Biaxially Self-Reinforced High-Density Polyethylene Prepared by Dynamic Packing Injection Molding. I. Processing Parameters and Mechanical Properties

Jun Lei,[1] Chaodong Jiang,[1] Kaizhi Shen[1,2]

[1]*College of Polymer Science and Engineering, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China*
[2]*Key Laboratory of Polymer Engineering, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China*

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ABSTRACT: Uniaxial oscillating stress field by dynamic packing injection molding (DPIM) is well established as a means of producing uniaxially self-reinforced polyethylene and polypropylene. Here, the effects on the mechanical properties of high-density polyethylene (HDPE) in both flow direction (MD) and transverse direction (TD) of packing modules and processing parameters in DPIM are described. Both biaxially and uniaxially self-reinforced HDPE samples are obtained by uniaxial shear injection molding. The most remarkable biaxially self-reinforced HDPE specimens show a 42% increase of the tensile strength in both MD and TD. The difference of stress–strain behavior and impact strength between MD and TD for the DPIM moldings indicates the asymmetry of microstructure in the two directions.
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Key words: reinforcement; polyethylene (PE); injection molding; mechanical properties; dynamic packing

INTRODUCTION

There have been several methods used to attain self-reinforcement of polyolefin through the injection molding process. High-pressure injection molding was investigated by Kubát and coworkers,[1,2] and elongational flow injection molding was carried out by Bayer et al.[3–5] High-modulus, high-strength polyethylenes were produced in both cases.

An alternative method is dynamic packing injection molding (DPIM), which was originated by Allan and Bevis et al.[6–9] Contrary to static packing injection molding (SPIM) (i.e., conventional injection molding), DPIM exerts reciprocal packing pressure to the polymer melt, forcing it to flow back and forth through the cavity before solidification. Well-controlled stress and temperature fields are produced, which helps to induce and solidify preferable orientation of crystals and molecules and realize self-reinforcement of polymer. Until now, there are considerable reports on attaining uniaxial self-reinforcment by using DPIM. Self-reinforced isotactic polypropylene (iPP) and copolymer of ethylene and propylene (P/E) were obtained by Bevis et al.[6–9] and self-reinforced high-density polyethylene (HDPE), low-density polyethylene (LDPE) and composite of HDPE and PP were developed by Shen et al.[10–13]

The idea of attaining biaxial self-reinforcement of HDPE by uniaxial stress field was stimulated by the work of Bashir and Odell[14,15] Elongational flow field by capillary extrusion was used to produce thick oriented PE filaments. The filament attained 1.2 GPa strength and did not splinter, which was unusual because normally a uniaxially oriented polymer will splinter if the filament is thick. This implied that the filament was self-reinforced in both flow direction (MD) and transverse direction (TD). After carrying out extensive studies on the morphology of high modulus PE filaments, they attributed biaxial self-reinforcement to the existence of interlocking shish kebab morphology, which is schematically shown in Figure 1. Crack propagation in the transverse direction is arrested by the fibrils, while, in the longitudinal direction, it is difficult for a crack to thread its way through the intermeshing lamellae. They expected that a wide sheet-formed specimen would have good mechanical properties in both MD and TD if such a morphology was established in it.[15] Based on the above-mentioned research results, the authors designed the dynamic packing injection molding device and successfully realized biaxial self-reinforcement of sheet-formed HDPE through uniaxial oscillating stress field by the mold.

Correspondence to: K. Shen (leijun10@263.net).

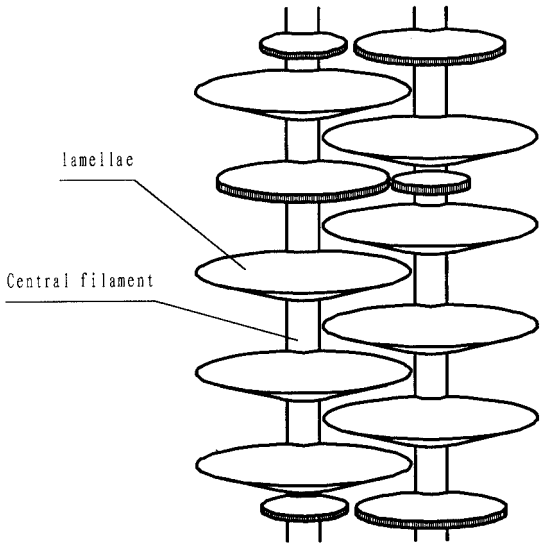

Figure 1 Schematic diagram of the interlocking shish kebabs (reproduced from López Cabarcos et al.[4]).

EXPERIMENTAL

Materials

The material used in this work was HDPE (grade 7006A) with a flow index of 6.8 g/10 min produced by Qilu Petrochemical Corp.

Dynamic packing injection molding (DPIM) device

The principle of the DPIM technique is similar to that of SCORIM originated by Bevis and Allan. It is a pilot hot-runner mold consisting of two parts (Fig. 2)–one double live-feed device with two hydrodriven pistons to keep the polymer in the melting state and to pack the polymer melt in a preferred mode and one molding unit to shape the specimen. To measure the mechanical properties in both MD and TD, the specimen is designed to be a 60 × 60 × 4 mm thin square plate with two thickened fan gates (Fig. 3). The thick fan gates are used to induce elongational flow within the transitional zones from the gates to the cavity, to ensure enough packing time before solidification of the plate, and to guarantee uniform flow distribution along the TD. The thin square plate form of the cavity helps to induce considerable macroshear strain rate within the cavity and also contributes to the uniform velocity distribution along the TD. Two pressure transducers are located to the ends of the cavity to monitor the cavity pressure.

DPIM and static packing injection molding (SPIM)

Two basic packing modes used to process two groups of comparative samples, namely DPIM mode and SPIM mode, are shown schematically in Figure 2. Although the procedures of DPIM and SPIM were described in our previous papers,[16–20] here, we would like to recapitulate them to give a comprehensive view of our work. The procedure of DPIM is as follows:

1. the pistons are set backward initially;
2. the cavity is filled with melt from the gates;
3. the pistons reciprocate in their respective chambers with a phase difference of 180°, according to the predetermined oscillating frequencies;
4. after the solidification of the plate, the mold is opened and the specimen is ejected.

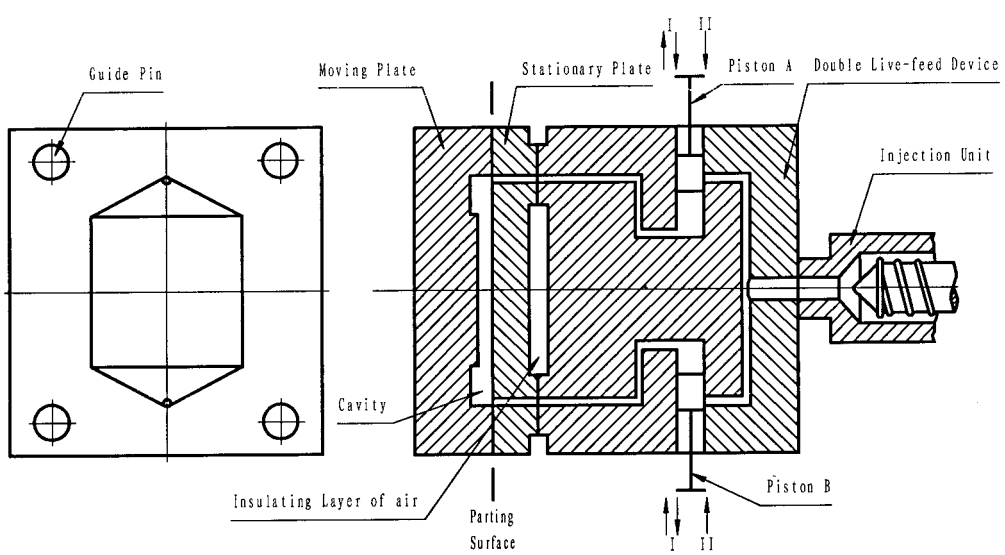

Figure 2 Device for DPIM (I. two pistons reciprocate with a difference of 180°) and SPIM (II. two pistons push forward simultaneously).

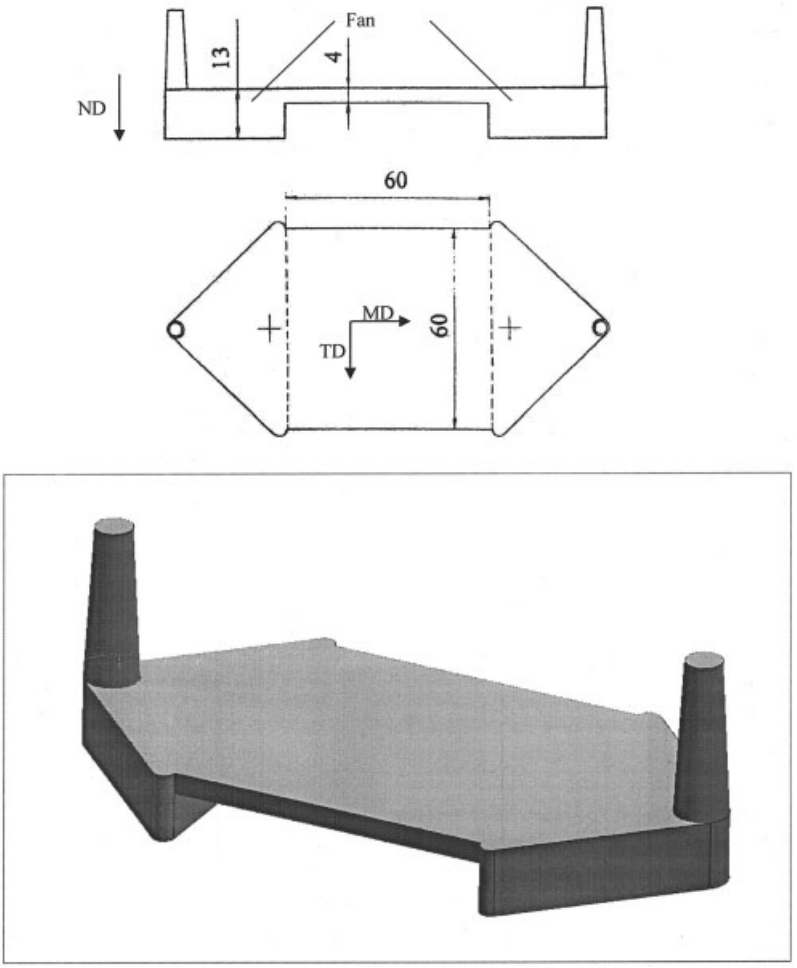

Figure 3 Outline of the square plate specimen. The dimensions are in millimeters. The locations of the two pressure transducers are indicated by the cross marks.

In contrast to DPIM, step 3 in SPIM is different–the pistons are activated by a static pressure, and thus they push forward simultaneously rather than reciprocate. Obviously, the procedure of SPIM is similar to that of conventional injection molding (CIM) and SPIM samples can therefore be used as comparative samples of DPIM ones. This viewpoint can also be supported by the similarity between cavity pressure curves of SPIM process [Fig. 4(a)] and CIM process.

According to Bassett's work, shear rate, melt temperature, cooling time, and temperature are critical factors in deciding the morphology of shear-induced shish kebab.[21–25] Bashir and Odell[14] regarded the presence of longitudinal and transverse velocity gradients, the strain rate, the strain time, and the temperature of the flow as important parameters to extend the chains by the flow.

Apparently, four parameters in DPIM process, the packing pressure, the melt temperature, the mold temperature, and the packing frequency, are decisive factors to determine the morphology of the flow-induced shish kebab. For the SPIM process, the former three are critical.

Preparation of specimens

The processing parameters for selected SPIM and DPIM samples are listed in Tables I and II, respec-

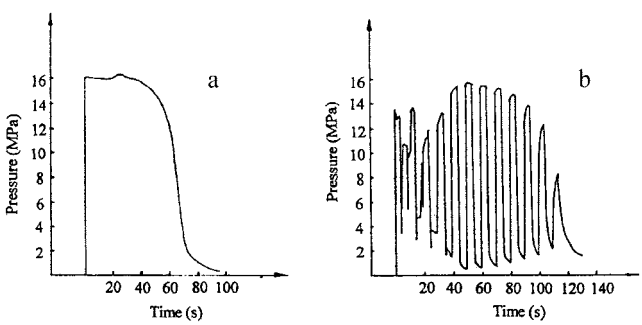

Figure 4 Cavity pressure curves of (a) static packing mode and (b) dynamic packing mode.

TABLE I
Processing Parameters of SPIM

Sample no.	Melt temperature (°C)	Mold temperature (°C)	Packing pressure (MPa)
SPIM-1	140	40	25
SPIM-2	140	60	28
SPIM-3	180	40	28
SPIM-4	180	60	28
SPIM-5	140	40	28

tively. To compare the properties of SPIM and DPIM, the SPIM and DPIM samples with the same sequence number have the same melt temperature, mold temperature, and packing pressure.

Tensile testing

Square plates (60 × 60 × 4 mm) were obtained after cutting off the fan gates of SPIM and DPIM moldings. The tensile test specimens were prepared by machining the plates into 60 × 10 × 4 mm bars along MD and TD, respectively (shown in Fig. 5). The SHIMADZU Universal Testing Machine (Model AG-10) was used to measure the tensile strength and stiffness (the slope of the proportional part of the stress–strain curve) at a room temperature of 23°C. The crosshead speed was 50 mm/min.

Impact testing

The SPIM and DPIM (in MD and TD) impact testing specimens were obtained by machining the plates into 60 × 10 × 4 mm bars along MD and TD (also shown by Fig. 5) and notching the bars with a single-tooth cutter according to GB/T1043–1993. A Charpy-type impact machine was employed to measure the impact strength of SPIM and DPIM specimens at room temperature (23°C). The impact speed was 2.9 m/s.

RESULTS AND DISCUSSION

The tensile and impact testing results for SPIM and DPIM samples are shown in Tables III and IV, respectively.

As expected, the DPIM process has a remarkable self-reinforcement effect on the tensile strength of HDPE in MD. Each DPIM sample has much higher tensile strength in MD than that of the SPIM sample having the same sequence number. More importantly, biaxial self-reinforcement of HDPE was realized under uniaxial flow field. The tensile strengths in both MD and TD of DPIM-1, DPIM-2, and DPIM-3 are much higher than those of SPIM-1, SPIM-2, and SPIM-3, respectively. Thus, they are named as biaxially self-reinforced samples. Among them, DPIM-1 has the most notable biaxial self-reinforcement effect, whose tensile strengths in both directions are about 44% higher than those of SPIM-1. In contrast, DPIM-4 and DPIM-5 show a striking increase (about 100%) over SPIM-4 and SPIM-5 in tensile strength along MD, but exhibit a substantial reduction (about 10–20%) in tensile strength along TD. Samples of this kind are called uniaxially self-reinforced samples.

In Tables III and IV, the stiffness refers to the slope of the proportional part in the stress–strain curve during tensile testing. The DPIM samples exhibit 20–30% higher stiffness than the SPIM ones, either in MD or TD. Also, DPIM samples have a much lower strain at break than SPIM ones, especially in TD (Fig. 6). This suggests that DPIM samples break in a brittle manner, whereas SPIM samples are ductile.

As for impact property, the DPIM samples have a 1 time higher value of impact strength in MD but 50% lower values of impact strength in TD compared with the SPIM samples. The SPIM samples have approximately equal impact strength values in TD and MD, whereas for the DPIM ones, the impact strength in MD is 2.4–7 times that in TD.

The self-reinforcement effect of DPIM samples is mainly due to the existence of stress-induced crystallization and molecular orientation. Figure 7 (based on the observation of cross section of DPIM moldings) shows the typical cross section freezing-off contours of biaxially self-reinforced moldings and uniaxially self-reinforced moldings. For either uniaxially self-reinforced or biaxially self-reinforced moldings, a multilayered structure has been formed due to their repeated packing and cooling stages during preparation. On the contrary, the nonreinforced moldings prepared by CIM or SPIM have no multilayered structure owing to its packing and cooling character. Obviously, during the packing stage of DPIM moldings, the melt flows reciprocally through a shrinking channel, different from a basically constant flow channel in the SPIM process. Thus, the elongational and shearing strain rates within the DPIM moldings are substantially higher than those within the SPIM moldings, especially in the center of the cross section. As a result, the stress-induced crystallization and orientation effect is more notable in DPIM moldings. Further-

TABLE II
Processing Parameters of DPIM

Sample no.	Melt temperature (°C)	Mold temperature (°C)	Packing pressure (MPa)	Oscillating frequency (Hz)
DPIM-1	140	40	25	0.2
DPIM-2	140	60	28	0.2
DPIM-3	180	40	28	0.2
DPIM-4	180	60	28	0.2
DPIM-5	140	40	28	0.5

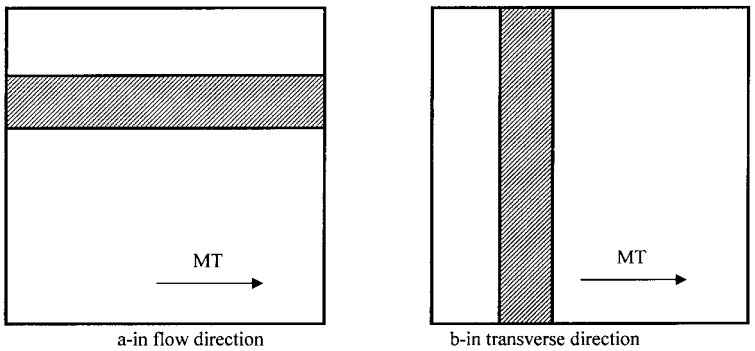

Figure 5 Preparation of specimens for tensile testing.

more, the flow channel of uniaxially self-reinforced moldings shrinks more rapidly but less uniformly along than that of biaxially self-reinforced moldings. This explains the higher tensile strengths in MD but lower tensile strengths in TD of uniaxially self-reinforced samples compared with those of biaxially self-reinforced moldings. Apparently, the uniformly distributed freezing-off process plays an important role in producing biaxially self-reinforced moldings with enhanced tensile strengths along both MD and TD.

As mentioned above, DPIM technology could produce both uniaxially and biaxially self-reinforced moldings. But whether to obtain the former or the latter depends on the processing conditions. By analyzing the processing parameters (Table II) and the corresponding mechanical properties (Table IV) of the samples, it can be found that higher melt temperature, mold temperature, and packing pressure tends to produce uniaxially self-reinforced samples (i.e., DPIM-4 and DPIM-5). In such cases, the viscosity of the melt is lower and the elongational and shearing rates of melt are higher. Thus, the flow velocity distribution along TD is highly uneven–the MD flow velocity near the centerline is much higher than that near the borders, as a result, the cross sections of the moldings shrink much more quickly in TD than in MD. This makes the core region much more highly oriented than the outer region. Furthermore, the formed shish kebab morphology has a higher percentage of extended-chain crystals and less that of chain-folded platelets. Obviously, this structure reinforces MD properties intensively but impairs TD properties. On the other hand, biaxially self-reinforced moldings (i.e., DPIM-1, DPIM-2, and DPIM-3) are generally obtained under moderate melt temperature, mold temperature, and packing pressure. Moderate viscosity and elongational and shearing rates result in uniformly distributed temperature and stress fields, causing evenly distributed freezing speed along TD. The extended-chain crystals and tapering chain-folded platelets grow in a rational way and interlocking shish kebab morphology structures are formed (refer to our next paper for the characterization of this morphology).

Another noticeable trait of DPIM moldings is anisotropy. It can be seen from Figures 6(c and d) and Table III that the SPIM moldings are basically isotropic. They have approximately equal tensile strengths, stiffness, and impact strengths along MD and TD. The samples along both directions fail in a typical plastic way during tensile tests. There are distinguished yielding and necking processes during the tensile tests and the strains at break are more than 200%. Nevertheless the situation is different for DPIM moldings; even samples having nearly the same strengths along MD and TD such as DPIM-1 are not essentially isotropic. First, DPIM tensile samples have the typical brittle failure in TD with an elongation of 10% and a ductile failure (failure between brittle failure and plastic fail-

TABLE III
Mechanical Properties of SPIM Specimens

Specimen no.	Tensile strength (MPa)		Stiffness (MPa)		Impact Strength (kJ/m^2)	
	MD	TD	MD	TD	MD	TD
SPIM-1	25.2	25.4	—	—	5.6	5.8
SPIM-2	29.1	30.0	—	—	5.4	5.1
SPIM-3	28.8	28.0	419	447	5.9	5.4
SPIM-4	24.3	29.3	393	499	5.7	5.3
SPIM-5	26.6	27.1	438	408	5.6	5.8

TABLE IV
Mechanical Properties of DPIM Specimens

Specimen no.	Tensile strength (MPa)		Stiffness (MPa)		Impact strength (kJ/m^2)	
	MD	TD	MD	TD	MD	TD
DPIM-1	35.9	35.9	—	—	8.1	3.4
DPIM-2	41.4	35.0	496	598	13.9	2.0
DPIM-3	39.2	35.0	552	576	13.2	1.8
DPIM-4	56.3	22.6	588	605	9.0	1.5
DPIM-5	48.5	24.2	534	631	9.3	1.6

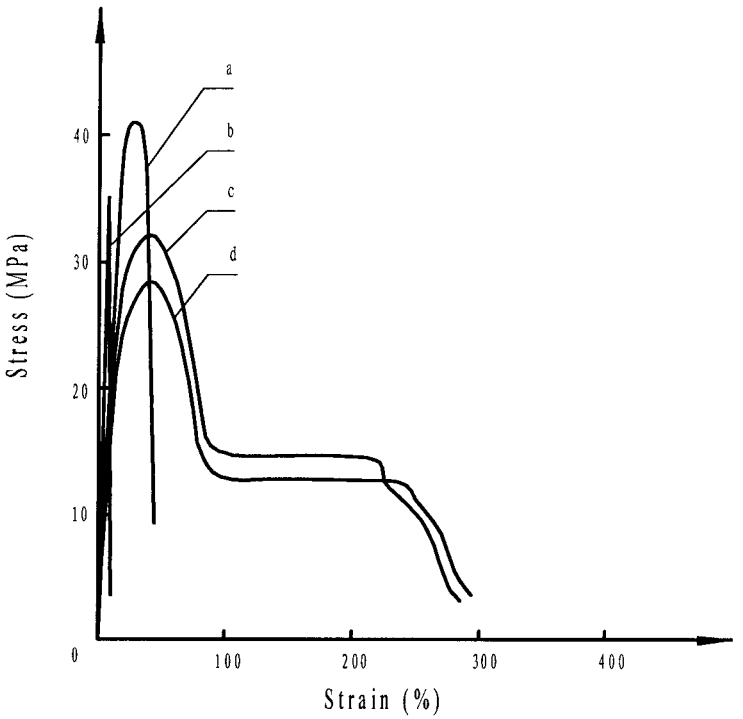

Figure 6 (a) Stress–strain curves for dynamic packing moldings (DPIM-2) in MD, (b) dynamic packing moldings (DPIM-2) in TD, (c) static packing moldings (SPIM-2) in TD, and (d) static packing molding (SPIM-2) in MD.

ure) in MD, with an elongation of 50% and inconspicuous yielding and necking processes. Second, the anisotropy of DPIM samples can also be reflected from the obvious difference between impact strengths along MD and TD. Table IV shows that for DPIM samples the impact strength in MD is two to six times that in TD. So it is a significant study to improve on the devices for producing moldings with almost equally high strength. The anisotropic structure is caused by orientation of molecules and crystals in MD, which can be seen in detail in our next paper.

CONCLUSION

The conclusion of this research can be summarized as follows:

1. By uniaxially oscillating injection molding, biaxially self-reinforced HDPE moldings can be produced, as well as uniaxially self-reinforced HDPE moldings. The tensile strengths in both MD and TD are enhanced remarkably for biaxially self-reinforced samples.
2. DPIM moldings have a multilayered structure due to repeated packing cycles [Fig. 4(b)]. Owing to moderate packing pressure and melt and mold temperatures, biaxially self-reinforced samples have well-distributed cross section freezing-off contours in TD; while cross section freezing-off contours of uniaxially self-reinforced samples shrink much more rapidly in TD than in ND, resulting from higher packing pressure and melt and mold temperatures.
3. Even though the biaxially self-reinforced samples have higher tensile strength in both MD and TD, they have different tensile failure modes and notably unbalanced impact strengths in the two directions. This characterization indicates that biaxially self-reinforced samples have anisotropic microstructure.

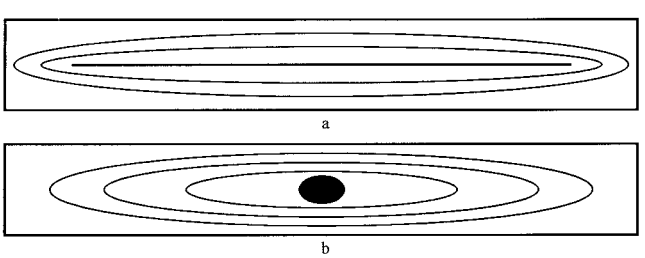

Figure 7 Cross section freezing-off contours of (a) biaxially self-reinforced samples and (b) uniaxially self-reinforced samples.

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