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The Effect of PEW on Properties of Solid State Drawn UHMWPE

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Abstract. UHMWPE is known for its excellent properties but its applications are limited due to its low tensile strength. Solid state drawing enhances the mechanical properties of UHMWPE by orienting its molecular chains. Polyethylene wax (PEW) improves UHMWPE's fluidity and processability. This study investigates the effect of PEW on the crystalline structure, morphology, thermal behavior, and mechanical properties of UHMWPE. The results show that PEW-modified samples exhibit enhanced tensile strength and better ductility, which make solid state drawing an efficient method for producing high-strength UHMWPE.

Keywords: UHMWPE; transparency; drawing; morphology; Polyethylene wax.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is renowned for its exceptional properties, including impact resistance, corrosion resistance, low-temperature resistance, and biocompatibility, making it suitable for applications in chemical, mechanical, and medical fields[1,2]. Despite these advantages, the relatively low tensile strength (≤50 MPa) of UHMWPE hinders its broader applications.

Various methods have been explored to enhance its mechanical properties, such as blending with nanomaterials including carbon nanofibers, carbon nanotubes, and graphene[3,4]. However, these methods often require complex processing steps to achieve good dispersion, and inadequate dispersion can lead to stress concentration points, causing premature failure[5].

Some researchers have focused on the influence of mold, pressure, and temperature. Truss[6] studied the effects of sintering temperature, time and pressure on the hot press process. By tuning such factors, the tensile strength can reach 43.5MPa. Some scholars have studied the influence of crystallization on mechanical properties of UHMWPE. To control crystallization, fish-tail shaped die[7] and equal channel angular die[8] were designed for continuous extrusion of UHMWPE sheets, but it was found that no improvement in tensile strength under the same process condition compared to normal extrusion. Controlling the crystal morphology of UHMWPE to enhance the mechanical properties is not an efficient way, due to the relatively high crystallization rate of UHMWPE, conventional methods cannot show a significant effect[9,10].

The solid state process is an efficient way to reinforce mechanical properties of polymers during continuous process[11]. Under the action of tensile stress, molecular chains oriented, initial spherulitic structure transformed into fibrils, leading to the obvious change in mechanical properties[12]. Chen[7] found that by setting the mold temperature near the melting temperature of UHMWPE, the mechanical properties improved several times. Polyethylene wax (PEW) is widely used to improve the fluidity and processability of UHMWPE. Shen[13] found that with the increase in polyethylene wax content, the flowability of blends was improved, and the maximum draw ratio can be achieved, with a decrease in tensile stress.

In this work, high strength UHMWPE sheets both with and without PEW were manufactured utilizing a self-designed solid state die drawing apparatus. The effect of different contents of PEW on the crystalline structure, morphology, thermal behavior and mechanical properties was studied. By adjusting the content of PEW, the drawn samples achieved significantly higher tensile strength

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compared to the undrawn samples. Solid state drawing of UHMWPE provides an efficient processing method for high strength UHMWPE.

2. Materials and Methods

2.1 Materials

The materials used in this work included UHMWPE (POLIMAXX-U511, molecular weight = 5×10^6, powder state), polyethylene wax (PEW, A-C 617). The UHMWPE was supplied by IRPC Public Co., Thailand. The polyethylene wax was purchased from Honeywell Co., Ltd., China.

2.2 Experiment

The UHMWPE plates were prepared using compression molding technology. UHMWPE and PEW were weighed according to the weight percentage listed in Table 1 and then mixed in a high-speed mixer (SHR-25A, Zhangjiagang Yongli Machinery Co., Ltd., China) at 25,000 rpm for 15 min. The mixture was molded by a hot press (Zhengzhou Xinhai Machinery Manufacturing Co., Ltd., Zhengzhou, China) at a temperature of 230 °C and a pressure of 5 MPa for 30 min. Subsequently, the mold filled with the melt was transferred to a water-cooled press (Zhengzhou Xinhai Machinery Manufacturing Co., Ltd., Zhengzhou, China) and quenched to room temperature under the pressure of 10 MPa. The UHMWPE plates were then machined into sheets with a breadth of 18mm and a thickness of 12mm for die drawing process.

Table 1. The formulation of UHMWPE and PEW

	UHMWPE	PEW
UH5	100	0
P5	95	5
P10	90	10
P15	85	15

The solid state drawing process of UHMWPE was carried out in a self-developed device, including a heating chamber, a heated converging die and a caterpillar tractor. The pre-heated temperature and drawing temperature were set at 130 °C and the drawing speed was 50 mm/min. The drawing ratio was controlled by a self-designed die shown in Fig. 1(a). The nominal drawing ratio is defined as the ratio of the cross-sectional area of the initial plate to the cross-sectional area at the die exit (18mm×12mm versus 9mm×6mm). The drawing ratio was uniformly set to 4 to investigate the influence of varying content of PEW on the drawn samples. The undrawn and drawn UHMWPE samples are shown in Fig. 1(b) and 1(c).

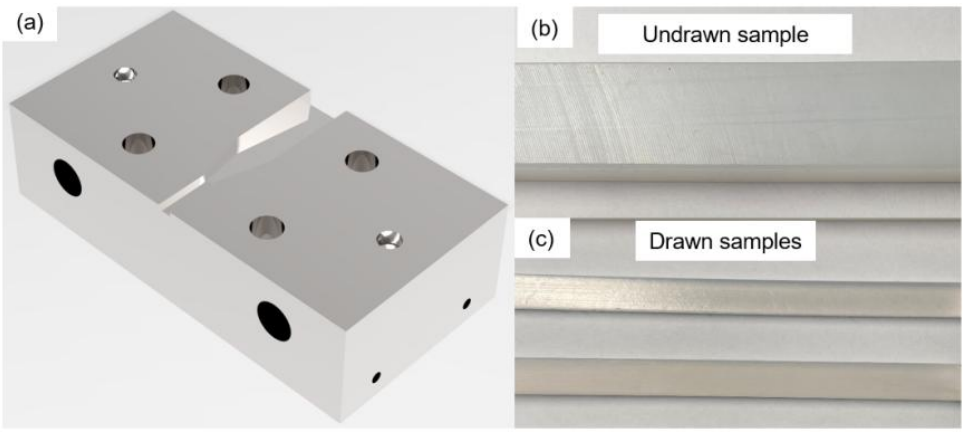

Fig. 1 (a) structure of solid state drawing die; (b) and (c) undrawn and drawn UHMWPE samples.

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2.3 Characterization Method

X-ray diffraction analysis (XRD): The XRD was characterized using an X-ray diffractometer (D8A25, Bruker Co., Germany) with Cu Kα radiation (λ = 0.154 nm) at a generator voltage of 40 kV. The scanned 2θ range was from 5° to 50° at a scanning rate of 10°/min.

Scanning electron microscopy (SEM): The UHMWPE samples were fractured at low temperature in liquid nitrogen. Gold coating was treated the cross section along drawing direction of the samples. The fractured surface morphology analysis of the samples was observed by scanning electron microscopy (MAIA3 XMU, TESCAN Co., Czech Republic) at room temperature and the acceleration voltage was 5 kV.

Differential scanning calorimetry (DSC): The thermal behavior of samples was tested by a differential scanning calorimeter (DSC 214, Netzsch Co., Germany). The thermal behavior of the samples was obtained by heating from 20 to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Mechanical properties: Tensile strength and Young's modulus of all samples were measured using an universal tensile tester (Instron 5966, Shanghai Instron Testing Equipment Trading Co., Ltd, China) with pneumatic side action tensile grips at room temperature according to GB/T 1040-2006. Specimens with a length of 200mm were cut from the samples. The tensile tests were carried out at a crosshead speed of 50mm min-1.

Transmission spectra: Transmission spectra of the die-drawn samples were measured using a UV−vis spectrometer (TU-1810, Beijing Puxi General Instrument Co., Ltd., China) in the wavelength range of 300−700 nm at an interval of 1 nm.

3. Results and Discussion

3.1 Crystalline Structure

The evolution of crystal structure occurs during solid state drawing, affecting the micro structure of the sample and leading to differences in macroscopic properties and performance. The XRD patterns of undrawn and drawn samples with different contents of PEW are shown in Fig. 2. As can be seen, the typical XRD peaks for all samples were around 2θ=21.4°、23.8°、36.1°, corresponding to the (110), (200) and (020) diffraction planes of orthorhombic, respectively, indicating that no crystal type transformation occurred due to the addition of PEW or the solid state drawing process[14].

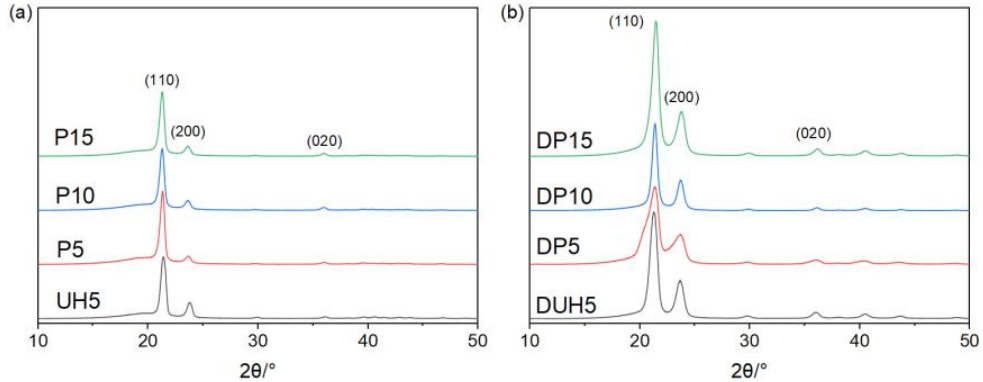

Fig. 2 XRD profiles of UHMWPE samples modified by PEW: (a) undrawn samples (b) drawn samples

Crystalline domain size of (110), (200) and (020) diffraction planes was calculated according to XRD curves, as shown in Table 1. For undrawn samples, the addition of PEW did not show a significant effect on hot press, and the domain size is almost the same as that of UH5. For drawn samples, the domain size decreased and then increased with the content of PEW. It can be

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concluded that PEW played the role of lubricant during solid state drawing process. Due to the polymerization of the same monomer, there is excellent compatibility between PEW and UHMWPE, leading to an increased slip of the entire crystal while the deformation and fragmentation gradually decreased.

Table 1. Crystalline structure parameters of undrawn and drawn samples

Undrawn Samples	Crystalline domain size(nm)			Drawn samples	Crystalline domain size(nm)		
	110 plane	200 plane	020 plane		110 plane	200 plane	020 plane
UH5	13.64	12.53	19.35	UH5	7.59	7.00	8.78
P5	13.95	8.22	18.13	P5	5.17	6.40	7.34
P10	13.68	8.57	16.38	P10	9.19	7.25	10.50
P15	14.02	9.10	16.47	P15	12.39	9.83	15.00

3.2 Mirco Morphology

The micro morphology of undrawn and drawn UHMWPE samples was characterized by SEM, as shown in Fig. 3. Cross section along drawing direction of all samples was observed to explore the effect of PEW on the structure. The micro structure of undrawn samples is similar, with no second phase observed. PEW and UHMWPE are well bonded, consisting of isotropic spherulites and amorphous regions. Fig 3 (a2) to (d2) presents the SEM images of drawn samples with different PEW contents. In the drawn samples, the spherulite structure was replaced by a microfiber structure, indicating that molecular chains were stretched and rearranged[15]. The micro fiber structures in the sample without lubricants vary in size and are loosely arranged, while the microfiber structures in the modified samples are more uniform, dense, and neatly arranged. During the solid state drawing process, molecular chains were stretched, rotated and fibril structures formed. If the fluidity of molecular chains is insufficient, the microfiber structure cannot be tightly arranged, resulting in the formation of voids[16]. This indicates that PEW are beneficial for the formation of microfiber structures, less microdefects and further regular arrangement.

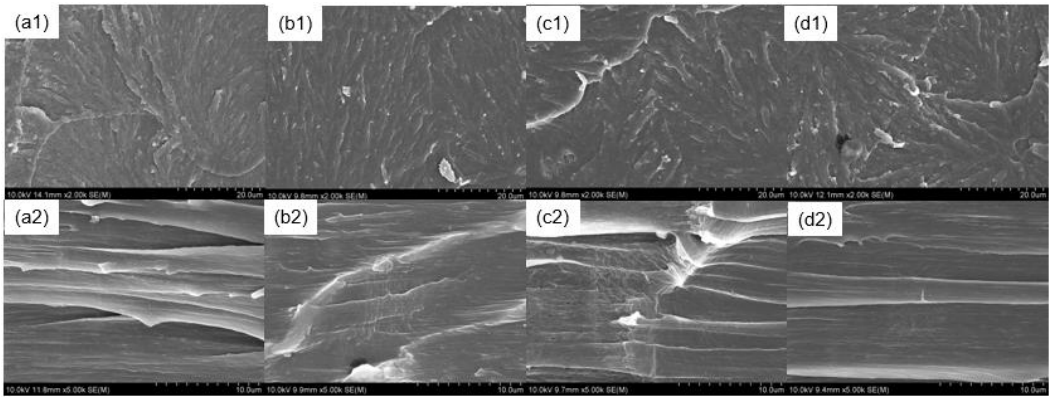

Fig. 3 SEM graphs of UHMWPE with different PEW contents, where 1 represents the series of un-drawn samples and 2 represents the series of drawn samples (a-d) UH5, P5, P10, P15

3.3 Thermal properties

Fig. 4 presents the DSC heating curves of undrawn and drawn samples. The crystallinity first gradually increased and then slightly decreased with the increase in the content of PEW, but it was still higher than that of pure UHMWPE. This indicates that the addition of PEW improved the mobility of the molecular chains of the raw material, enabling more molecular chains to be regularly arranged and forming more crystalline regions. However, the melting peak shifted to a lower temperature position. This is because the melting point of PEW is relatively low, and PEW and UHMWPE are extremely compatible. After long-time high-temperature molding process under pressure, a stable homogeneous system was formed, resulting in the DSC curve of the blend not

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showing a double peak but a melting peak at a lower temperature than that of UH5. Combined with Table 2, it can be seen that the crystallinity and Tm of the modified UHMWPE drawn samples increased by 5.3 - 5.9% and 3.5 - 5.2°C, respectively. The variation tendency of crystallinity with the amount of PEW was still an increase first and then a slight decrease. At the same time, the melting peak splitted. This indicates that after solid state drawing of P15, the regularity and perfection of the internal crystal structure of the drawn samples were severely damaged.

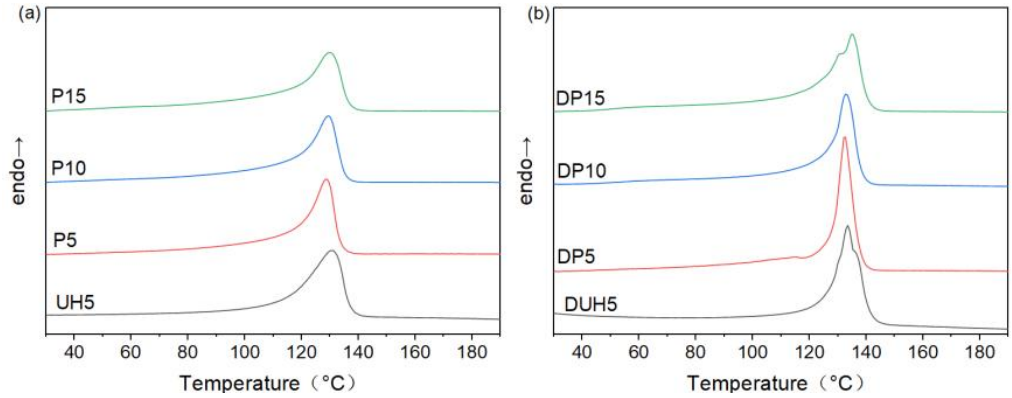

Fig. 4 DSC heating curves of UHMWPE samples modified by PEW: (a) undrawn samples (b) drawn samples

Table 2. DSC analysis data of UHMWPE samples with different lubricant contents

Undrawn Samples	Tm (°C)	ΔHm	Xc (%)	Drawn samples	Tm (°C)	ΔHm	Xc (%)
UH5	130.7	124.7	43.15	UH5	133.6	144.0	49.83
P5	128.7	138.5	47.92	P5	132.2	154.6	53.50
P10	129.1	145.3	50.27	P10	132.8	160.5	55.53
P15	129.8	136.4	47.20	P15	134.0	153.6	53.15

3.4 Mechanical Properties

Fig. 5 shows various mechanical properties of undrawn and drawn samples. The lubrication of PEW changed the movement mode of molecular chains. The elongation at break of PEW modified samples is obviously higher than that of UH5. The chains of pure materials mainly move in segments, while the chains in modified samples show more slippage. According to Fig. 5(a) and (b), an increase in PEW results in a higher elongation at break. The tensile strength of P5 is greatly affected by lubricants, with only 22.1 MPa. The tensile strength of other samples ranges from 25.6 to 27.2 MPa. the tensile stress of samples containing lubricants under the same strain is lower than that of UH5, but due to the ability to achieve higher elongation at break, the orientation of the molecular chains makes its tensile strength not lower than that of pure UHMWPE.

As shown in Fig. 5(c) and (d), the solid state drawing produced significant increase in tensile strength and Young's modulus. But elongation at break of the materials decreased after drawing process. The tensile strength and Young's modulus can reach up to 116.3MPa and 1.02GPa, increased 1.74 and 6.45 times in P5, respectively. High orientation of molecular chains and the increase of crystallinity enhance the material's ability to resist deformation[17]. But such transformation of molecular chains also restricted the further movement of the molecular chains, resulting in a decrease in the elongation at break. The tensile strength and Young's modulus of all PEW modified samples are lower than that of UH5, while the elongation at break is higher.

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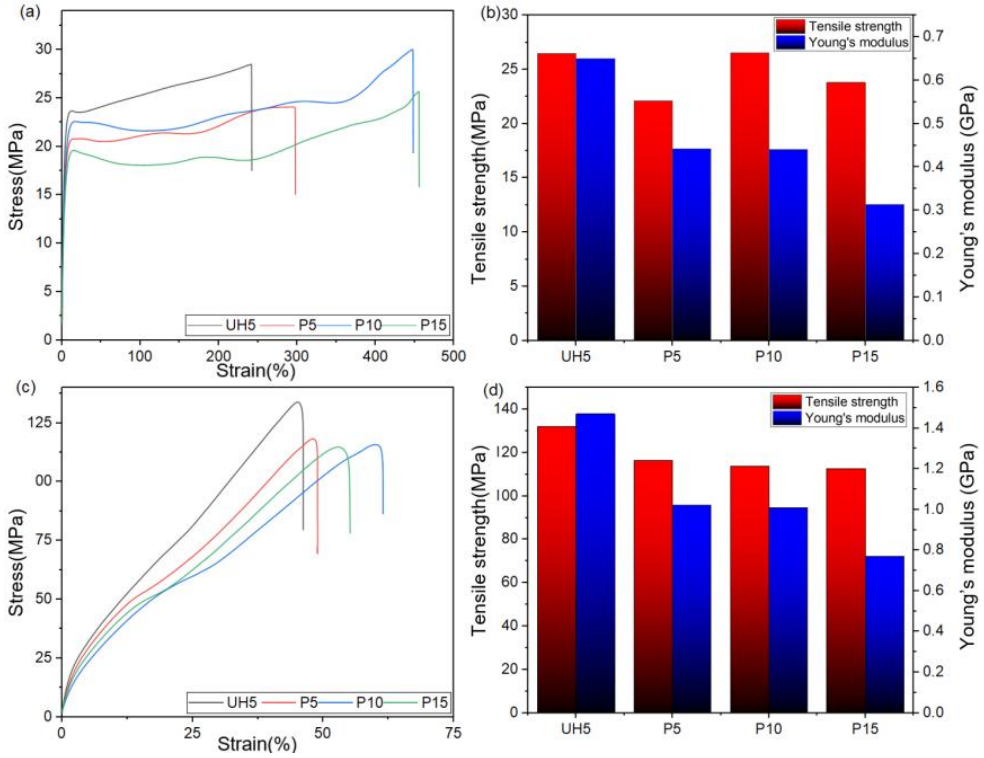

Fig. 5 Tensile properties of UHMWPE samples modified by PEW: (a) strain-stress curves and (b) tensile strength and Young's modulus of undrawn samples; (c) strain-stress curves and (d) tensile strength and Young's modulus of drawn samples

Conclusion

This study demonstrates that adding PEW during solid state drawing improves UHMWPE's crystalline structure and mechanical properties. Modified samples show more uniform microfibers and higher tensile strength (up to 116.3 MPa) and Young's modulus (1.02 GPa). PEW-modified samples have higher elongation at break, indicating better ductility. Solid state drawing with PEW is an effective method to enhance UHMWPE's strength and maintain ductility.

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