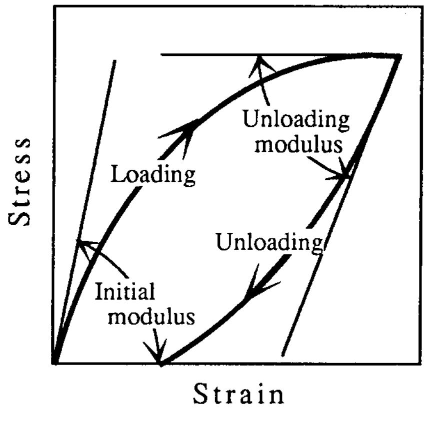

Figure 1 Estimation of longitudinal elastic modulus from gradient of unloading curve at an arbitrary strain

The toughness of the specimen was evaluated by a three-point bending test on a U-notched bar. 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).

Morphological analysis of deformation mode

To discuss the deformation processes of U-notched bars in the three-point bending test 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 microstructure of the plastic deformation zone was observed with a scanning electron microscope for the surfaces of cryogenically fractured samples. Samples, which were 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 influenced significantly 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 (refs 1 and 6). Specimens were treated by ion spattering to give adhesiveness to the interfaces.

RESULTS AND DISCUSSION

Toughness and plastic deformation ahead of the U-notch

Figure 2 shows the toughness evaluated by the three-point bending test for both PP and PE. The PE fractured before general yielding in a ductile manner and the toughness of PE was lower than that of PP over the molecular weight examined. The toughness of polyolefin was obviously increased as the molecular weight increased. It has been suggested that the brittle fracture of polymers originates from the breakdown of fibrillar bundles in the craze[1,7]. The stress required for the breaking of fibrils was caused, of course, by the constraint of strain[8-10] on the crack. Since the ratio of the strength of the fibril (σ_{fib}) to the yield stress (σ_Y) was smaller for PE than for PP, as shown in *Table 1*, crack nucleation occurred easily. Therefore, the toughness of PE is low in comparison with that of PP.

Figures 3 and *4* show the plastic deformation zone developed at the U-notched tip for PE and PP, respectively. Observations were carried out for the microtomed sections by an optical microscope and for the surfaces of cryogenically fractured samples by a scanning electron microscope. For both PE and PP, the highest molecular weight materials were examined. For PE, the load was applied first until crack nucleation ahead of the local plastic zone at the notch tip and then the deformation zone was given back to the bending displacement of 2.0 mm to prevent cracking by the delay fracture. The structure of deformed PE was fixed by casting in epoxy resin. The plastic deformation zone contained the craze, as shown in the electron micrographs. The morphology of the craze depends on the kind of polymer. The craze of PP clearly revealed the unstable concentration of plastic strain and fibril within the craze. On the other hand, the craze of PE was stable

Table 1 Mechanical properties[a] of PE and PP

Sample		MFI	M_n ($\times 10^4$)	ν	E (GPa)	σ_{fib} (MPa)	τ/μ	σ_{fib}/σ_Y
	A	5	1.30	0.37	1.12	33.1	0.0373	1.28
PE	B	7.5	1.22	0.33	1.16	30.0	0.0347	1.16
	C	20	0.89	0.39	1.16	25.5	0.0347	1.02
	A	0.7	7.86	0.36	1.42	40.5	0.0443	1.41
PP	B	3.8	5.02	0.36	1.63	43.4	0.0455	1.34
	C	23	3.63	0.35	1.67	40.0	0.0345	1.14

[a] M_n, molecular weight; ν, Poisson's ratio; E, elastic modulus; σ_{fib}, strength of fibril; τ, shear yield stress; μ, shear modulus; σ_Y, uniaxial yield stress; MFI, melt flow index

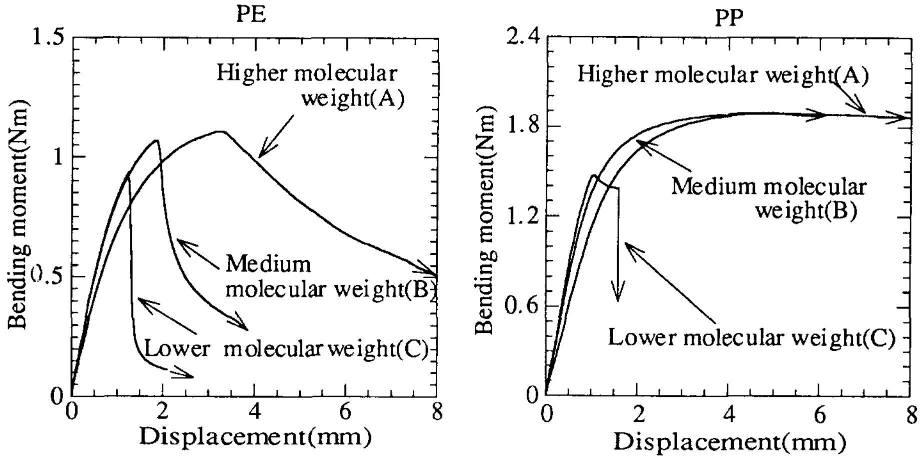

Figure 2 Toughness evaluated by the three-point bending test of U-notched bar in PP and PE

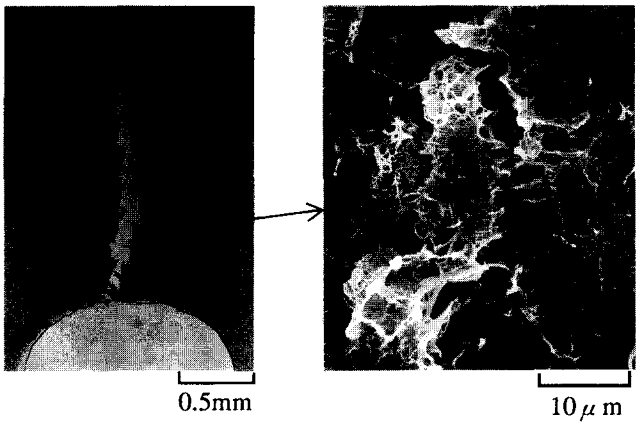

Figure 3 Plastic deformation zone developed at U-notched tip for PE

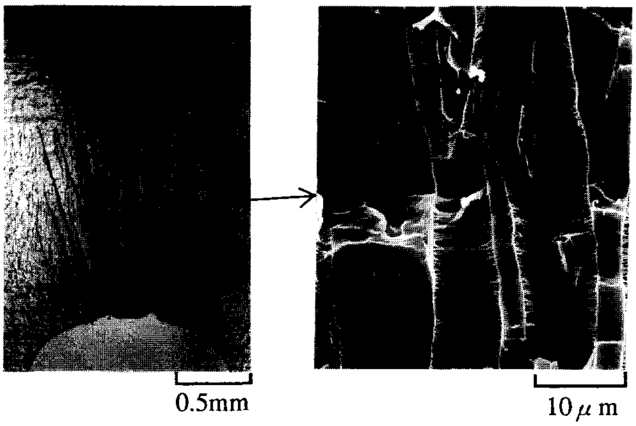

Figure 4 Plastic deformation zone developed at U-notched tip for PP

and finer than that of PP. It seems that the craze of PE is analogous to the void. It has been pointed out that the craze of a crystalline polymer first develops at the equatorial planes of spherulites because a high dilatational stress occurs due to the constraint of strain originating from the structure of the spherulite[10,11]. This region, which contains the numerous microcrazes, can be stably deformed by 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[8–10]. 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 is locally concentrated between neighbouring microcrazes, occurs at the tip of the local plastic zone. If the stress ahead of the local plastic zone reaches the strength of the fibrils, then the microrupture of the craze fibrils leads to catastrophic brittle fracture. In this study, PE shows fracture from the craze and PP shows general yielding which occurred in preference to fracture of the craze. Since the constraint of strain in a crystalline polymer depends on the structure of the spherulites, the size of the microcraze, which is nucleated at the first stage, may be influenced by the size of the spherulites. The size of spherulites was about 50 μm and 10 μm for PP and PE, respectively. It was suggested that the craze could grow beyond these spherulite sizes in either case. Therefore the stability of plastic deformation or toughness was not associated directly with the size of the spherulites.

Stability of plastic deformation

The mode of deformation of PP on the dilatational stress was obviously unstable in comparison with that of PE. The instability of plastic deformation between adjacent voids is strictly governed by a compliance (i.e. ratio of shear yield stress (τ) to shear elastic modulus (μ))[12]. This ratio (τ/μ) is influenced by the temperature, strain rate and the structure of polymer, and a decrease of the ratio introduces stable plastic deformation such as the plastic deformation at high temperature. The value of τ/μ for PP shown in *Table 1* is slightly larger than that of PE. It may be premature to decide from only this result that the unstable plastic deformation of PP is governed by the mechanism described above, because the difference of τ/μ between these samples is very small. Necking, which is known as a typical unstable plastic deformation, occurred at high strain of about 20–30% in both samples. It is reasonable to expect a large plastic strain ahead of the notch tip, although estimation of strain is difficult. The change of microstructure due to the large plastic strain may introduce a variation of the material constant from the original value evaluated by the conventional method.

Figure 5 shows the unloading curves of PP when the stress was removed beyond the yield strain. The longitudinal elastic modulus was estimated from the gradient of these unloading curves. The shear modulus (μ) was calculated by the use of both longitudinal elastic modulus and Poisson's ratio. In this calculation, the Poisson's ratio used was an initial value because its change with strain was negligible. *Figure 6* shows the variation of the longitudinal elastic modulus with increase of the unloading strain. It was clearly observed that the decrease of elastic modulus with strain was more obvious for PP than for PE. *Figure 7* shows the variation of τ/μ with strain at unloading. For both PP and PE, τ/μ increases with increase of the strain. It is suggested from this result that the mode of plastic deformation becomes unstable with increasing strain. This change is especially remarkable in PP. The variation due to molecular weight is slight in either case. It could be concluded from this discussion that the unstable plastic deformation of PP compared with that of PE is the result of a sharp increase of τ/μ related to the change of microstructure with the increase of strain.

It is reasonable to understand that the change of structure in the crystalline polymer was caused by plastic deformation as the applied strain increased. The spherulites of a crystalline polymer are plastically deformed by shear plastic deformation which is exhibited by tilting of the lamellae and slipping of the crystal[13]. A spherulite in a semicrystalline polymer 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 resistance against deformation by compressing the spherulite is large. Consequently the constraint

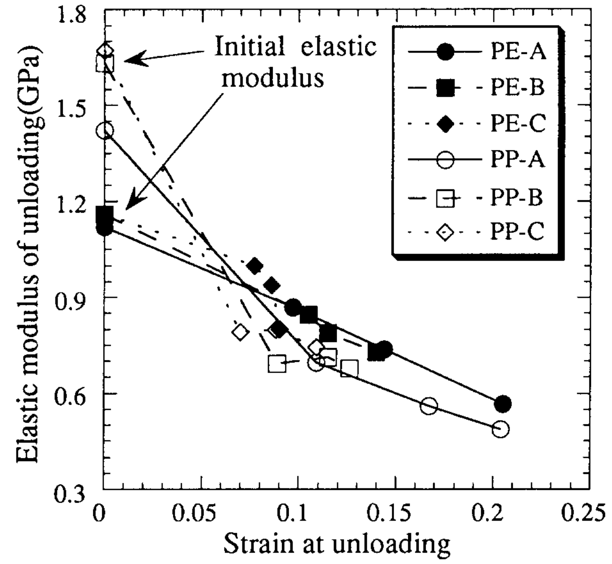

Figure 6 Variation of the longitudinal elastic modulus with the increase of strain at unloading

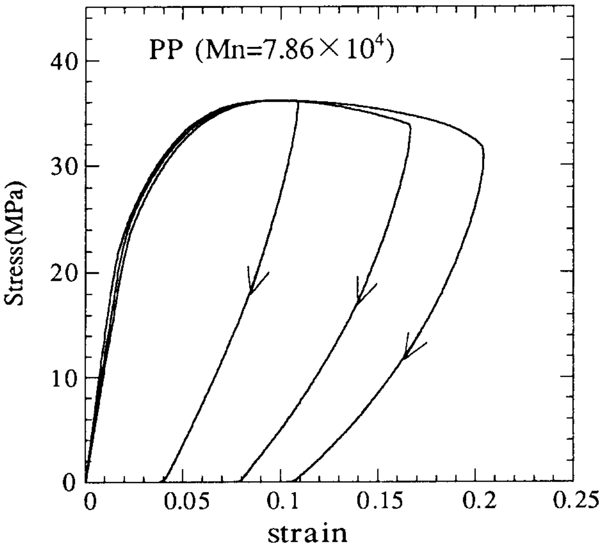

Figure 5 Unloading curves of PP when the stress was removed beyond the yield strain

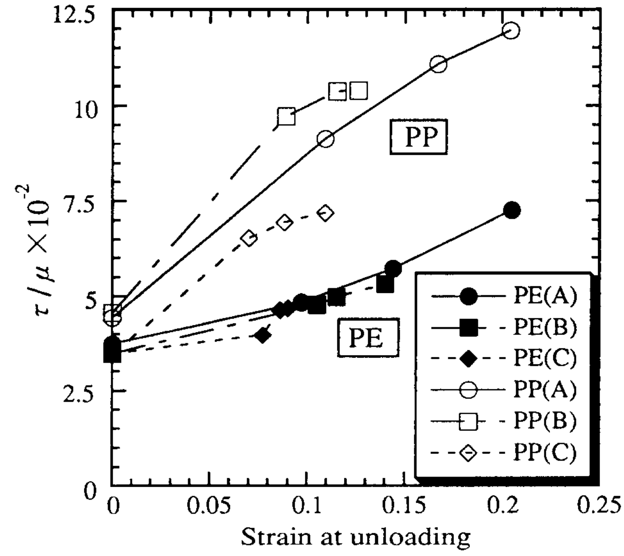

Figure 7 Variation of the ratio τ/μ with the increase of strain at unloading

of strain gives rise to high dilatational stress on the equatorial planes of spherulites. Therefore, it is difficult to keep the volume of such a region constant during plastic deformation, and the development of voids initiates easily on the equatorial planes of spherulites together with yielding by fracture of lamellar crystals. The diffraction of X-rays caused by lamellar crystals was broadened by the fracture of lamellar crystals. The change of microstructure due to nucleation of voids has provided strong evidence of the factors involved in the decrease of shear modulus. It is well known now that the spherulite of PE grows in the direction of the *a*-axis in a lamellar crystal and the growth is accompanied by twisting of the lamellar crystal as shown by the extinction ring under crossed nicols. On the other hand, because the spherulite of PP grows in the direction of the *b*-axis in a lamellar crystal and twisting of the lamellar crystal does not occur, the spherulite of PP does not have an extinction ring. It seems that twisting of the lamellar crystals inhibited the propagation of craze due to fracture of the lamellar crystal because the direction of the *c*-axis in the lamellar crystal was different from the direction of maximum principal stress. It is reasonable to point out that the difference of the material constant at high strain owing to the difference in microstructure between PE and PP is the main factor causing the different stability of plastic deformation.

CONCLUSIONS

The stability of plastic deformation of both PE and PP was analysed by a theory of plastic instability. It could be concluded that the unstable plastic deformation of PP compared with that of PE is the result of the high value of τ/μ relating to the change of structure with an increase of strain.

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