JOURNAL OF APPLIED POLYMER SCIENCE VOL. 21, 3291–3309 (1977)

Mechanical Anisotropy in Injection-Molded Polypropylene

MITSUYOSHI FUJIYAMA and HIROSHI AWAYA, *Research and Development Division, Tokuyama Soda Co., Ltd., Tokuyama-shi, Yamaguchi-ken, Japan,* and SHUKICHI KIMURA, *Plastic Division, Tokuyama Soda Co., Ltd., Tokuyama-shi, Yamaguchi-ken, Japan*

Synopsis

By use of a mod with a film gate, two straight polypropylenes (PP) with different melt flow index (*MFI*) and a glass fiber-reinforced polypropylene (FRPP) were injection molded at various temperatures into square plates with orientational anisotropy. The anisotropies of tensile property, tensile impact strength, and flexural property were studied on the molded sample cut mainly in the machine direction (MD), 45°-direction (45°), and transverse direction (TD). Both the orders of the yield strength and tensile impact strength of the FRPP, and those of the necking stress and tensile impact strength of the straight PP, were MD >45° >TD, which are reasonable tendencies. The orders of the yield strength and flexural modulus of the straight PP were MD > TD > 45°, which suggests the presence of shear deformation between the lamellae in the skin layer. The variation of the flexural modulus with the angle to the MD fitted well to Hearmon's equation. Generally, for straight PP, the anisotropy of various properties increased as the *MFI* and cylinder temperature became lower, or as the skin layer became thicker. For the FRPP, the anisotropy increased as the cylinder temperature became higher, or as the degree of the orientation of glass fibers became higher.

INTRODUCTION

Since polymer melt crystallizes under high shear stress, molecular chain orientation occurs on injection molding. Accordingly, the properties of the processed article may be affected by its direction, namely, by anisotropy. Many studies have been done on the mechanical anisotropies of oriented films.[1–15] However, studies on the mechanical anisotropies of injection-molded articles are few.[16–18] This may be due to the orientational inhomogeneity in injection-molded articles. According to Ballman et al.,[16] as the degree of the orientation of injection-molded polystyrene increases, the tensile strength, elongation, and Izod impact strength in the MD increase and those in the TD slightly decrease. Ogorkiewicz et al.[17] injection molded polypropylene into wide-bottom trays, cut the specimens in various directions, measured the variations of tensile and shear moduli with angle, and found that their variations fitted well to Hearmon's equation.[19] Krebs[18] measured the variations of the tensile yield strength and ultimate elongation of an injection-molded low-pressure polyethylene with angle, and found that the yield strength was the lowest and the ultimate elongation was the highest in the 45°-direction.

In the previous paper,[20] we showed that an injection-molded PP showed a clear two-phase structure of skin and core when its cross section was observed with a polarized microscope; and we estimated the higher-order structures of the skin and core layers by means of wide-angle x-ray diffraction, small-angle x-ray scattering, melting behavior, density, dynamic viscoelasticity, and tensile test. In the skin layer, the *c*-axis highly oriented parallel to the MD, and the plane of the lamellar structure of about 160 Å in thickness was normal to the MD. The density was about 0.907 g/cm^3, which was nearly equal to that of the core layer. Although the major part of crystallites melted in the same temperature range as that of the core layer, there was about 5.3% of a high-temperature melting structure (T_m = 182°C). The dynamic tensile modulus E' in the MD decreased more slowly with increasing temperature than that of the core layer, and held high in the range of ca. 30°C, just above the temperature at which E' of the core layer suddenly dropped. The tensile yield strength in the MD was about 1.5 times higher than that of the core layer. In general, PP melt crystallizes under high shear stress on injection molding. From these experimental results, it was concluded that the skin layer was composed of, or contained, a so-called "shish kebab" structure which was in parallel to the MD and was imbedded in a row structure. The core layer was composed of spherulites.

In other papers,[21,22] we studied the effect of molecular weight and molding conditions on the mechanical properties of injection-molded PP's through the skin/core morphology. The thickness of the skin layer increased with decreases in cylinder temperature, injection speed, and *MFI*. It was practically not affected by injection pressure and mold temperature. The tensile yield strength, necking stress, tensile modulus, flexural modulus, flexural strength, mold shrinkage, and annealing shrinkage increased with decreasing cylinder temperature and were in linear relationships with the thickness of the skin layer, regardless of the *MFI*.

However, only one direction was studied in previous papers[21,22] (flow direction = orientation direction). When we are to evaluate the strength, rigidity, shrinkage, and other properties of actually processed articles, we need to study the properties of all directions. Thus, in this investigation we studied the anisotropies of injection-molded PP. Since the molecular orientation of the injection-molded PP is concentrated in the skin layer, we chose the thickness of the skin layer as an internal structure parameter as in the previous papers[21,22] and discuss the experimental results from the viewpoint of the skin/core morphology. Although the thickness of the skin layer was influenced by the kind of resin and processing conditions, it was most influenced by the *MFI* and cylinder temperature.[21] Then, in this work, we studied the latter two factors. Furthermore, since the orientation of glass fibers as well as molecular chains participated in the properties of FRPP, it was also studied. The properties studied here were all mechanical ones, namely, tensile yield strength, necking stress, tensile impact strength, flexural modulus, and flexural strength. The directions studied were generally the MD, 45°-direction, and TD for all samples, and 22.5°- and 67.5°-directions were also added in some cases.

EXPERIMENTAL

Materials

The resins used in this study were three commercial isotactic polypropylenes: L (low-*MFI* straight PP, *MFI* = 1.6 dg/min); H (high-*MFI* straight PP, *MFI* = 8.2 dg/min); and G (FRPP, glass fiber content = 20 wt-%), which were manufactured by Tokuyama Soda Co., Ltd.

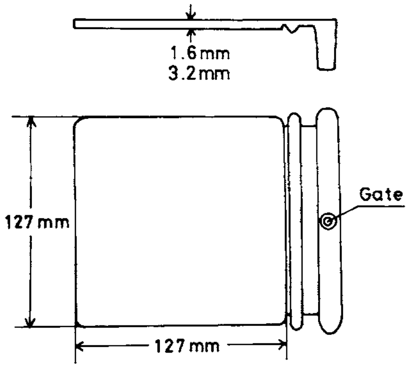


Fig. 1. Shape of mold cavity.

Molding

To obtain specimens of uniform anisotropy, square plates were injection-molded by use of a mold with a film gate. The shape of the mold cavity is shown in Figure 1. Injection molding was carried out with a Toshiba IS 200A-Type

TABLE I
Injection-Molding Conditions[a]

Plate thickness, mm	Sample	Cylinder temperature, °C				Injection pressure, kg/cm^2
		FZ	CZ	MZ	AD	
1.6	L	180	170	190	170	860
		180	200	220	200	680
		180	230	250	230	480
		180	260	280	260	460
	H	180	170	190	170	460
		180	200	220	200	400
		180	230	250	230	350
		180	260	280	260	350
	C	180	170	190	170	570
		180	200	220	200	460
		180	230	250	230	370
		180	260	280	260	350
3.2	L	180	180	190	180	450
		180	200	220	200	400
		180	230	250	230	350
		180	260	280	260	350
	H	180	180	190	180	400
		180	200	220	200	400
		180	230	250	230	350
		180	260	280	260	350
	G	180	180	190	180	400
		180	200	220	200	420
		180	230	250	230	350
		180	260	280	260	350

[a] FZ = feed zone; CZ = compression zone; MZ = metering zone; AD = adaptor. Mold temperature: 40°C, cooling time; 30 sec; injection speed; max.

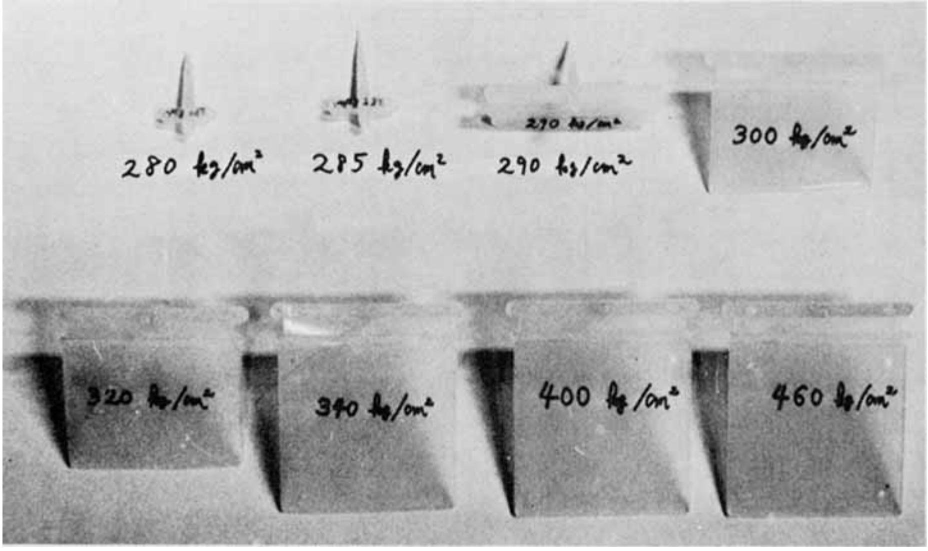


Fig. 2. Short-shot test; $3.2\ \text{mm}^t$ plate, L sample molded at 250°C.

20-ounce reciprocating-screw injection-molding machine. The molding conditions are shown in Table I. The cylinder temperature was measured at the metering zone (MZ). To obtain fine articles, the injection pressure was changed since the short-shots occurred when low-*MFI* resins were molded at low cylinder temperatures, and the flashes occurred when high-*MFI* resins were molded at high cylinder temperatures. We have already confirmed that the injection pressure has little effect on the thickness of the skin layer and mechanical properties.[21]

To confirm whether the specimen of uniform anisotropy was actually obtained by the mold cavity, a short-shot injection-molding test was carried out. The results are shown in Figure 2. Below the injection pressure of 285 kg/cm^2, resins enter into only the sprue and runner. They do not enter into the cavity until the injection pressure reaches 290 kg/cm^2. Flow length increases with increase in injection pressure. Above an injection pressure of 400 kg/cm^2, the cavity is completely filled with resins. The short-shot test indicates that the resins flow uniformly from the film gate. This suggests that the orientation state is also uniform. The isotropic specimens were obtained by compression molding at 215°C under a pressure of 100 kg/cm^2 for 10 min, followed by cooling with water.

Measurements

Thickness of Skin Layer. The injection-molded plate was cut about 0.1 mm thick in the TD, and was observed by a universal projecter (Olympus UT350) under cross-Nikols with a magnification of 50×. A clear skin/core morphology was observed. Since the thickness of the skin layer was not uniform, the center area was used as representative area.

Tensile Property (JIS K6758-1968). To obtain specimens for tensile tests, square plates 1.6-mm thick were cut at the center in the MD, 45°-direction, and TD with a JIS Type-3 dumbbell cutter. For the L sample molded at 250°C and the G sample molded at 220°C, the 22.5°- and 67.5°-directions were also added

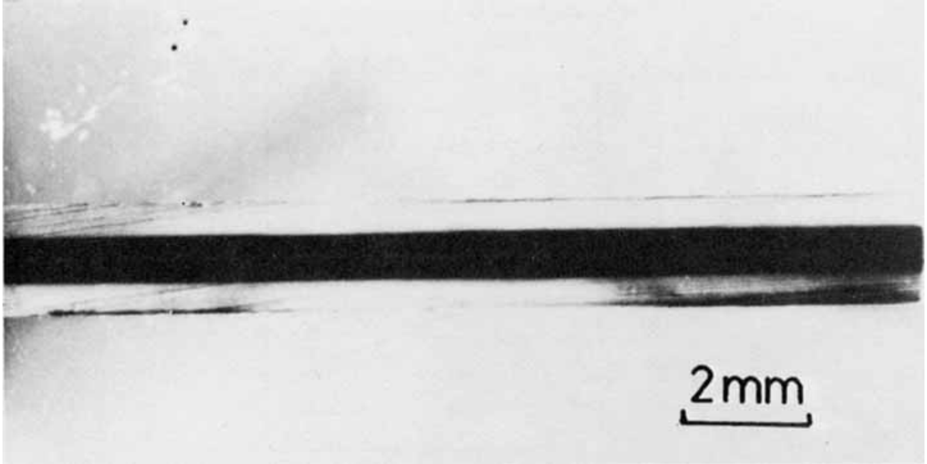


Fig. 3. Example of polarized micrograph of the cross section of injection-molded PP. L Sample molded at 250°C.

to the above directions. The tensile properties were measured with a Shimazu Autograph IS-5000 Type at 23°C. The chuck distance was 6 cm; the mark-line distance, 1 cm; and the tensile speed, 20 mm/min. The average value of three samples was adopted.

Tensile Impact Strength (ASTM 1961 Part 9). To obtain the specimens for tensile impact strength (*TIS*), square plates 1.6-mm thick were cut at the center in the MD, 45°-direction, and TD with a *TIS* dumbbell cutter. The *TIS* was measured at 23°C. The average value of six samples was adopted.

Flexural Property (ASTM D790). To obtain the specimens for flexural tests, square plates 3.2-mm thick were cut at the center in the MD, 45°-direction, and TD with a saw. For the L sample molded at 190°C and the G sample molded at 220°C, the 22.5°- and 67.5°-directions were also added to the above directions. The flexural properties were measured with a Shimazu Autograph IS-5000 Type at 23°C. Span length L was 5 cm, and bending speed was 10 mm/min. Flexural modulus E and flexural strength FS were calculated by eqs. (1) and (2), respectively:

$$E = \frac{PL^3}{4\delta bh^3} \tag{1}$$

$$FS = \frac{3P_Y L}{2bh^2} \tag{2}$$

where P is load, P_Y is yielding load, δ is flexion amount, and b and h are, respectively, width and thickness of the specimen.

RESULTS AND DISCUSSION

ThicKness of Skin Layer

An example of the polarized micrograph of the cross section of an injection-molded PP is shown in Figure 3; since it was printed by a quick copier, darkness is inverted. A clear two-phase structure with skin (outer bright portion) and core (inner dark portion) is observed.

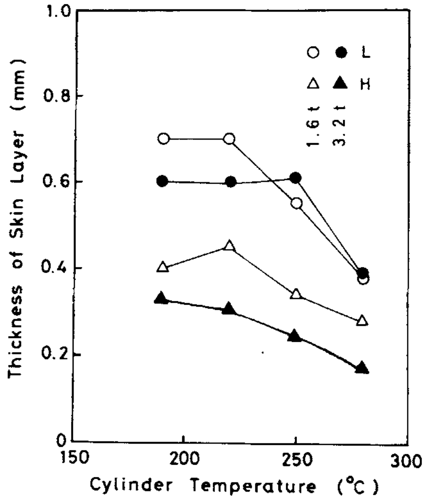


Fig. 4. Effect of cylinder temperature on thickness of the skin layers.

The effect of cylinder temperature on the thickness of the skin layer is shown in Figure 4. Although the thickness of the skin layer generally decreases with increase in cylinder temperature, there are exceptional cases where the thickness of the skin layer does not change, or even increases, with increase in cylinder temperature. This is probably so because the injection pressure is reduced when the cylinder temperature is raised as shown in Table I. On pressure-controlling-type injection molding, the thickness of the skin layer increases as the injection pressure decreases.[21] Since the injection moldings in this work were carried out under pressure slightly higher than the short-shot pressure, they were possibly controlled by pressure in contrast to the previous work.[21]

No skin layer was observed in the G sample.

Tensile Property

Yield Strength. The effect of cylinder temperature on the yield strengths in various directions for the L, H, and G samples is shown in Figure 5(a)–5(c), respectively. The variations of the yield strengths of the L sample molded at 250°C and the G sample molded at 220°C with the angle to the MD are shown in Figures 6 and 7, respectively. While the yield strength of the G sample decreases gradually from the MD to the TD, those of the L sample and H sample are MD ≫ TD > 45°; the 45°-direction is the lowest. This fact is worth noting.

When the tensile stress σ is applied to the specimen as shown in the upper part of Figure 8, the normal stress σ_N and shear stress τ, both of which act in the plane whose angle is $(90° - \theta)$ against σ, are represented by eqs. (3) and (4), respectively:

$$\sigma_N = \sigma \cos^2 \theta \tag{3}$$

$$\tau = \sigma \sin \theta \cos \theta \tag{4}$$

The variations of σ_N and τ with θ are shown in the lower part of Figure 8. The shear stress τ shows a maximum at $\theta = 45°$ with a value of $\sigma/2$.

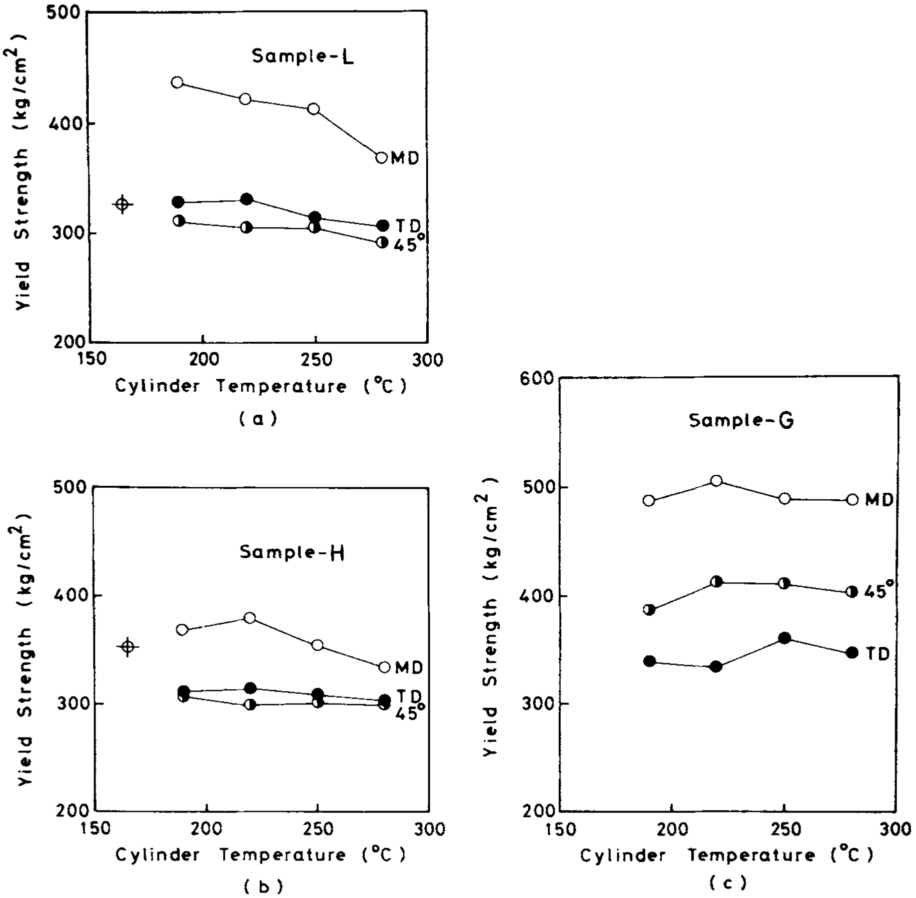


Fig. 5. Effect of cylinder temperatures on yield strengths in various directions. Cross-marked points are for compression-molded materials: (a) L sample; (b) H sample; (c) G sample.

The orientation direction of the molecular chains and lamellae in the skin layer of the MD-, 45°-, and TD-specimens are shown in Figure 9. (It was shown in the previous paper[20] that the lamellae in the skin layer were perpendicular to the MD.) Since the orientation directions of the molecular chains and/or lamellae in the skin layer of the 45°-specimen coincide with the 45°-direction at which the shear stress τ is maximum, the 45°-specimen is under the state where slips between the oriented molecular chains or lamellae most easily occur. However, it is difficult to elucidate the yield phenomenon in terms of intermolecular deformation, which pulls apart the van der Waals bonds, since it is observed under considerably large deformation. It is rather reasonable to elucidate it by interlamellar deformation. On interlamellar deformation, it might be easier to make the lamellae slip by shear stress than to pull them apart by tensile stress. Both facts, that the 45°-direction is under the state where the shear deformation most easily occurs and that the shear deformation can be done with a weak force due to the higher-order structure of injection-molded PP, indicate that the yield strength in the 45°-direction is the lowest.

Ward et al.[8] showed that the modulus of an anisotropic polyethylene sheet

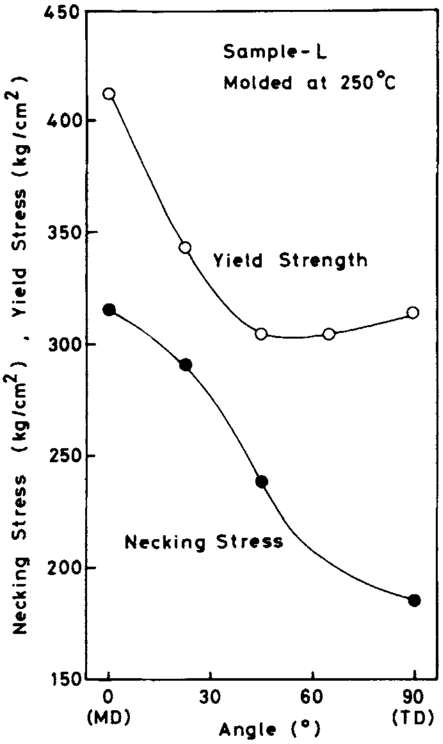


Fig. 6. Variations of yield strength and necking stress with angle to the MD; L sample molded at 250°C.

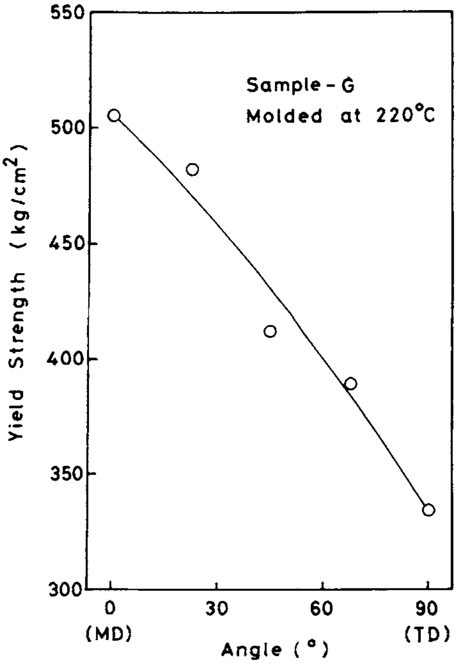


Fig. 7. Variation of yield strength with angle to the MD; G sample molded at 220°C.

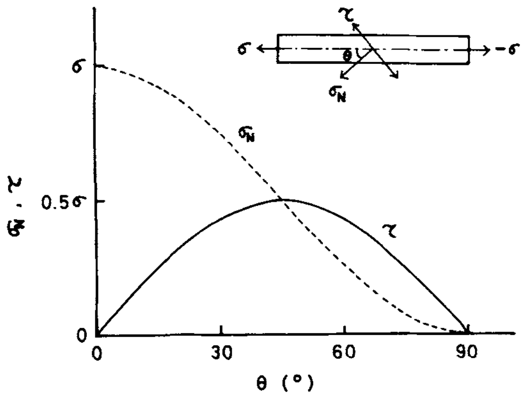


Fig. 8. Variations of normal stress σ_N and shear stress τ with angle θ.

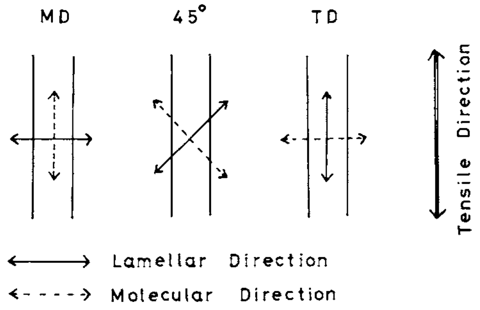


Fig. 9. Orientation directions of molecular chains and lamellae in the individual specimen.

was the lowest at 45°-direction and elucidated it with the concept of interlamellar shear deformation.

On the assumption that the yield of the skin layer originates in the interdirections are schematically drawn in Figure 10. In the MD, the interlamellar materials (amorphous chains) are elongated by tensile stress. In the 45°-direction, the lamellae slip past each other by shear stress; and in the TD, by tensile stress. Furthermore, at the center of the injection-molded PP, there is not only a skin layer but also a core layer composed of spherulites. The yield of the core layer may be ascribed to the overlapping of spherulite and interspherulite deformations.

The order of the yield strength of the G sample (FRPP) is reasonably MD > 45° > TD. It is assumed that the yield strength of the FRPP is rather governed by the glass fiber orientation than by the molecular orientation or the higher order structure of base resin. The fact that the order of the yield strength of the FRPP is 45° > TD, in contrast to the straight PP, suggests that the yield does not occur by shear stress but by tensile stress in all cases in the FRPP.

The yield strengths in the MD, 45°-direction, and TD of the straight PP increase with the decrease in cylinder temperature. Consequently, all the directions become strong if the MD is strengthened. Such tendency has been observed also for T-die film.[15] For such resins as polyethylene and polystyrene, the TD is weakened when the MD is strengthened by molecular orientation.[16] Such tendency for the orientation-crystallized polypropylene is ascribed to a

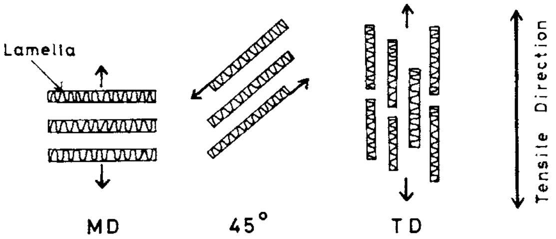


Fig. 10. Elementary processes of yield phenomena in various directions.

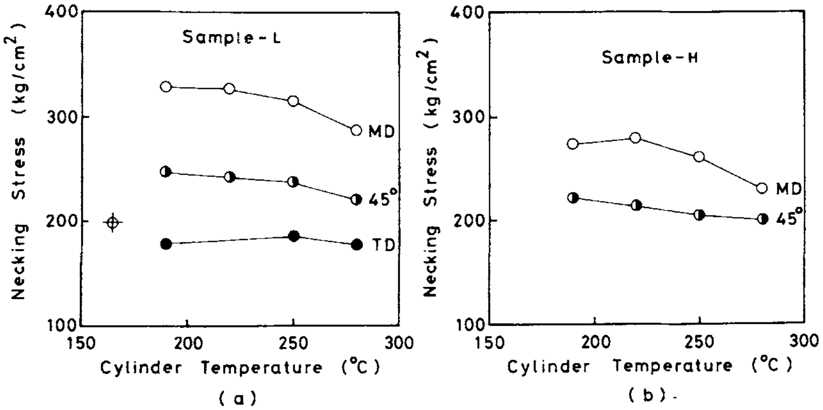


Fig. 11. Effect of cylinder temperatures on necking stresses in various directions. Cross-marked point is for compression-molded material: (a) L sample; (b) H sample.

"woven structure."[20,23] However, the previous results[20] and the fact that the yield strength in the MD is far higher than that in the TD suggest that the woven structure is mainly composed of the warp, and the woof component is very small. The order of the dependence of the yield strength on cylinder temperature is MD $\gg$ TD $>$ 45°, which is in accordance with the order of the yield strength of the skin layer (*vide infra*). The yield strength of the G sample is practically independent of cylinder temperature. It is assumed that the reduction of the yield strength which originates in the decrease of the molecular chain orientation caused by the increase in cylinder temperature and the reduction in yield strength caused by the decrease in injection pressure[21] may balance the increase in yield strength which originates in the increase in glass fiber orientation caused by the increase in cylinder temperature.

Necking Stress. The effect of cylinder temperature on necking stress in various directions for the L and H samples is shown in Figure 11(a) and (b), respectively. The variation of the necking stress of the L sample molded at 250°C with the angle to the MD is shown in Figure 6. The L sample molded at 220°C in the TD ruptured soon after the yield point and did not show necking. Since one of the three specimens showed necking for the L sample molded at 190°C in the TD, its value was adopted. The H sample in the TD and the G sample in all directions ruptured soon after the yield points and did not show necking. For the L sample, the der of the necking stress is 9 or MD $>$ 45° $>$ compression-molded $>$ TD. This is reasonable, for the difficulty of the unfolding of the lamellae is in this order, as shown in Figure 12. According to the theory of Kasai

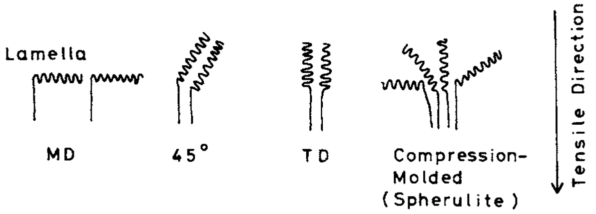


Fig. 12. Unfolding of the lamellae in the skin layer of an injection-molded article in various directions and in a compression-molded one.

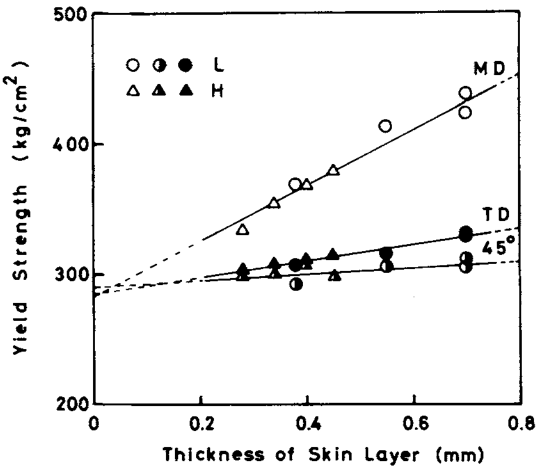


Fig. 13. Relationship between yield strengths in various directions and thickness of the skin layer.

et al.,[24] since the molecular unfolding occurs after the lamellae change to elongation direction, the lamellae must rotate by 90° and 45° in the MD- and 45°-specimens, respectively. On the other hand, they need not rotate in the TD specimen. Consequently, the order of difficulty of the necking is MD > 45° > TD, and hence the necking stress is also in the same order.

The necking stress, just like the thickness of the skin layers, tends to decrease with increasing cylinder temperature. From this fact, a certain relationship between the necking stress and the thickness of the skin layer (*vide infra*) is expected.

Relations Between Tensile Properties and Thickness of Skin Layer. The relation between the yield strength or necking stress and the thickness of the skin layer is shown in Figures 13 and 14. The yield strengths and necking stresses in all directions correlate linearly with the thickness of the skin layer, having positive slopes, regardless of the *MFI* of the resins. By extrapolating the thickness of the skin layer to 0.8 mm and zero, the values for the various tensile properties of the skin and core layers were obtained, as shown in Table II. The yield strengths of the skin and core layers obtained from the injection-molded dumbbell (one-directional specimen) in the previous paper[22] were, respectively, 450 kg/cm^2 and 260 kg/cm^2, agreeing perfectly with those in the MD in Table II. However, the yield strength of the core layer obtained here is slightly higher than that in the previous paper.[22] This is probably so because the specimen

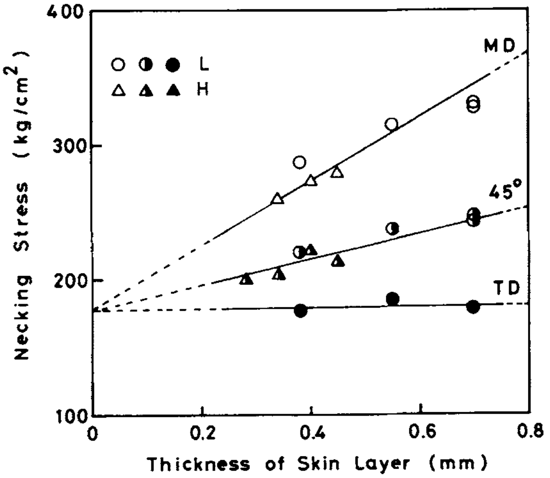


Fig. 14. Relationship between necking stresses in various directions and thickness of the skin layer.

molded at the mold temperature of 40°C in this work was cooled more slowly than that molded at 13°C in the previous paper.[22] The necking stresses of the skin and core layers obtained in the previous paper[22] were, respectively, 390 kg/cm^2 and 200 kg/cm^2, which were higher than those in the MD in Table II. This is probably so because the specimen in the previous paper, the ASTM dumbbell, had a higher cross-sectional area than the JIS Type-3 dumbbell in this work.

For the tensile strength, it is advantageous to injection mold the skin layer as thick as possible since the yield strength of the skin layer is higher than that of the core layer in all directions, as shown in Table II. Since the skin layer of the 45°-specimen had a strong possibility to yield by shear deformation as mentioned above, we tried to calculate the shear yield strength of the skin layer from the tensile yield strength of the skin layer of the 45°-specimen. As shown in Figure 8, when the tensile stress σ is applied to the specimen, the shear stress on the plane at 45° is $\sigma/2$. Namely, the shear yield strength of the skin layer is one half of the tensile yield strength of the skin layer of the 45°-specimen. The shear yield strength of the skin layer, calculated in this way, is 155 kg/cm^2. The shear yield strength of the skin layer corresponds to the interlamellar slipping yield strength, and the tensile yield strength in the MD of the skin layer corresponds to the interlamellar pulling-apart yield strength. The former is about one third of the latter.

TABLE II

Values of the Various Tensile Properties of Skin and Core Layers

Tensile property	Layer	MD	45°	TD
Yield strength, kg/cm^2	skin	452	309	334
	core	282	290	284
Necking stress, kg/cm^2	skin	368	254	180
	core	176	176	176

Tensile Impact Strength (TIS)

The effect of the cylinder temperatures on the *TIS* values in various directions for the L, H, and G samples is shown in Figure 15(a)–15(c), respectively. For all the samples, the order of the *TIS* is MD > 45° > TD. Since the *TIS* is proportional to the integral of the tensile stress at high-speed tensile deformation (about 3 m/sec) from zero to rupture elongation, i.e., the area of the stress–strain curve at high speed elongation, the *TIS* shows a low value when the stress is high but the elongation is low. Since the skin layer occupies a considerably wide part in the injection-molded PP and the lamellae in the skin layer are arranged as shown in Figure 10, the order of the ease of stress propagation is MD > 45° > TD. Further, since the difference in the ease of the stress propagation is magnified at the high-speed deformation, the elongation at high speed should also be in the same order. Furthermore, since the order of the stress is MD > 45° > TD, the order of the multiplied value of the stress by the elongation should be MD > 45° > TD, and, consequently, the *TIS* is also in the same order.

The *TIS* of the L sample shows a notable maximum at 250°C in the MD and 45°-direction and a small maximum at the same temperature in the TD. The *TIS* values of the H and G samples are practically independent of the cylinder temperature. Since the thickness of the skin layer decreases gradually with increasing cylinder temperature, the *TIS* is almost independent of the thickness of the skin layer, and the structural factor which governs the *TIS* is not obvious. However, as clearly observed on the L sample in the usual cylinder temperature range, the *TIS* values of an injection-molded PP in all directions become higher when the *TIS* in one direction becomes higher. This is in contrast to the injection-molded polystyrene.[16] Thus, so far as the impact strength is concerned, it is better to mold the MD as tough as possible on injection molding PP.

For the resins studied here, the order of the *TIS* is L sample≫ H sample > G sample in the MD and 45°-direction, and G sample >L sample ≈ H sample in the TD. When an injection-molded article fractures by impact, the strength depends on the impact direction. If the impact is added mainly in the MD, the order of the strength will be L sample ≫H sample > G SAMPLE/ If the impact is added mainly in the TD, the order will be G sample > L sample ≈ H sample. Although the impact direction is not known in most cases, a fracture should occur along the impact direction when the impact energy in a certain direction exceeds the impact strength in the direction. If the impact strengths in the TD of two materials are equal, the one which has higher impact strength in the MD and/or 45°-direction will have higher total impact strength. For example, the L sample, which has nearly equal *TIS* as the H sample in the TD and has higher *TIS* than the H sample in the MD and 45°-direction, will have higher total impact strength.

Finally, we will compare the *TIS* of the injection-molded PP with that of the compression-molded PP, which is regarded as an isotropic sample. As for the *TIS,* the compression-molded material is situated between °C for the L sample. Also it is situated between the MD and 45°-direction of the injection-molded material molded at 250°C for the H sample.

Since the compression-molded material is isotropic, it shows same impact strength in any direction. If an isotropic article is obtained by injection molding, the *TIS* will be the same as that of the compression-molded article in any direction. (Strictly speaking, they are not exactly the same since cooling conditions

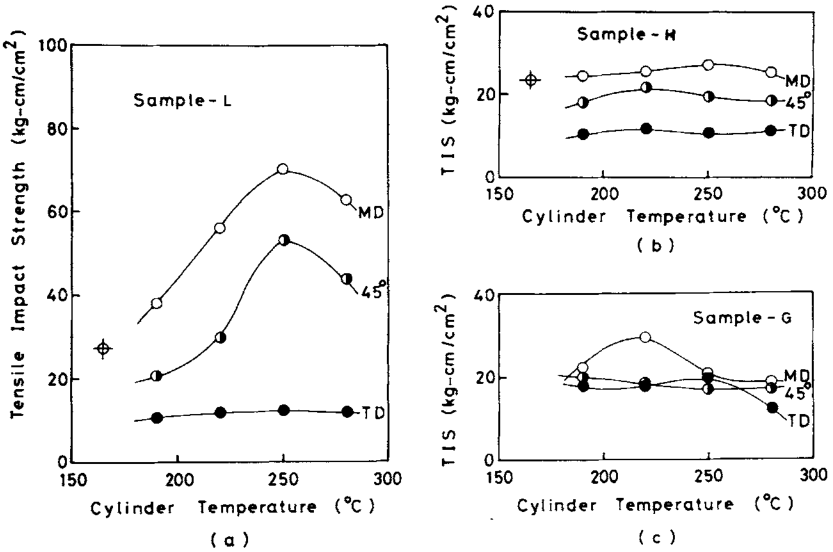


Fig. 15. Effect of cylinder temperatures on tensile impact strengths in various directions. Cross-marked points are for compression-molded materials: (a) L sample; (b) H sample; (c) G sample.

differ.) Consequently, in comparison with the usual anisotropic injection-molded article, the isotropic one may have higher impact strength in the TD though it may have lower impact strength in the MD and 45°-direction. In other words, it cannot be essential that the isotropic injection-molded article has higher impact strength than the usual anisotropic one. However, it seems to be safe to adopt the isotropic one since its impact strength in the TD is higher. For the injection-molded PP, as shown in Figure 15(a) and 15(b), it might be better to mold the MD as tough as possible, since the impact strength in the TD tends to increase with increase of the impact strength in the MD.

Flexural Property

Flexural Modulus. The effect of the cylinder temperatures on the flexural moduli in various directions for the L, H, and G samples is shown in Figure 16(a)–16(c), respectively. The order of the flexural moduli of the straight PP's is MD > TD > 45°; the 45°-direction is the lowest, as in the case of the tensile yield strength. This fact can be elucidated by the shear deformation in the skin layer, as in the case of the tensile yield strength.

The order of the flexural modulus of the FRPP is reasonably MD $\gg$ 45° > TD. The flexural modulus of the FRPP might be governed mainly by the orientation of glass fibers rather than by the molecular orientation or the higher order structure of base resin.

The flexural moduli of the straight PP's decrease in the MD and TD and slightly increase in the 45°-direction with increase in cylinder temperature. Since the flexural modulus in the 45°-direction decreases slightly with increase in cylinder temperature, it is of advantage to injection mold the straight PP's so that the skin layer is as thick as possible when the cylinder temperature is as low as possible. The flexural moduli of the G sample vary irregularly and in-

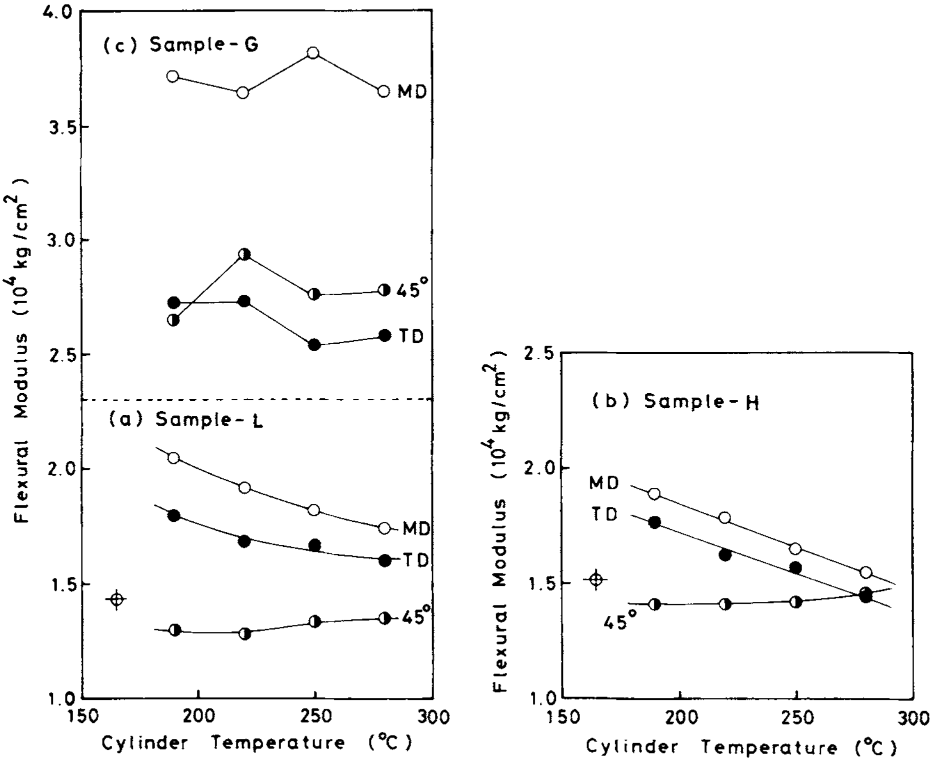


Fig. 16. Effect of cylinder temperatures on flexural moduli in various directions. Cross-marked points are for compression-molded materials: (a) L sample; (b) H sample; (c) G sample.

dependently with cylinder temperature. The reduction of the flexural modulus which originates in the decrease of the molecular orientation caused by the increase in cylinder temperature and the reduction of the flexural modulus caused by the decrease in injection pressure may balance the increase of the flexural modulus which originates in the increase in glass fiber orientation caused by the increase in cylinder temperature.

In comparison with the compression-molded PP, which is regarded as an isotropic sample, the flexural modulus of the injection-molded PP is slightly lower in the 45°-direction.

Finally, flexural moduli of the resins will be compared with one another. As for the flexural moduli of the L sample and the H sample, both being stlatter is higher in the 45°-direction. This is probably so because the L sample possesses a thicker skin layer than the H sample. The skin layer shows higher flexural modulus in the MD and TD and a lower one in the 45°-direction than the core layer (*vide infra*). As for the flexural moduli of the straight PP and FRPP, the latter is higher than the former in all directions. The discrepancy is most noticeable in the MD.

Flexural Strength. The effect of the cylinder temperatures on the flexural strengths in various directions for the L, H, and G samples is shown in Figure 17(a)–17(c), respectively. The order of the flexural strengths of the straight PP's is TD $\gtrsim$ MD $\gg$ 45°; the 45°-direction is by far lowest. The fact that the flexural

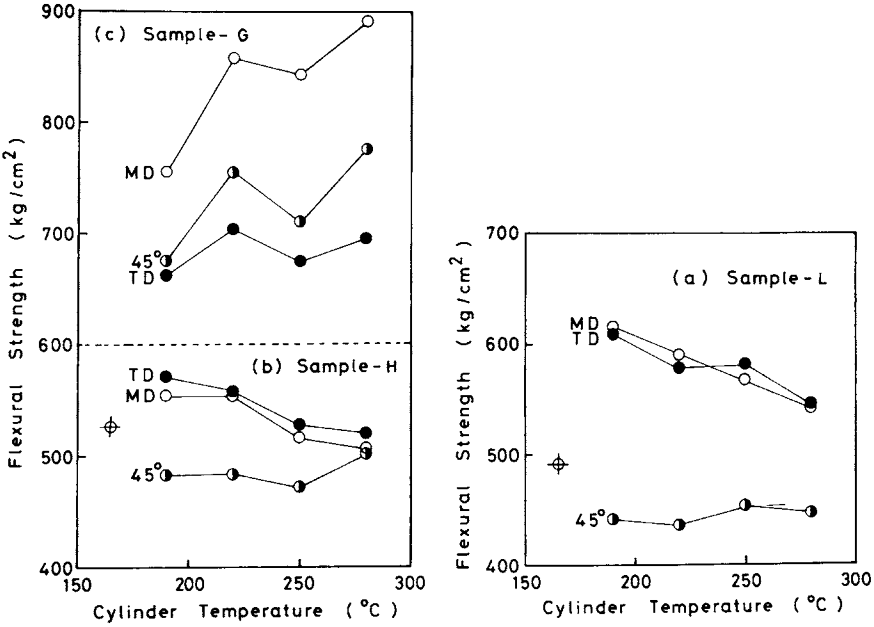


Fig. 17. Effect of cylinder temperatures on flexural strengths in various directions. Cross-marked points are for compression-molded materials: (a) L sample; (b) H sample; (c) G sample.

strength is the lowest in the 45°-direction is ascribed to the shear deformation in the skin layer as in the case of the tensile yield strength. The reason why the flexural strength in the MD is nearly equal to that in the TD and is by far the lowest in the 45°-direction is not known.

The flexural strength decreases with increase in cylinder temperature in the MD and TD, and is almost independent of the cylinder temperature or slightly increases with increase in cylinder temperature in the 45°-direction. Since the thickness of the skin layer decreases with increase in cylinder temperature, as shown in Figure 4, it is assumed that the flexural strength of the skin layer is higher than that of the core layer in the MD and TD, and the latter is higher in the 45°-direction. The details will be discussed later.

The flexural strength in the 45°-direction of the injection-molded sample is lower than that of the compression-molded one. This may be explained by the fact that the flexural strength in the 45°-direction of the skin layer is lower than that of the core layer, which is composed of spherulites as in the compression-molded one.

As for the flexural strengths of the L sample and the H sample, the former is higher than the latter in the MD and TD, while the latter is higher in the 45°-direction. This is because the L sample possesses a thicker skin layer than the H sample.

The order of the flexural strength of the G sample is MD > 45° > TD, which is a reasonable tendency, as in the case of the tensile yield strength. The flexural strength of the G sample increases with increase in cylinder temperature, which is probably because the orientation of glass fibers increases with increase in cylinder temperature. The flexural strength of the G sample varies irregularly with cylinder temperature. This is due to the variation of the injection pressure.

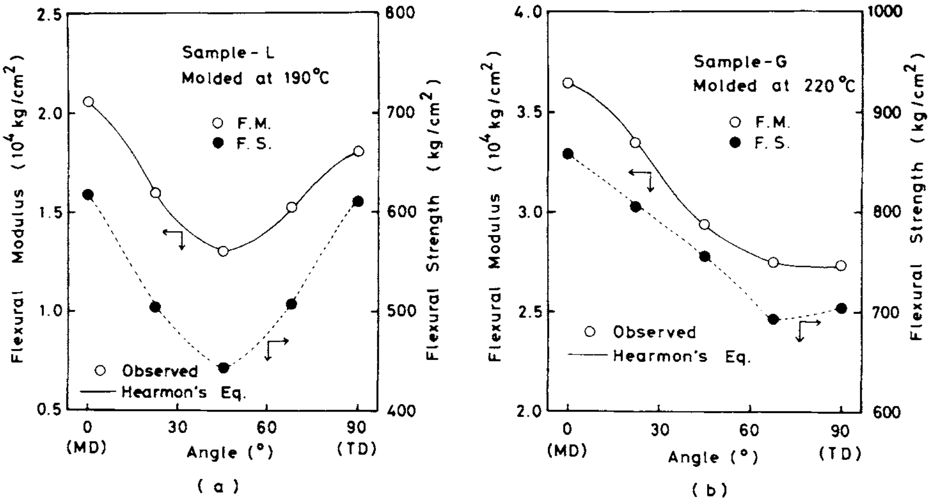


Fig. 18. Variations of flexural moduli and flexural strengths with the angle to the MD: (a) L sample molded at 190°C; (b) G sample molded at 220°C.

Variations of Flexural Modulus and Flexural Strength with Angle

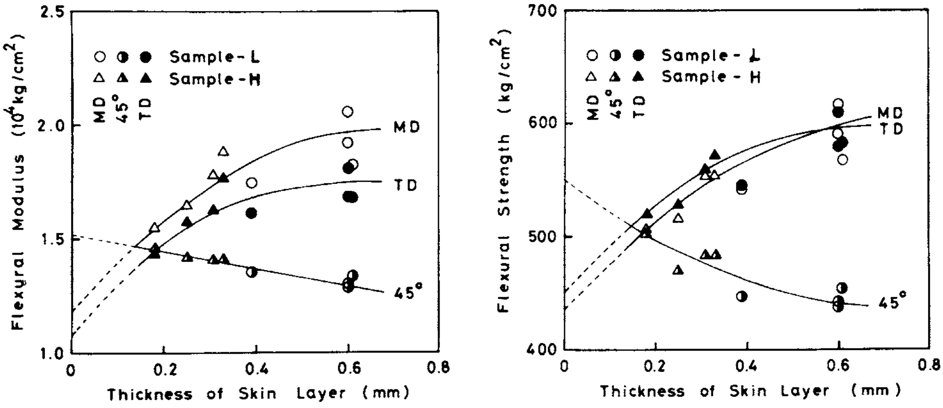
The variations of the flexural moduli and flexural strengths of the L sample and the G sample with the angle to the MD are shown in Figure 18(a) and 18(b) respectively. The flexural modulus and flexural strength show a similar tendency together. Both the flexural modulus and flexural strength of the L sample show minima in the 45°-direction, while those of the G sample gradually decrease in a reverse S-shape with increase in the angle.

According to Hearmon,[19] the tensile modulus E_θ, at arbitrary angle θ, of the material of uniform anisotropy can be calculated from the tensile moduli E_0, E_{45}, and E_{90} in the 0°-, 45°- and 90°-directions through eq. (5):

$$\frac{1}{E_\theta} = \frac{\cos^4\theta}{E_0} + \frac{\sin^4\theta}{E_{90}} + \left(\frac{4}{E_{45}} - \frac{1}{E_0} - \frac{1}{E_{90}}\right) \sin^2\theta \cos^2\theta \tag{5}$$

Although it may not be proper to apply eq. (5) to an injection-molded article since it gets a skin/core morphology and/or the orientation of glass fibers is not uniform in the FRPP, we try to apply eq. (5) to the injection-molded PP. The variations of E_θ values with θ, calculated by eq. (5) for the L sample molded at 190°C and G sample molded at 220°C, are shown by solid lines in Figure 18(a) and 18(b), respectively. The calculated values fit fairly well with experimental ones. Since in the injection-molded article (like the injection-molded plate with the film gate as in this work) anisotropy is regarded uniform in the lengthwise direction, while it is not uniform thicknesswise, eq. (5) seems to be meaningful.

Relations Between Flexural Modulus or Flexural Strength and Thickness of the Skin Layer. The relations between the flexural moduli in various directions and the thickness of the skin layer are shown in Figure 19(a). The flexural modulus increases with increase in thickness of the skin layer in the MD and TD, and it decreases with increase in the thickness of the skin layer in the 45°-direction. This fact indicates that the flexural modulus of the skin layer is higher than that of the core layer in the MD and TD, while the latter is



(a) (b)

Fig. 19. (a) Relations between flexural moduli in various directions and thickness of the skin layer. (b) Relations between flexural strengths in various directions and thickness of the skin layer.

higher in the 45°-direction. The flexural modulus of the core layer, which is obtained by extrapolating the thickness of the skin layer to zero, is different among in the MD, 45°-direction, and TD. The reason for this discrepancy is not obvious. Since in the 45°-direction the relation between the flexural modulus and the thickness of the skin layer is linear and the scattering of the points is small, extrapolation can be carried out with considerably high precision. The flexural modulus of the core layer, obtained in this way, is ca. 15000 kg/cm^2, which is nearly equal to that of the compression-molded specimen [cf. Fig. 16(a) and 16(b)]. On the contrary, since in the MD and TD the points scatter considerably, extrapolation is inaccurate.

The relations between the flexural strengths in various directions and the thickness of the skin layer are shown in Figure 19(b). As the flexural modulus, the flexural strength increases with increase in the thickness of the skin layer in the MD and TD and decreases with increase in the thickness of the skin layer in the 45°-direction. These facts indicate that the flexural strength of the skin layer is higher than that of the core layer in the MD and TD and the latter is higher in the 45°-direction. This is in contrast to the fact that the tensile yield strength of the skin layer is higher than that of the core layer also in the 45°-direction, though the reason is not obvious.

CONCLUSIONS

The anisotropies of the tensile property, tensile impact strength, and flexural property of injection-molded PP were studied. The results are summarized in Table III.

TABLE III
Anisotropies of Tensile Property, Tensile Impact Strength, and Flexural Property

Property	Straight PP	FRPP
Yield strength	MD ≫ TD > 45°	MD > 45° > TD
Necking stress	MD > 45° > TD	—
Tensile impact strength	MD > 45° > TD	MD > 45° > TD
Flexural modulus	MD > TD > 45°	MD ≫ 45° > TD
Flexural strength	TD ≳ MD ≫ 45°	MD > 45° > TD

The orders of the yield strength, tensile impact strength, flexural modulus, and flexural strength of the FRPP were MD > 45° > TD, which were reasonable tendencies. On the other hand, the orders of the yield strength and flexural modulus of the straight PP were MD > TD > 45°; the 45°-direction was the lowest. This seems to be due to the shear deformation between the lamellae in the skin layer. The order of the necking stress of the straight PP was MD > 45° > TD. This is probably so because the lamellae in the skin layer are perpendicular to the MD. The unfolding of the lamellae becomes difficult in the same order. Regardless of the *MFI* of the resin, the yield strengths and necking stresses in various directions were respectively in a linear relationship with the thickness of the skin layer, having positive slopes and the same zero intercepts. The variation of the flexural modulus with the angle to the MD fitted well to Hearmon's equation. The degree of the anisotropies of various properties for the straight PP generally became higher as the *MFI* and cylinder temperature became lower, or as the skin layer became thicker. On the other hand, for the FRPP, it generally became higher as the cylinder temperature became higher, or as the degree of the orientation of glass fibers became higher.

The authors would like to thank the Tokuyama Soda Co., Ltd., for permission to publish this paper.

References

1. Y. Ito, *Kobunshi Kagaku,* **18,** 220 (1961).
2. G. Rauman and D. W. Saunders, *Proc. Phys. Soc. (London),* **77,** 1028 (1961).
3. G. Rauman, *Brit. J. Appl. Phys.,* **14,** 795 (1963).
4. V. S. Kim and A. N. Levin, *Sov. Plast.,* **3,** 52 (1966).
5. M. Takayanagi, K. Imada, and T. Kajiyama, *J. Polym. Sci. C,* **no. 15,** 263 (1966).
6. V. B. Gupta and I. M. Ward, *J. Macromol. Sci., Phys.,* **B1,** 373 (1967).
7. V. B. Gupta, A. Keller, and I. M. Ward, *J. Macromol. Sci., Phys.,* **B2,** 139 (1968).
8. V. B. Gupta and I. M. Ward, *J. Macromol. Sci., Phys.,* **B2,** 89 (1968).
9. Z. H. Stachurski and I. M. Ward, *J. Polym. Sci. A-2,* **6,** 1083 (1968).
10. Z. H. Stachurski and I. M. Ward, *J. Polym. Sci. A-2,* **6,** 1817 (1968).
11. Z. H. Stachurski and I. M. Ward, *J. Macromol. Sci., Phys.,* **B3,** 445 (1968).
12. W. W. Darlington and D. W. Saunders, *J. Macromol. Sci. Phys.,* **B5,** 207 (1971).
13. G. R. Davies, A. J. Owen, I. M. Ward, and V. B. Gupta, *J. Macromol. Sci., Phys.,* **B6,** 215 (1972).
14. A. J. Owen and I. M. Ward, *J. Macromol. Sci., Phys.,* **B7,** 279 (1973).
15. H. Awaya and T. Isobe, *Kobunshi Kagaku,* **29,** 196 (1972).
16. G. B. Jackson and R. L. Ballman, *SPE J.,* 1147 (Oct. 1960).
17. R. M. Ogorkiewicz and G. W. Wiedmann, *Plastics & Polymers,* 337 (Dec. 1971).
18. J. Krebs, *Kunststoffe,* **60,** 185 (1970).
19. R. F. S. Hearmon, *An Introduction to Applied Anisotropic Elasticity,* Oxford University Press, London, 1961.
20. M. Fujiyama, *Kobunshi Ronbunshu,* **32,** 411 (1975).
21. M. Fujiyama and S. Kimura, *Kobunshi Ronbunshu,* **32,** 581 (1975).
22. M. Fujiyama and S. Kimura, *Kobunshi Ronbunshu,* **32,** 591 (1975).
23. M. Kojima, *Kobunshi Kagaku,* **25,** 276 (1968).
24. N. Kasai, S. Fujiwara, S. Morioka, H. Kurose, M. Kakudo, and T. Watase, *Kogyo Kagaku Zasshi,* **64,** 55 (1961).

Received November 10, 1975
Revised October 15, 1976