

# Construction of Pressure-resistance Polyethylene-based Pipes with Highly Biaxially Oriented Structure and Self-reinforcing Mechanism

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**Abstract** Fabrication of polyethylene (PE) pipe with significantly enhanced hoop strength and burst pressure is essential necessary for high transportation requirements. In this work, biaxially oriented PE/ultrahigh molecular weight polyethylene (PE/UHMWPE) blend pipes were fabricated on self-made pipe solid-phase die drawing apparatus. Due to formation of chain entanglement network and enhanced viscoelasticity, incorporation of UHMWPE chains improved stretchability and biaxial orientation degree of blend pipe. During die drawing, formation of more miscible blend system make long UHMWPE chains be sufficiently stretched under load, and such extended-chain conformation of UHMWPE acted as shish structure and induced short PE chains to array orderly and form kebab crystals. With increasing axial draw ratio, the lamellae remarkably deviated from hoop to axial direction, while the blend pipe exhibited higher crystallinity and orientation degree than that of PE pipe, presenting a more uniform and dense biaxial orientation structure with shish-kebab crystals. As a result, the blend pipe showed roughly 99% increase in tensile strength along hoop direction and 25% increase in burst pressure, respectively. Such biaxial self-reinforced PE/UHMWPE blend pipes exhibit promising application prospect as high-pressure transportation pipelines in civil engineering.

**Keywords** PE/UHMWPE blend pipe; Viscoelasticity; Solid-phase die drawing process; Biaxially oriented crystalline structure; Self-reinforcing mechanism

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## INTRODUCTION

In civil engineering, a large number of polymer pipes are widely applied in water supply and drainage, and gas transport of the building, while the mechanical strength and pressure resistance of pipes are the most issues of concern for satisfying the requirement on the pressurized natural gas and water. Polyethylene (PE100S) pipe resin with bimodal molecular weight distribution has been widely used to fabricate pipes owing to its excellent mechanical properties, long-term servicing stability and easy processability.<sup>[1–6]</sup> However, the commercially available PE100 pipes were difficult to meet high transportation requirements due to remarkable increase of transporting distances and pressure.<sup>[7–9]</sup> Therefore, fabrication of PE100 pipe with significantly enhanced mechanical property is essentially necessary.

For normal PE100 pipes, only axial orientation occurred, and axial strength of pipe was enhanced. However, the pressure that pipe can bear, is directly proportional to its hoop strength.<sup>[10]</sup> Therefore, it is essential to obtain biaxial orientation of PE pipes with biaxial enhanced mechanical strength,

especially hoop strength, while few literatures can be available on this issue.<sup>[11–14]</sup> Nie *et al.* prepared HDPE pipes by rotational extrusion, and found that shish-kebab crystal structure formed for pipe sample during processing, and the tensile strength along hoop direction increased by 10%.<sup>[11]</sup> Chen *et al.* fabricated HDPE pipes by vibration extrusion, exhibiting larger crystal sizes and perfect crystals for pipe sample under vibration force, causing 5.3% increase in hoop tensile strength.<sup>[12]</sup> Up to now, study on preparation of biaxially oriented PE pipes with improved mechanical performance along both hoop and axial direction was scarcely reported. Moreover, most biaxially oriented PE pipes were prepared in melt state, and orientation structure was not easily retained due to high mobility of molecular chains, leading to low orientation degree and enhancing efficiency.<sup>[12–15]</sup>

Solid-phase die drawing technology has been developed to obtain and maintain high molecular orientation for polymer pipes oriented in solid phase.<sup>[9,16]</sup> In process of die drawing, the pipe billet is heated to temperature below its melting point and then drawn through expanding die under axial load, which promoted formation of a high biaxial molecular orientation structure for pipe, leading to great enhancement on mechanical strength of pipe along both axial and hoop directions. Since large deformation for pipe wall is encountered during solid-phase processing, in order to avoid

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rupture of the pipe samples, moderately high molecular entanglement and enhanced melt viscoelasticity of the pipe samples are desired.<sup>[17,18]</sup>

Ultrahigh molecular weight polyethylene (UHMWPE) with extremely high molecular weight ( $>10^6$  g/mol) and massive entanglement showed outstanding mechanical performance, excellent fatigue and wear resistance.<sup>[19–24]</sup> In this work, firstly, due to similar molecular architecture, UHMWPE was introduced to fabricate PE/UHMWPE blend in order to improve molecular entanglement and viscoelasticity of PE, and an enhanced stretchability for the blend would be expected. The highly biaxially oriented PE/UHMWPE blend pipes were fabricated on self-made solid-phase die drawing apparatus for pipe, and thus the mechanical strength both along axial/hoop direction would be significantly enhanced. The evolution of the biaxially oriented crystalline structure of the pipe samples in presence or absence of UHMWPE was studied, and the self-reinforcing mechanism of the blend pipe was explored. Such biaxial self-reinforced PE/UHMWPE blend pipes exhibit promising application prospect as high-pressure transportation pipelines in civil engineering.

## EXPERIMENTAL

### Materials

Polyethylene (PE, 100S) was purchased from Jilin Petrochemical Company (China). UHMWPE with molecular weight of  $1.5 \times 10^6$ – $3.5 \times 10^6$  g/mol was purchased from Celanese Corporation (United States).

### Preparation of Biaxially Oriented PE/UHMWPE Blend Pipes

PE/UHMWPE blend pipe resin was prepared by extrusion under temperature of 200–230 °C and screw speed of 180 r/min. Then, the pipe resin was employed to fabricate pipes billet via extruder with a rotational speed of 150 r/min at 200–230 °C. Furthermore, the biaxially oriented PE/UHMWPE blend pipes were prepared. The pipe billets were put into pre-heater under 100–125 °C for 5–20 min, and then the billets were drawn through an expanding die at temperature of 110–125 °C, while the traction (drawing)/propulsion speed ratio was 1.5–2.5. After the desired pipe length was obtained, the pipe sample was cooled down to room temperature.

The draw ratio along axial direction ( $DR_{\text{axial}}$ ) is defined as ratio of cross-sectional area of the pipe billet ( $A_{\text{billet}}$ ) to that of the drawn pipe ( $A_{\text{product}}$ ):<sup>[25]</sup>

$$DR_{\text{axial}} = \frac{A_{\text{billet}}}{A_{\text{product}}} \quad (1)$$

The draw ratio along hoop direction ( $DR_{\text{hoop}}$ ) is defined as ratio of inner diameter of the drawn pipe ( $D_{\text{product}}$ ) to that of the pipe billet ( $D_{\text{billet}}$ ):<sup>[25]</sup>

$$DR_{\text{hoop}} = \frac{D_{\text{product}}}{D_{\text{billet}}} \quad (2)$$

$DR_{\text{axial}}/DR_{\text{hoop}}$  of the resultant biaxially oriented PE/UHMWPE blend pipes varied as follows: 1.1/1.8, 1.2/1.8, 1.3/1.8 and 1.5/1.8, which were designated as PE/UHMWPE-x, where x represented  $DR_{\text{axial}}$  of pipe samples, respectively, while the undrawn sample was designated as PE/UHMWPE-0. For comparison, the PE pipe samples in absence of UHMWPE with the

same  $DR_{\text{axial}}/DR_{\text{hoop}}$  were designated as PE-x.

### Measurements

Tensile strength of PE pipe samples was measured with 5567 universal material testing machine (USA) at room temperature according to ISO 6259-3-1997. The specimen was dumbbell shaped thin strip with the size of 60 mm × 20 mm × 2.5 mm, and 5 specimens were tested for each pipe sample. The tensile speed of 50 mm/min was applied. The burst pressure performance of pipe was tested with IPT 1443 hydrostatic pressure testing equipment (Germany) at 20 °C by following the standard of ISO1167-1-2006.<sup>[12,26,27]</sup> Five specimens with the size of 1000 mm in length, 90 mm in outer diameter and 2.5 mm in wall thickness were measured for each pipe sample.

Two-dimensional wide-angle X-ray diffraction (WAXD) analysis of PE pipe was conducted with D8 Discover X-ray diffractometer (Germany). The orientation factor ( $f$ ) was calculated with Herman's Eqs. (3) and (4):<sup>[28,29]</sup>

$$f = \frac{3 \langle \cos^2 \theta \rangle - 1}{2} \quad (3)$$

$$\langle \cos^2 \theta \rangle = \frac{\int_{\theta}^{\pi/2} I(\theta) \sin \theta \cos^2 \theta d\theta}{\int_{\theta}^{\pi/2} I(\theta) \sin \theta d\theta} \quad (4)$$

where  $I(\theta)$  is scattering intensity along angle  $\theta$ .

The crystallinity ( $X_c$ ) of PE pipe was calculated as the area ratio of diffraction of (110) and (200) planes to the whole diffraction of sample.

Two-dimensional small-angle X-ray scattering analysis of PE pipe was performed with Xeuss 2.0 system of Xenocs company (France). The long period ( $L_{\text{ac}}$ ) of lamellae was calculated from peak position ( $q_{\text{max}}$ ) of scattering intensity-vectors ( $I$ - $q$ ) curves (Fig. 1a) with Bragg's law:<sup>[9]</sup>

$$L_{\text{ac}} = 2\pi/q_{\text{max}} \quad (5)$$

Electron density correlation function  $K(z)$  (Eq. 6) was employed to investigate crystalline and amorphous regions of pipe samples:<sup>[30,31]</sup>

$$K(z) = \frac{\int_0^\infty I(q) q^2 \cos(qz) dq}{\int_0^\infty I(q) q^2 dq} \quad (6)$$

where  $z$  is perpendicular to drawing direction. In Fig. 1(b), the fitting line of the decline region of curves had an intersection with horizontal baseline of the minimum point, corresponding to amorphous layers thickness ( $L_a$ ) for pipe samples, and lamellae layers thickness ( $L_c$ ) was obtained by the relation  $L_c = L_{\text{ac}} - L_a$ .<sup>[30,31]</sup>

The lateral size of lamellae ( $L_{\text{lateral}}$ ) was derived from scattering intensity distribution ( $I(q_y)$ ) along  $q_y$  direction (Fig. 2), and obtained with Eq. (7):<sup>[32]</sup>

$$L_{\text{lateral}} = 2\pi/\Delta q_y \quad (7)$$

where  $\Delta q_y$  is half-height width of peak.

The morphologies of PE pipe were observed with JEOL JSM-5900LV microscope (Japan). The viscoelasticity was analyzed on AR 1500ex dynamic stress rheometer (USA) at 200 °C, while the average entanglement density ( $\nu_e$ ) was estimated with the following equations:<sup>[33]</sup>

$$\nu_e = \frac{\rho}{M_e} \quad (8)$$

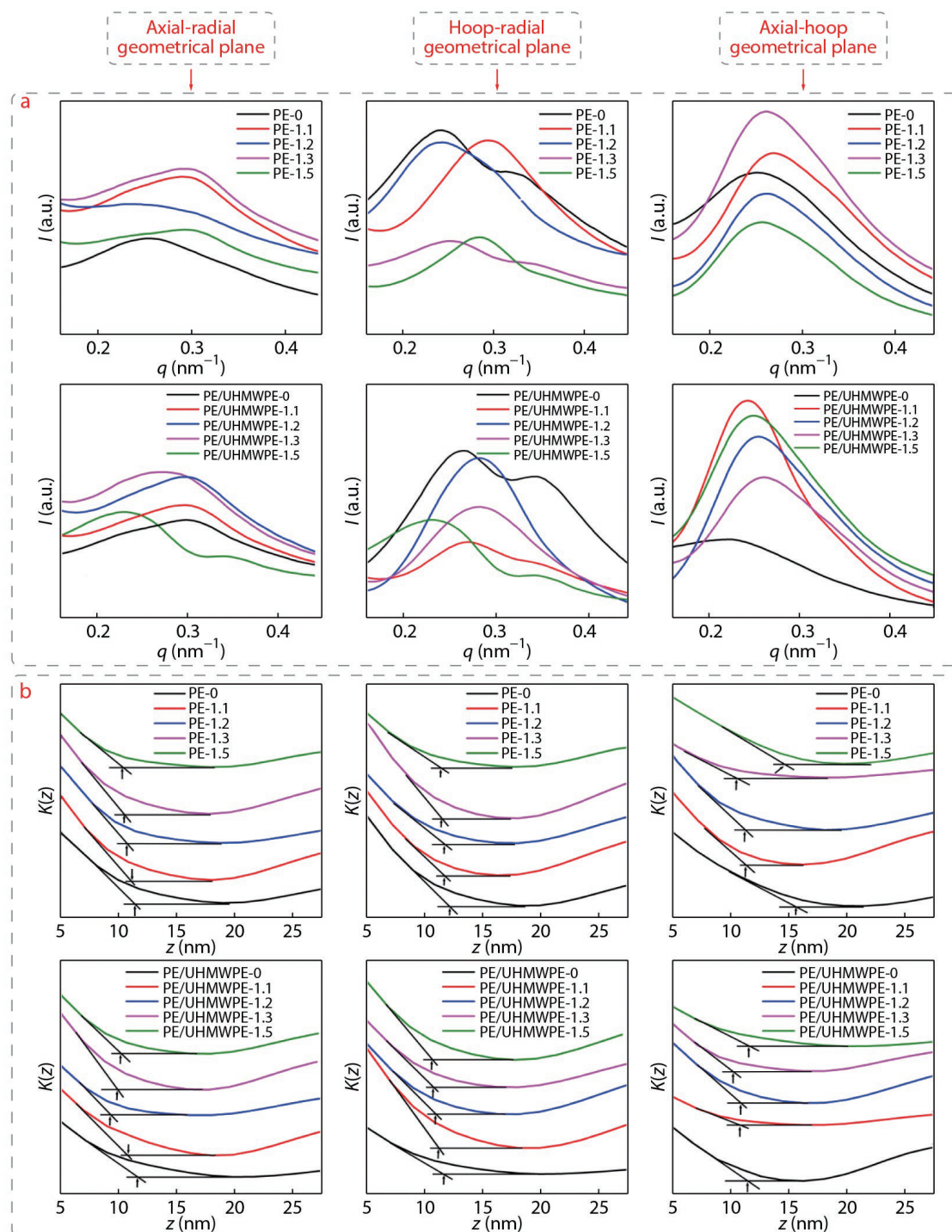


**Fig. 1** Scattering intensity-scattering vectors ( $I$ - $q$ ) curves (a) and electron density correlation function ( $K(z)$ ) curves (b) of PE and PE/UHMWPE blend pipe in different geometrical planes.

$$M_e = \frac{4\rho RT}{5G_N} \quad (9)$$

where  $M_e$  is average molecular weight between entanglements;  $G_N$  is plateau modulus;  $\rho$  is density of pipe;  $R$  is gas constant;  $T$  is absolute temperature.

## RESULTS AND DISCUSSION

### Construction of Biaxially Oriented PE/UHMWPE Blend Pipes and Highly Reinforcing Effect

Biaxially oriented PE and PE/UHMWPE blend pipes were fabricated on self-made pipe solid-phase die drawing apparatus of our group. As illustrated in Fig. 3, PE/UHMWPE blend pipe billets with inner diameter of 50 mm were put into the pre-

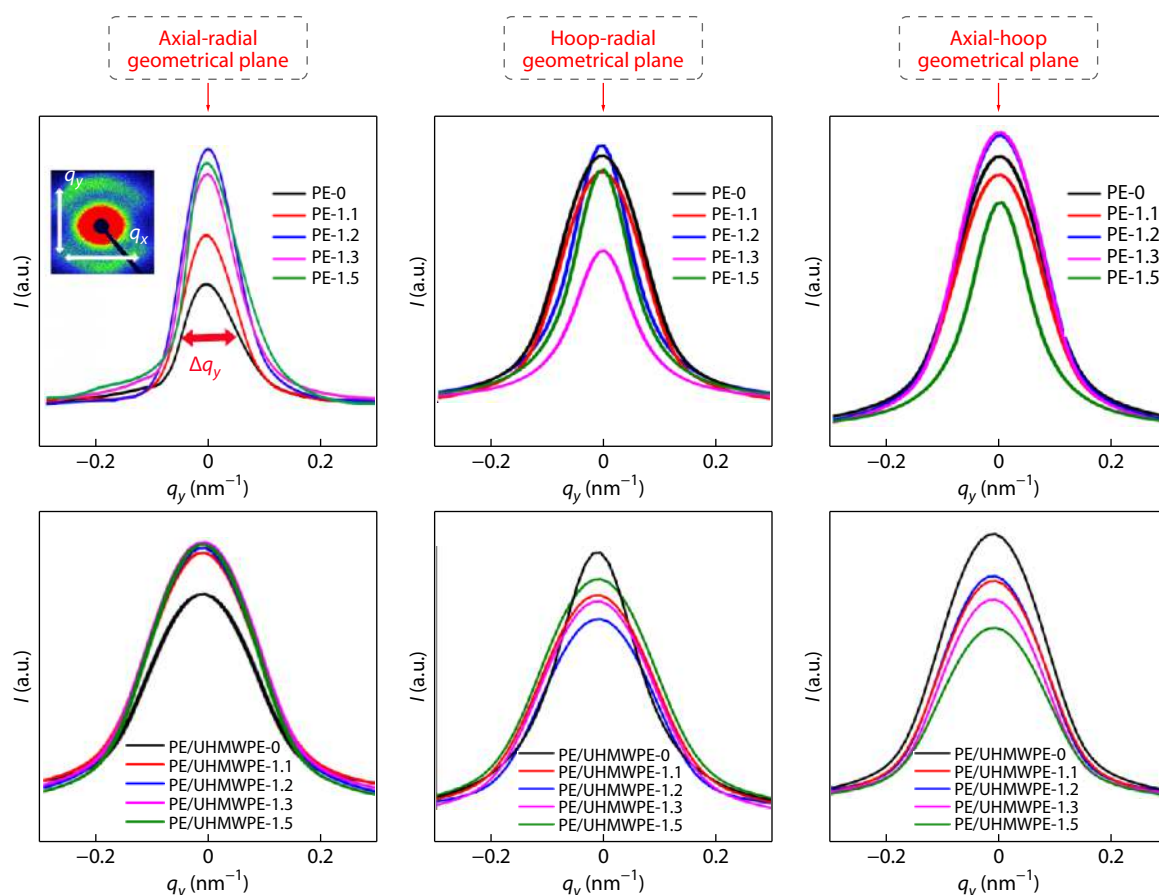


**Fig. 2** The azimuthal scan of the lamellar peaks along  $q_y$  of PE and PE/UHMWPE blend pipe samples in different geometrical planes.

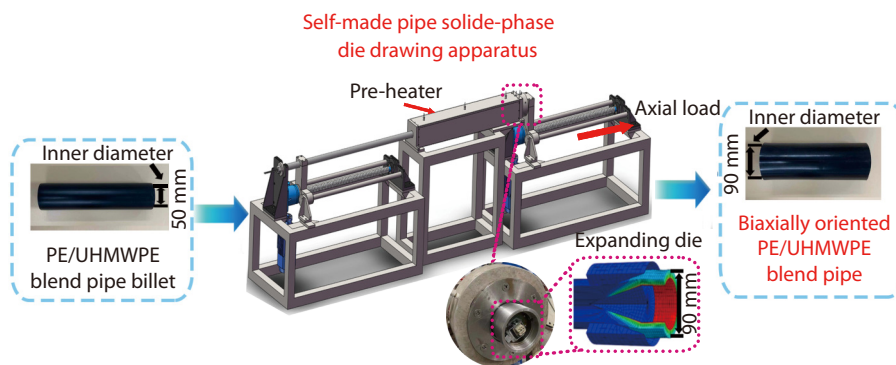


**Fig. 3** Scheme of preparation process of biaxially oriented PE/UHMWPE blend pipes.

heater, and then drawn through an expanding die with outer diameter of 90 mm under an axial load.  $DR_{hoop}$  of pipes was a definite value of 1.8 determined by the size and configuration of the expanding die, while variations of  $DR_{axial}$  in range of 1.1–1.5 were obtained by adjusting drawing speed. The mechanical performance and evolution of biaxially oriented crystalline structure of PE and PE/UHMWPE blend pipes were studied.

Figs. 4(a) and 4(b) exhibit the mechanical performance of biaxially oriented PE and PE/UHMWPE blend pipe samples. Before drawing, the blend pipe showed higher tensile strength both along the axial/hoop direction when compared with PE pipe. With increasing  $DR_{axial}$  for both samples,

the tensile strength along axial direction increased, while along hoop direction it increased first and maintained almost stable at high  $DR_{axial}$ . Moreover, for pipe samples at the same  $DR_{axial}$ , the blend pipe sample displayed much higher biaxial mechanical property than that of PE pipe sample. The tensile strength along hoop/axial direction was 29.90/37.32 MPa for PE-1.3 pipe and 33.16/50.32 MPa for PE/UHMWPE-1.3 pipe sample, which showed roughly 24%/27% and 62%/99% increase than that of undrawn PE-0 and PE/UHMWPE-0 blend pipe, respectively, realizing a biaxial reinforcement for both PE and PE/UHMWPE blend pipes.

The burst pressures of PE-0, biaxially oriented PE-1.3 and

PE/UHMWPE-1.3 blend pipe are shown in Fig. 5(a). Compared with PE-0 pipe, the burst pressure of biaxially oriented samples was highly enhanced. Moreover, the burst pressure of biaxially oriented PE/UHMWPE-1.3 pipe reached up to 2.48 MPa, which exhibited an increase of 25% and 12% compared with PE-0 and PE-1.3 pipe samples, respectively, indicating significantly enhancing pressure resistance for such blend pipe.

Fig. 5(b) shows the digital photos of PE-0, PE-1.3, and PE/UHMWPE-1.3 blend pipe samples by subjected to burst pressure testing. Obvious yield deformation occurred under hydrostatic pressure for all pipe samples. For PE-0 pipe sample, there was a large burst crack extending along the axial direction, while the crack length decreased obviously for the biaxially oriented samples. In comparison, PE/UHMWPE-1.3 blend pipe sample exhibited the shortest damage crack, further demonstrating the remarkable improvement of pressure resistance of pipe.

### Evolution of Biaxially Oriented Crystalline Structure of PE/UHMWPE Blend Pipes

For biaxially oriented PE and PE/UHMWPE blend pipes, a three-dimensional coordinate system, including axial-radial, hoop-

radial and axial-hoop geometrical planes,<sup>[9]</sup> is shown in Fig. 6(a).

Figs. 6(b) and 6(c) show the 2D-WAXD patterns of biaxially oriented PE and PE/UHMWPE blend pipes. Before drawing, the pattern of PE-0 pipe showed two homogeneously distributed diffraction rings, ascribed to (110) and (200) planes of PE,<sup>[34]</sup> and no apparent orientation was observed. However, for PE/UHMWPE blend pipe, the diffraction intensity of (110) plane was slightly enhanced on equator (marked by grey rectangle) in all geometrical planes, demonstrating that introduction of UHMWPE promoted orderly arrangement of lamellae, presenting some anisotropic crystal structure.

After die drawing, in axial-radial geometrical plane, for both PE-1.1 and PE/UHMWPE-1.1 blend pipe samples, the pattern of both (110) and (200) planes showed 2-arc diffraction (marked by grey arrow) on equator and meridian, respectively. With increasing of  $DR_{axial}$ , apparent 4-arc (110) diffraction (marked by yellow rectangle) on the equator and 2-arc (200) diffraction on meridian were observed for both samples, and a distinct orientation structure formed in axial-radial geometrical plane. In hoop-radial geometrical plane, for all pipe samples, the diffraction of both (110) and (200) planes showed off-axis 4-arc pattern (marked by cyan arrow). With

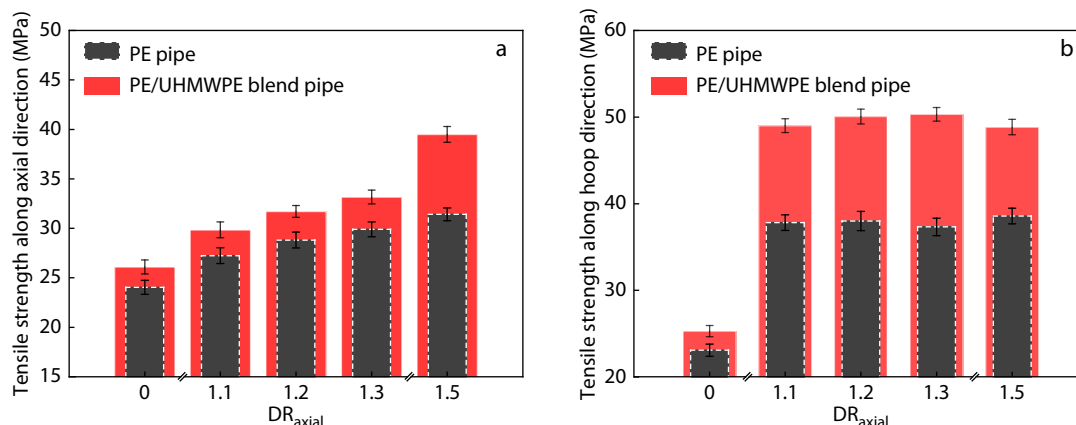


Fig. 4 Tensile strength along axial (a) and hoop (b) direction of biaxially oriented PE and PE/UHMWPE blend pipes.

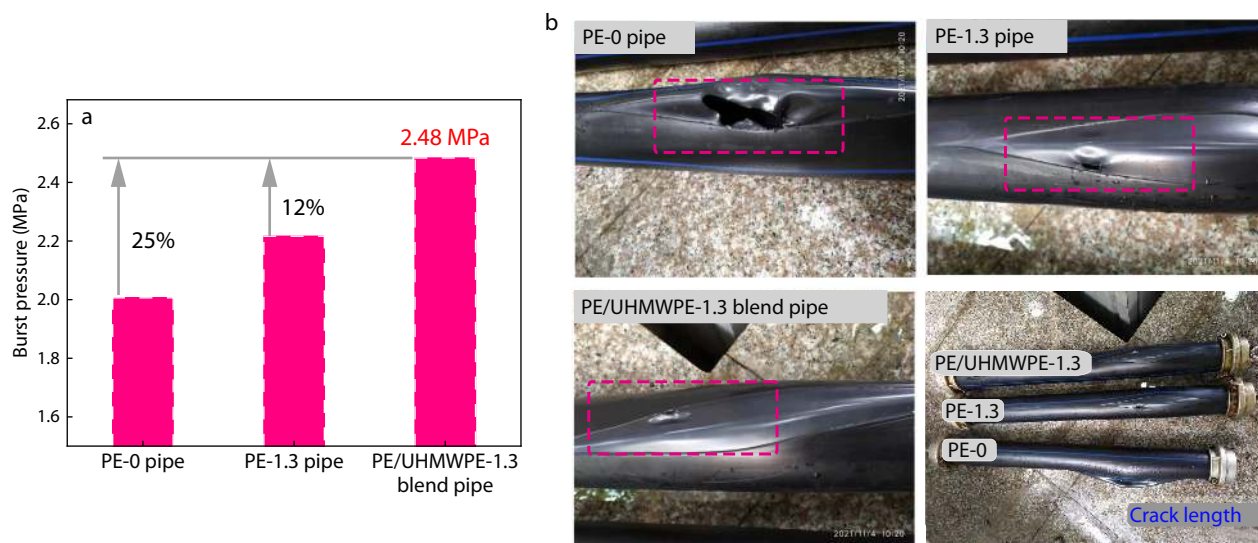


Fig. 5 Burst pressure resistance (a) and images of burst crack (b) of PE-0 and biaxially oriented PE-1.3 and PE/UHMWPE-1.3 blend pipe samples.

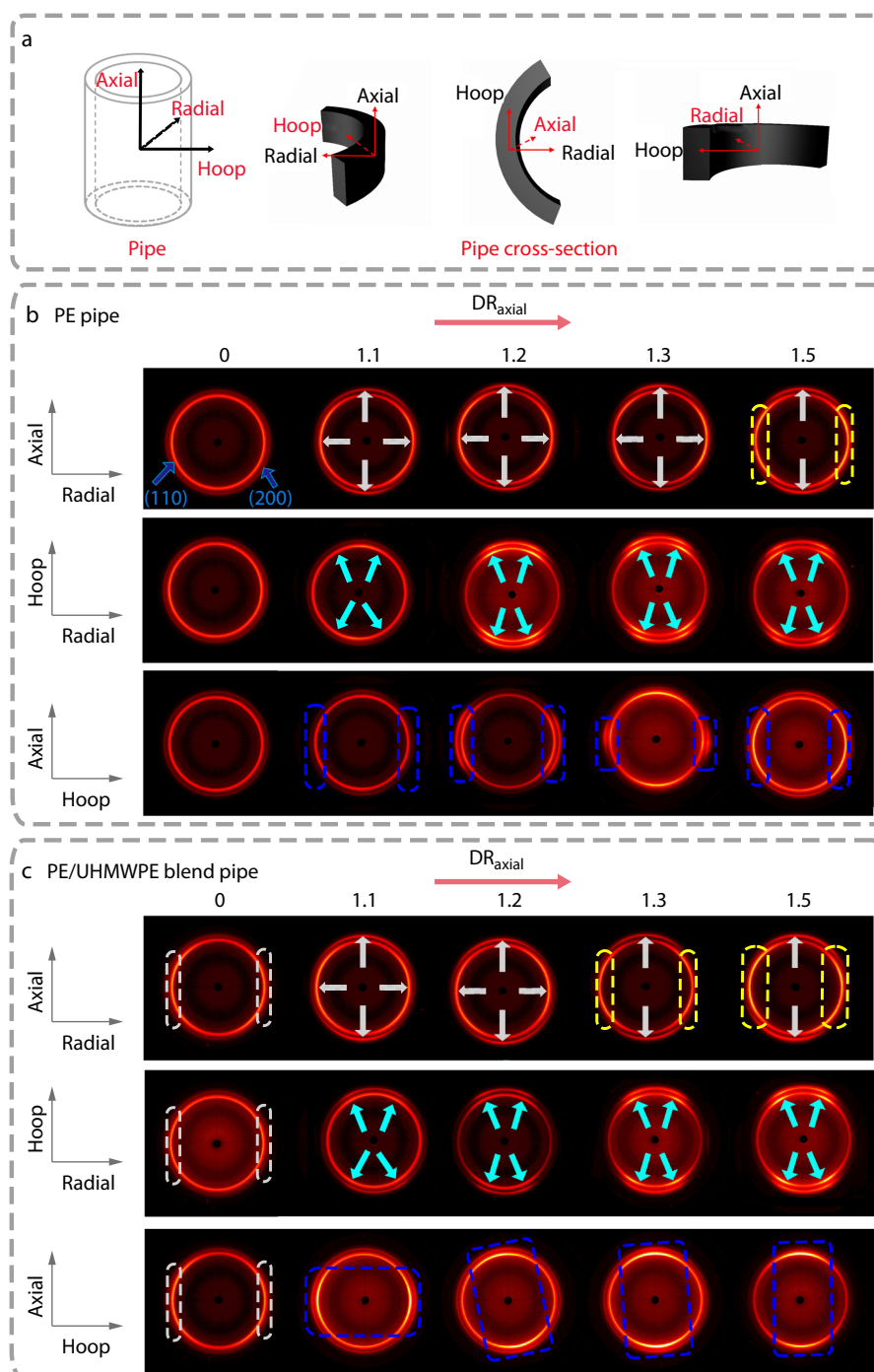


**Fig. 6** Experimental geometry employed for structure analysis (a), 2D-WAXD patterns of biaxially oriented PE (b) and PE/UHMWPE blend (c) pipe samples with different  $DR_{axial}$ .

increasing  $DR_{axial}$ , the diffraction arcs gradually became bright and concentrated first, and then the intensity of the arcs became weaker for PE-1.5 pipe sample, while for PE/UHMWPE blend pipe sample, the diffraction arcs became narrower in spread and more prominent, and crystals orientation along hoop direction greatly increased for pipe sample. In axial-hoop geometrical plane, for PE pipe sample, the diffraction of both (110) and (200) planes showed 2-arc pattern (marked by blue rectangle) on equator. With increasing of  $DR_{axial}$ , the in-

tensity of the arcs was enhanced first and then became weaker at high  $DR_{axial}$ , demonstrating that molecular orientation increased initially and then decreased along hoop direction. In contrast, PE/UHMWPE-1.1 blend pipe sample with low  $DR_{axial}$  showed 2-arc pattern, while with increasing  $DR_{axial}$ , the diffraction arcs deviated from equator to meridian, suggesting that lamellae orientation along axial direction was greatly enhanced, leading to formation of biaxial orientation structure for pipe sample.

1D X-ray diffraction curves are shown in Fig. 7. For both samples before drawing, two distinct diffraction peaks at  $2\theta \approx 21.3^\circ$  and  $23.8^\circ$ , attributed to diffraction of (110)/(200) plane, respectively, were observed in all geometrical planes. After die drawing, the peak position had no change, while

peak intensity was enhanced, suggesting that the crystallinity increased for pipe samples without affecting its crystal type during die drawing.

Orientation factor ( $f$ ) of pipe samples was calculated with Eqs. (3) and (4) (Fig. 7). Before drawing, the  $f$  value of PE

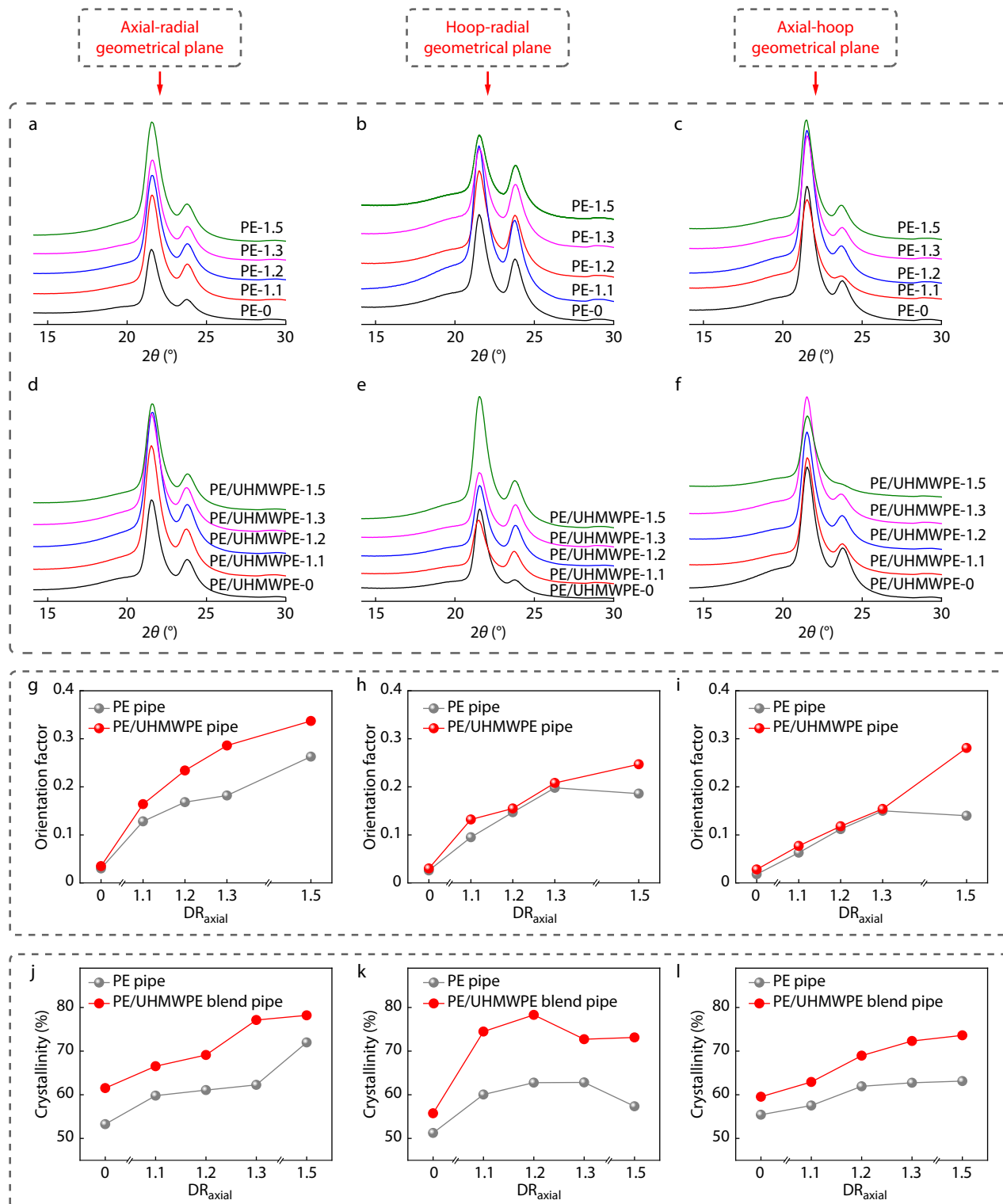


**Fig. 7** 1D WAXD curves (a–f), oriented factor ( $f$ , g–i) and crystallinity ( $X_c$ , j–l) of biaxially oriented PE and PE/UHMWPE blend pipe in different geometrical planes.

sample was as low as 0.030, 0.026 and 0.018 in axial-radial, hoop-radial and axial-hoop planes, respectively, while the  $f$  values of PE/UHMWPE blend was higher than those of PE sample in all geometrical planes, indicating a certain degree of anisotropy for blend sample formed during processing. With increasing  $DR_{axial}$  in axial-radial geometrical plane,  $f$  value of both samples greatly increased. In both hoop-radial and axial-hoop geometrical planes, with increasing  $DR_{axial}$ ,  $f$  value of PE sample increased first and then decreased, attributed to slippage of PE chains. For blend sample,  $f$  value increased steadily, presenting an enhanced stretchability. Moreover, at the same  $DR_{axial}$ ,  $f$  value of blend sample was much higher than that of PE sample in all geometrical planes, indicating that introduction of UHMWPE significantly promoted formation of oriented crystalline structure for blend sample during die drawing process.

Fig. 7 shows the crystallinity ( $X_c$ ) of pipe samples. With increasing  $DR_{axial}$ ,  $X_c$  of both pipe samples greatly increased in both axial-radial and axial-hoop geometrical planes, while  $X_c$

increased initially and then decreased slightly in hoop-radial geometrical plane. Because at high  $DR_{axial}$ , the orientation was inhibited by the motions of PE and PE/UHMWPE chains towards axial direction, the lamellae density was reduced in hoop-radial geometrical plane. Moreover, at the same  $DR_{axial}$ ,  $X_c$  of blend sample was much higher than that of PE sample, suggesting that, by incorporation of UHMWPE, the stress-induced crystallization of blend sample was improved effectively.

The 2D-SAXS patterns of pipe samples are shown in Fig. 8. Before drawing, the pattern of PE sample displayed an isotropic scattering ring in all geometrical planes, while for blend sample, a slightly elongated oval shaped pattern was observed. After die drawing, in axial-radial geometrical plane, the pattern of PE-1.1~PE-1.2 sample showed an oval scattering, while for blend sample, a trace of developing 4-arc pattern at  $DR_{axial}=1.1$  was seen. When  $DR_{axial}$  reached up to 1.2, the blend sample exhibited a clear 4-arc pattern, indicating that the lamellae began to rotate toward radial direction for

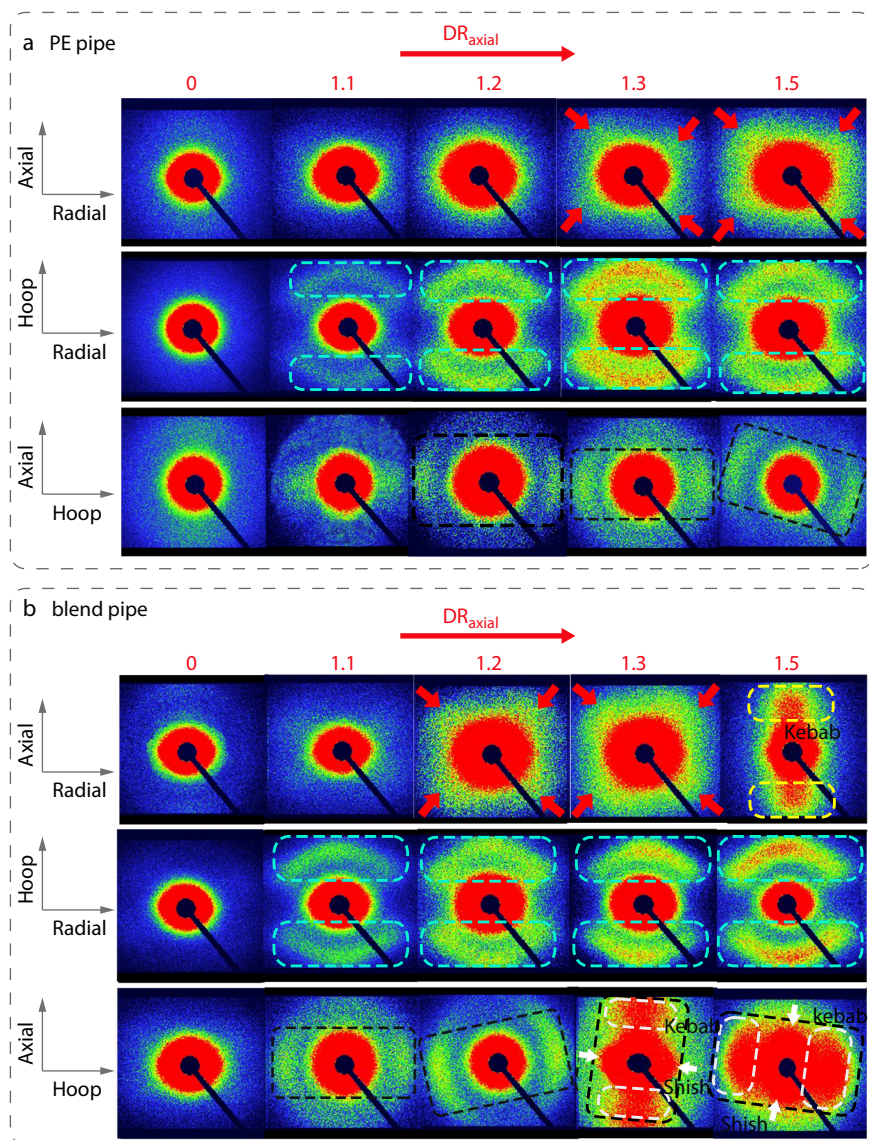


**Fig. 8** 2D-SAXS patterns of biaxially oriented PE (a) and PE/UHMWPE blend (b) pipes in different geometrical planes.

blend. With further increasing  $DR_{axial}$ , PE-1.3~PE-1.5 samples exhibited 4-arc pattern (marked by red arrow). In comparison, for PE/UHMWPE-1.3 blend, 4-arc pattern could also be observed, while its intensity was much higher than that of PE-1.3 sample. Moreover, the PE/UHMWPE-1.5 blend pipe with high  $DR_{axial}$  exhibited a pair of maximum on meridian (marked by yellow rectangle), and a highly oriented structure with kebab crystals formed in blend.<sup>[35,36]</sup> In hoop-radial geometrical plane, for both samples, an oval shaped pattern together with strong 4-arc pattern can be observed. With the increasing  $DR_{axial}$ , the scattering intensity increased first and then de-

creased for PE samples, while the intensity increased significantly for blend. In axial-hoop plane, the PE-1.1 sample showed a trace of developing a pair of maxima in equatorial direction, while a pair of clear emergence maximum can be observed for blend (marked by black rectangle), and the lamellae were highly oriented perpendicular to hoop direction for blend.<sup>[37]</sup> With increasing  $DR_{axial}$ , a pair of maximum patterns was seen for both samples, and the pattern deviated from equator to meridian gradually, especially for blend sample. Moreover, at the same  $DR_{axial}$ , the intensity of the two scattering maximum (kebab structure) of blend was much

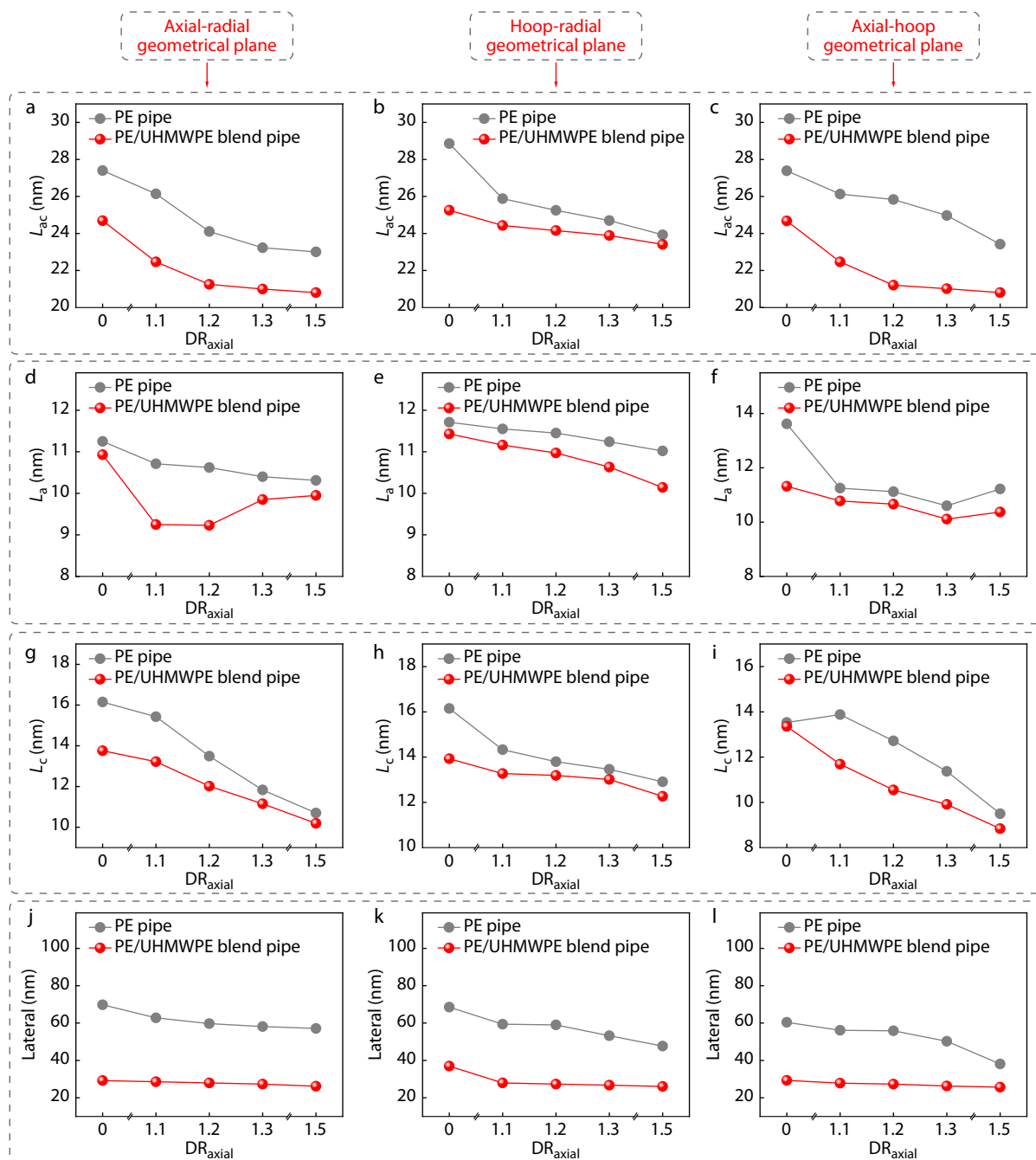


**Fig. 9** Long period ( $L_{ac}$ , a-c), amorphous layer thickness ( $L_a$ , d-f), lamellae layer thickness ( $L_c$ , g-i), and lateral size of lamellae ( $L_{lateral}$ , j-l) of biaxially oriented PE and PE/UHMWPE blend pipe in different geometrical planes.

higher than those of PE samples. For PE/UHMWPE-1.3 blend pipe sample, a spindle shaped pattern along the equator was also observed, indicating that the long UHMWPE chains were sufficiently stretched along the hoop direction during die drawing process, and then such extended-chain conformation of UHMWPE acted as shish structure (hoop direction), inducing short PE chains to array orderly and form kebab crystals (axial direction),<sup>[38,39]</sup> leading to forming a biaxially oriented chain-stretched network with shish-kebab structure for blend pipe. Besides, with increasing  $DR_{axial}$ , the shish structure gradually deviated from hoop to axial direction. For PE/UHMWPE blend pipe with high  $DR_{axial}$  of 1.5, the UHMWPE chains were rearranged and oriented primarily along the axial direction, resulting in a shish structure in the axial direction and kebab crystals in hoop direction for the blend pipe system.

The crystalline structural parameters of lamellae of pipe samples were obtained according to SAXS analysis and Eqs. (5)–(7). In Fig. 9, before drawing, the values of  $L_{ac}$ ,  $L_a$ ,  $L_c$  and  $L_{lateral}$  of PE/UHMWPE blend were lower than that of PE

sample in all geometrical planes, suggesting that incorporation of UHMWPE was beneficial for formation of fine crystalline structure. After die drawing, in both axial-radial and axial-hoop planes, with increasing  $DR_{axial}$ , the values of  $L_{ac}$ ,  $L_c$  and  $L_{lateral}$  of both PE and UHMWPE blend pipe samples decreased gradually, while the values of  $L_a$  first decreased to a minimum and increased slightly, indicating that the original crystals were destroyed, and stress-induced re-crystallization occurred during die drawing process, leading to forming dense lamellae structure. In hoop-radial geometrical plane, with increasing  $DR_{axial}$ , the values of  $L_{ac}$ ,  $L_a$ ,  $L_c$  and  $L_{lateral}$  displayed a downward trend. Moreover, at the same  $DR_{axial}$ , the lamellae size of blend was lower than that of PE sample in all geometrical planes, suggesting forming more dense oriented lamellae network in blend pipe.

SEM images of etched surfaces of pipe samples in axial-hoop plane are shown in Fig. 10. Before drawing, the lamellae of PE sample were randomly arranged, while for PE/UHMWPE blend, some orderly aligned crystals were observed. After die drawing, for both PE-1.1 and PE/UHMWPE-1.1 blend

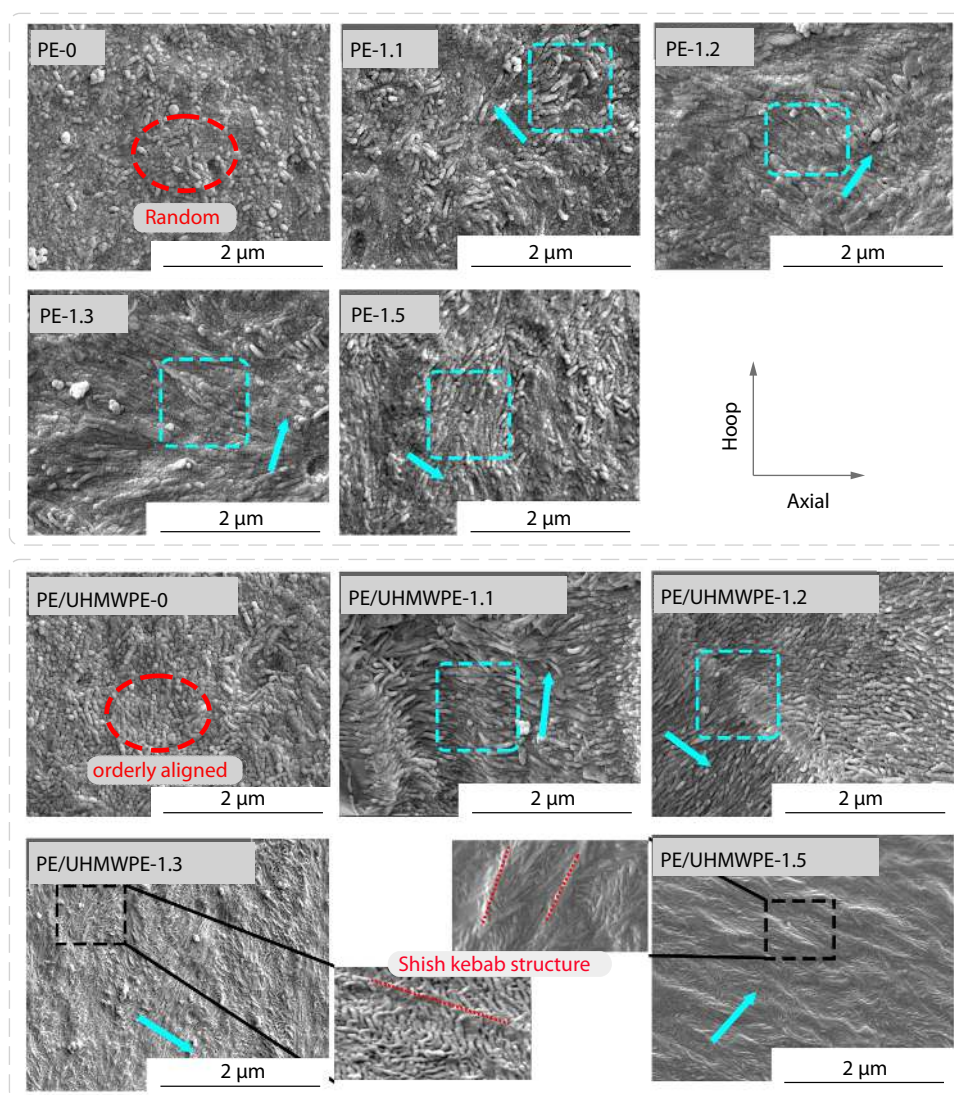


**Fig. 10** SEM micrographs of etched surfaces of biaxially oriented PE and PE/UHMWPE blend pipe in axial-hoop geometrical plane.

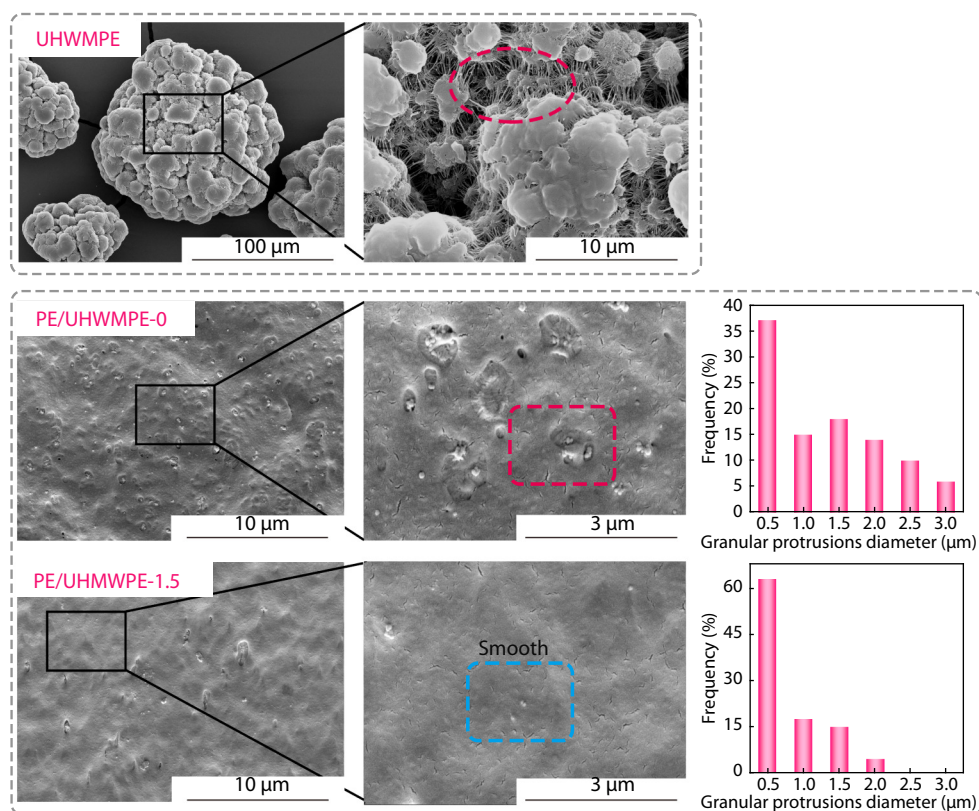


**Fig. 11** SEM images of UHMWPE particles, and the cryogenically fracture surfaces of PE/UHMWPE blend pipe and corresponding diameter distribution of granular protrusion.

samples with low  $DR_{axial}$ , the lamellae were preferentially arranged perpendicular to hoop direction. With increasing  $DR_{axial}$ , the lamellae deviated from hoop direction to axial direction gradually (marked by cyan rectangle), presenting a bi-axially oriented crystalline structure for both samples. Moreover, for PE/UHMWPE-1.3~PE/UHMWPE-1.5 blend with high  $DR_{axial}$ , a large number of oriented shish-kebab structures (marked by red dotted line), composed by long UHMWPE chains as shish and short PE chains as kebab after selectively etching the amorphous phase,<sup>[11,35]</sup> were observed, forming a dense oriented crystalline structure with fine and tiny crystals for blend pipe.

### Self-reinforcing Mechanism of Biaxially Oriented PE/UHMWPE Blend Pipes

Cryogenically fracture surfaces of PE/UHMWPE blend pipe before and after die drawing were studied by SEM analysis. As shown in Fig. 11, the UHMWPE particle was composed of lots of fibrillar entities and irregular nodulus units, and the average diameter of UHMWPE particles distributed in range of 50–100 μm.<sup>[35]</sup> For PE/UHMWPE blend pipe sample before drawing, a relatively rough fracture, accompanied by numerous granular protrusions formed by UHMWPE particles with average diameter of 1.31 μm (marked by red rectangle) was observed, while UHMWPE particles were uniformly dispersed in PE matrix. After die drawing, the PE/UHMWPE-1.5 blend displayed a flat and smooth cryogenically fracture surface (marked by cyan rectangle), and few granular protrusions with lower average diameter of 0.81 μm were seen on the fractured surface,

indicating that UHMWPE particles were almost completely dissolved in PE matrix by drawing, forming a more miscible blend pipe.

The stretchability of PE pipe sample was closely related to its viscoelasticity and molecular entanglement,<sup>[19,20]</sup> and the dynamic rheological properties of PE and PE/UHMWPE blend pipe samples before drawing were investigated (Fig. 12). With increasing frequency, the values of  $G'$  and  $G''$  increased greatly for both PE-0 and PE/UHMWPE-0 blend pipe samples. Moreover, compared with PE-0 pipe sample, PE/UHMWPE-0

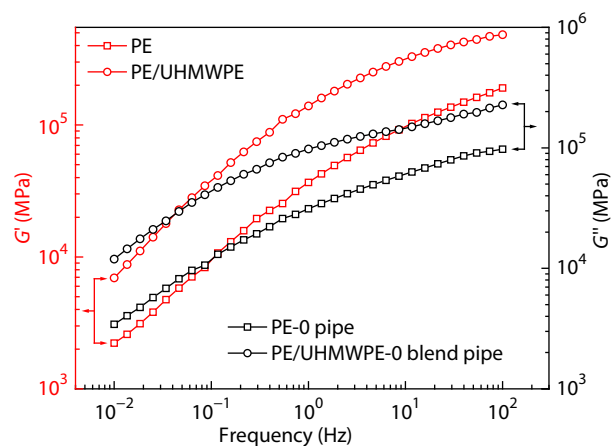


**Fig. 12** Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of PE-0 and PE/UHMWPE-0 blend pipe samples.

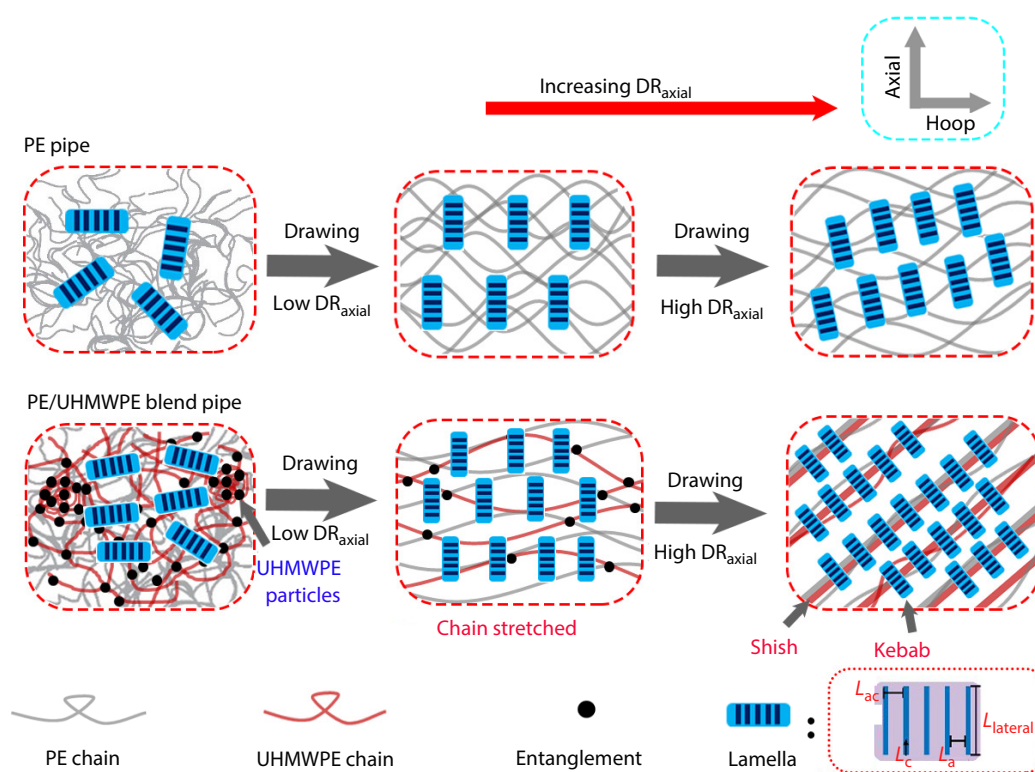


**Fig. 13** Scheme for self-reinforcing mechanism of biaxially oriented PE/UHMWPE blend pipe.

blend pipe sample showed higher  $G'$  and  $G''$  values in test frequency range.

The value of the average entanglement density ( $\nu_e$ ) was obtained based on Eqs. (8) and (9). The value of  $\nu_e$  of PE-0 pipe was 58.26 mol/m<sup>3</sup>, while that for PE/UHMWPE-0 blend pipe sample was much higher and reached up to 174.62 mol/m<sup>3</sup>, indicating that chains inter-diffusion and strong interfacial intermolecular entanglements occurred between components of PE and UHMWPE in blend, and thus a dense chain entanglement network with strong interfacial interaction between the two phases formed for blend pipe, leading to an enhancement of orientation degree for blend pipe.

The reinforcing mechanism of the biaxially oriented PE/UHMWPE blend pipes was explored (Fig. 13). Before drawing, PE pipe sample showed an isotropic structure with random arrangement crystals. After drawing, crystal fragmentation occurred, and the lamellae grew perpendicular to hoop direction for pipe sample. With increasing  $DR_{axial}$ , the lamellae were slightly deviated from hoop direction and approached axial direction. Moreover,  $X_c$  and  $f$  increased, and the lamellae size decreased, presenting a dense oriented structure with enhanced mechanical strength both along hoop/axial direction.

In comparison, for PE/UHMWPE blend pipe sample, due to formation of a chain entanglement network and enhanced viscoelasticity, incorporation of UHMWPE effectively promoted orderly arrangement of PE chains under stress, and improved the stretchability and orientation degree of blend pipe. During die drawing, formation of more miscible blend system make long UHMWPE chains be sufficiently stretched under load, and then such extended-chain conformation of

UHMWPE as shish structure induced short PE chains to crystallize on its surface and form oriented kebab crystals perpendicular to hoop direction during stress-induced re-crystallization process. Moreover, with increasing  $DR_{axial}$ , the lamellae were remarkably deviated from hoop direction to axial direction. Meanwhile, at the same  $DR_{axial}$ , the blend pipe sample exhibited much higher  $X_c$  and  $f$ , and lower values of  $L_{ac}$ ,  $L_c$ ,  $L_a$ ,  $L_{lateral}$  than that of PE pipe, leading to formation of uniform and dense biaxial orientation structure with shish-kebab crystals. Thus, the biaxial mechanical strength and burst pressure of blend pipe were improved significantly.

## CONCLUSIONS

Biaxially oriented PE/UHMWPE blend pipes were fabricated on self-made pipe solid-phase die drawing apparatus. Incorporation of UHMWPE improved the intermolecular entanglements and viscoelasticity of the blend, leading to an enhancement of stretchability and orientation degree for blend pipe. During die drawing, formation of more miscible blend system make long UHMWPE chains be sufficiently stretched under load, which induced short PE chains to array orderly, leading to formation of shish-kebab crystals. Moreover, with increasing  $DR_{axial}$ , the lamellae were deviated from hoop direction and approached axial direction gradually, and more dense and uniform biaxial orientation crystalline structure formed. As a consequence, the hoop strength and burst pressure of blend pipe were improved significantly, which exhibited wide application potentials as high-pressure transportation pipelines in civil engineering.

## NOTES

The authors declare no competing financial interest.

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