High Thermal Conductivity Ultra-High Molecular Weight Polyethylene (UHMWPE) Films

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ABSTRACT

Recently, high thermally conductive polymers have emerged as low cost and energy efficient alternatives to traditional use of metals in heat transfer applications. Here, we present development of ultra-high molecular weight polyethylene (UHMWPE) thin films with high thermal conductivity. The fabrication platform is based on sol-gel process accompanied by stretching process. After gel formation and partial drying, UHMWPE films are mechanically stretched at elevated temperatures, resulting in macroscopic plastic deformation as well as additional polymer chain alignment and crystallization. Both the extrusion and stretching procedures have been automated, and custom software incorporates parameter "recipes" to allow selection of a range of desired process variables. Structural characterization (XRD, DSC, and SEM) of these films suggests highly aligned polymer chains and crystallinity greater than 99%. The Angstrom method is utilized to measure thermal conductivity of these films along the drawing direction.

KEY WORDS: ultra-high molecular weight polyethylene, thermal conductivity

INTRODUCTION

Development of new materials with superior properties is a step toward a proper utilization of energy resources. Bulk polymers usually have low thermal conductivities, ~0.1-0.3 $Wm^{-1}K^{-1}$ compared to metals ~40 $Wm^{-1}K^{-1}$ for steel and ~400 $Wm^{-1}K^{-1}$ for copper. This low thermal conductivity has hindered widespread deployment of polymers in heat transfer applications. Traditional methods for improving thermal conductivity of polymers have typically focused on composite materials, where a high thermal conductive additive (such as carbon nanotubes) is added to the polymer matrix. However, due to high interfacial resistance between the polymer matrix and additive, thermal conductivity enhancement in these composite materials is limited to one order of magnitude [1].

A single polymer chain can have a very high thermal conductivity since it behaves like a one-dimensional conductor [2]. Substantial enhancement in thermal conductivity of polymers can be achieved by alignment of polymer chains. In bulk polyethylene (PE) which accounts for over 60% of plastics used worldwide, the defects (polymer chain ends, entanglement, voids, and impurities, etc.) act as stress concentration points and phonon scattering sites for heat transfer. Thus, bulk PE exhibits low strength and low thermal conductivity. Through molecular dynamic simulations, Henry and Chen [3] showed that an individual polymer chain can have very high or even divergent (in some cases) thermal conductivity. In the limit of an individual polyethylene chain, theoretical predictions suggest thermal conductivities as high as 300 $Wm^{-1}K^{-1}$. Fabrication of ultra-high molecular weight polyethylene (UHMWPE) fibers with high moduli of elasticity and thermal conductivities is reported through sol-gel process [4], [5]. Mergenthaler et al. [6] has fabricated ultraoriented polyethylene strips to achieve high values of thermal conductivity. The authors used a point-source heater and measured temperature distribution by monitoring spatial infrared radiation by In-Sb detector. The measured temperature field is fitted to 3-D solution of heat equation to obtain thermal diffusivity. As the size of the samples were small, an empirical correction factor is used to update the value of thermal diffusivity. The authors suggested thermal conductivity of up to 37.5 $Wm^{-1}K^{-1}$ for ultraoriented Polyethylene strips. Cao et al. [7] used a nano-template to fabricate polyethylene nanowires through a sol-gel process. They measured thermal conductivity of these nanowires by laser flash method and achieved a value of 10 $Wm^{-1}K^{-1}$.

Recently, molecular-aligned UHMWPE fibers were fabricated with diameters of 50 – 500 nm and thermal conductivity as high as 104 $Wm^{-1}K^{-1}$ [8]. These fibers

were fabricated utilizing a sol-gel process. In this method, an AFM cantilever or sharp tungsten tip (~100 nm diameter) is used to draw a fiber from a heated gel (UHMWPE + Decalin). The gel is kept at 120°C on a heated stage. Then the fiber is dried at temperature of 90°C to partially evaporate the solvent. Finally, the fiber is mechanically stretched up to 400 draw ratio at 90°C to achieve high thermal conductivity values.

However, for most practical heat transfer applications, a film (vice fibrous) form of these materials is needed. Here, we report the development of thin-film high thermal conductivity UHMWPE. The fabrication platform is based on sol-gel process followed by mechanical stretching. These films provide a new generation of materials that can replace metals in many heat transfer applications such as electronic packaging and heat exchangers, with the additional advantages of energy savings, weight reduction, chemical resistance, electrical insulation, and lower cost.

RESULTS AND DISCUSSION

1. Characterization of crystalline structure

Polymer films were fabricated from UHMWPE 3 wt% gels with different draw ratios (the length of final product to the intial film). The films have thickness of 4-10 μm. The crystallinity of the stretched films are examined by X-ray Diffraction (XRD) using a PANlytical X'Pert Pro, a conventional 1.8kW sealed X-ray tube source with a Cu target. The XRD pattern are shown in Fig 1. The patterns are analyzed in Highscore Plus software. The percentage of crystallinity in each pattern is determined by comparing the area of the amorphous hump and crystalline peaks. As shown, the initial crystallinity of the UHMWPE powder is 47%, Fig 1a. However, after going through a sol-gel process and extrusion, its crystallinity drops to 15%, Fig 1b. This suggests that the powder losses its crystalline structure in the sol-gel process. The high ratio of noise-to-signal ratio is a consequence of low crystallinity of this film. In Fig 1c, the XRD pattern of the UHMWPE film with draw ratio of 200 is shown. This film shows 99% crystalline structure which indicates the recovery of crystalline structure in the stretching process. Higher crystallinity is favorable for obtaining high thermal conductivity. However, it is not the only crucial parameter in determining thermal conductivity. The XRD results show that current processing approach leads to a significant increase in the crystallinity.
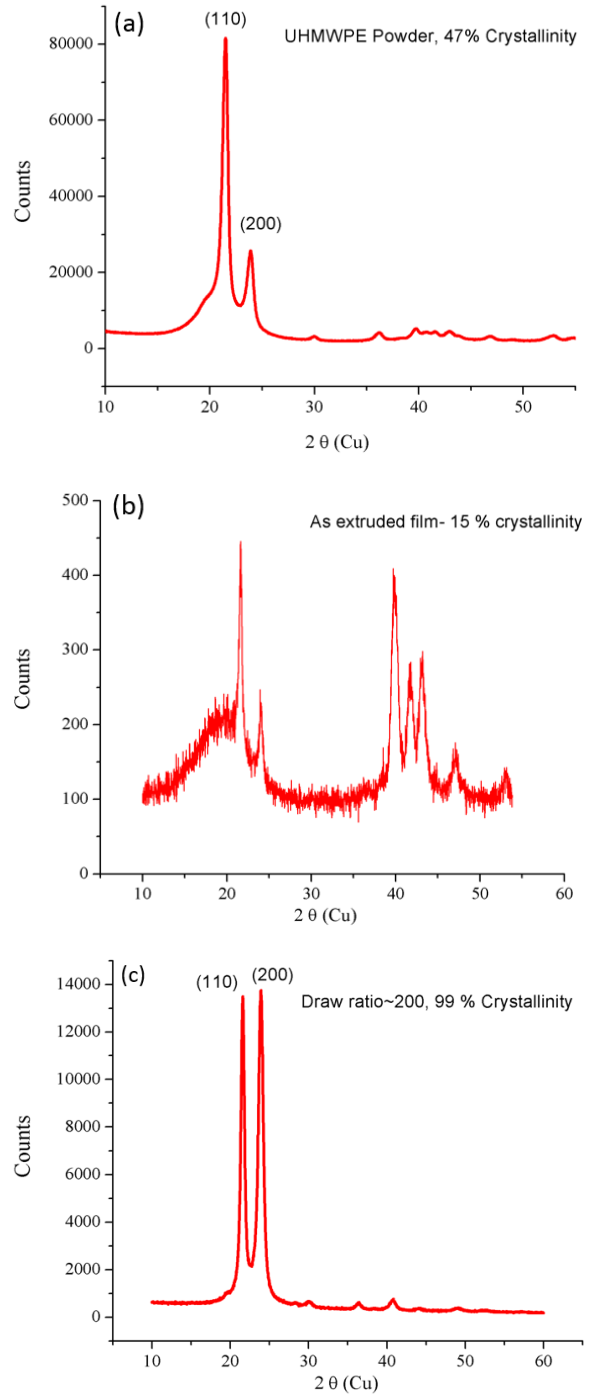

Fig. 1: The XRD pattern of three samples are shown: (a) UHMWPE powder (b) The as extruded UHMWPE film, and (c) a UHMWPE film with draw ratio of 200 (3% UHMWPE).

Furthermore, we examined distortion of the unit cell in UHMWPE structure in the extrusion process through analysis of XRD pattern by Highscore Plus software. The crystal structure of PE is orthorhombic with the unit

cell dimension of 0.741 nm × 0.494 nm × 0.255 nm. We determined the unit cell size at different draw ratios tabulated in Table 1. No detectable change in unit cell dimensions are observed. This demonstrates that the drawing process does not introduce any unit cell strain and serves only to crystalize the amorphous phase.

Table 1: The dimension of PE unit cell as a function of draw ratio

Initial Concentration of solution	Draw ratio	a (nm)	b (nm)	c (nm)
3 wt%	0	0.748	0.499	0.2554
3 wt%	5	0.742	0.499	0.2514
3 wt%	45	0.74	0.493	0.254

In the next step, we studied the dependence of the molecular stem length to draw ratio by studying the

melting temperature (T) of the films as a function of draw ratio. According to Thomson equation [9],

$$T = T_0 \left(1 - \frac{2\,\sigma}{H_m\,L}\right) \qquad (1)$$

where T_0 is the melting temperature of polyethylene with infinite stem length, σ is the surface free energy per unit area, H_m is the enthalpy of fusion per unit volume, and L is the stem length. All the parameters are taken from [9] and the Thomson equation is written as

$$T = 414.2 \left(1 - \frac{0.627}{L}\right) \qquad (2)$$

The dependence of the melting temperature on draw ratio is shown in Fig. 2a. Using the Thomson formula, the stem length at different draw ratios is calculated and shown in Fig 2b.
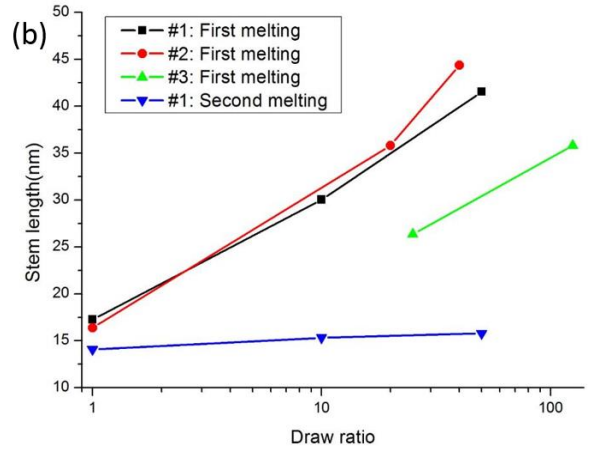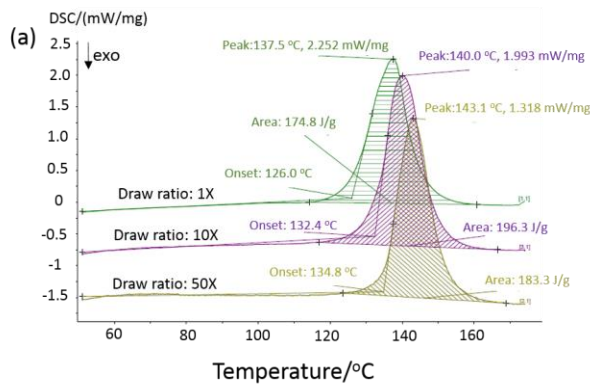

Fig 2: (a) The dependence of melting temperature on the draw ratio is studied by DSC. (b) The change of stem length as a function of draw ratio is shown.

As shown, in the first melting cycle of the film, there is a dependence of melting temperature on draw ratio. Thus, the stem length is calculated as a function of draw ratio. All the samples are processed from 1% wt UHMWPE solution. Samples 1 and 2 are from the same extrusion batch, while sample 3 is from a different batch. As expected, in subsequent re-melting, this dependence disappears. Stem length is increased by ~2.5 times at a 45 times draw ratio. Further analysis of steam length dependence on draw ratio will be presented in future work.

2. **Microstructural characterization**

The surface morphology of extruded and stretched films are examined to study the degree of alignment. The morphology of the UHMWPE film with the draw ratio of 200 is shown in Fig. 3(a) and 3(b). The cross section of a ruptured sample is shown in Fig 3(c). The fibrous nature of the cross section indicates formation of aligned structure in the UHMWPE film.
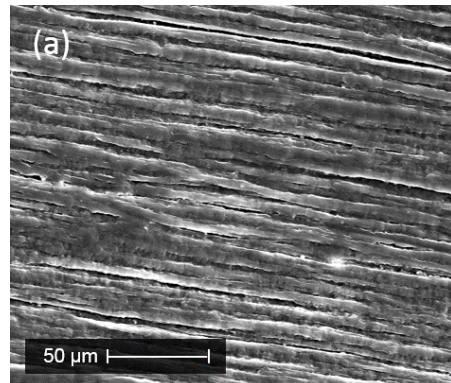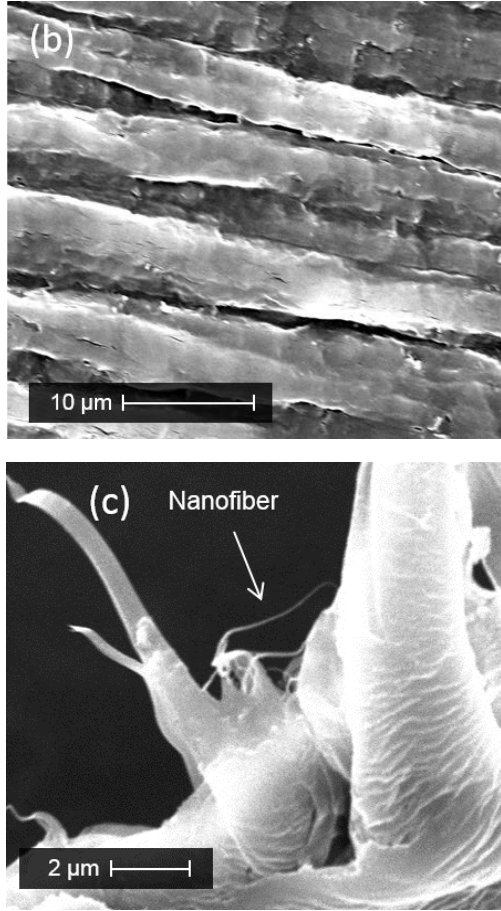
Fig. 3: (a) and (b) The morphology of stretched UHMWPE film at different magnifications are shown. (c) The cross section of the stretched film shows formation of nano-fibers in the structure.

3. Thermal conductivity measurements

Thermal conductivities of the stretched films are measured by the Angstrom method [10]. In this method, a customized small resistive heater is mounted on the middle of a suspending UHMWPE film strip. Two thermocouples are mounted on the sample at one side but at difference distances. The whole fixture is put in a vacuum below 10^{-4} Torr. As the heater is powered by a periodic current or voltage, heat will transport along the film producing periodic temperatures (with different amplitudes and phases) at different locations along the film. With knowledge of the distance between thermocouples and measured temperature amplitudes and phases, thermal diffusivity of the film is calculated. A representative of the set-up and the measurements of Angstrom method are shown in Fig. 4.
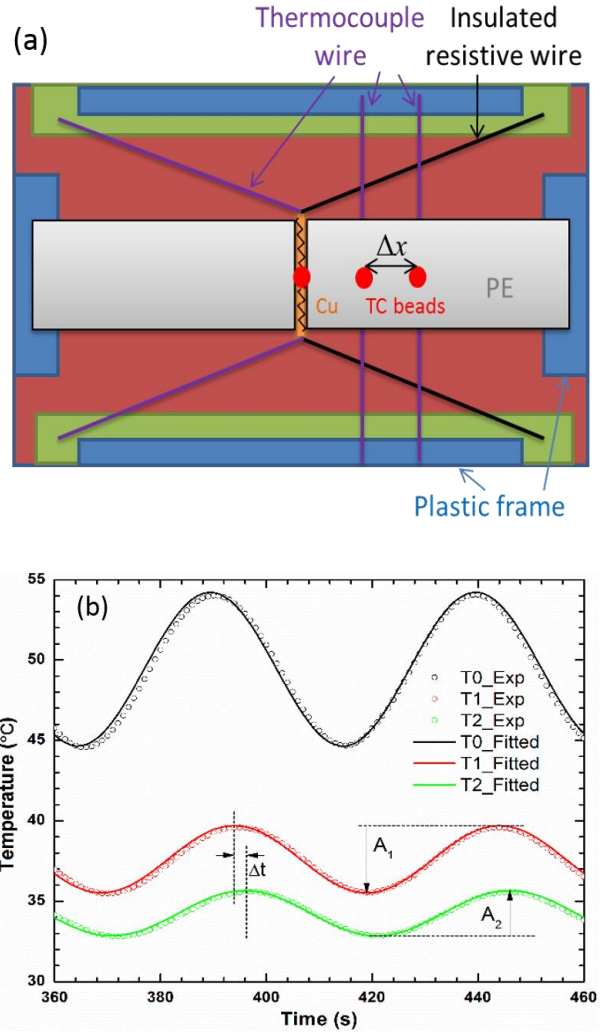

Fig. 4: (a) The set-up of Angstrom method for thermal conductivity measurements. (b) The typical temperature evolution in the UHMWPE film at different positions

The thermal diffusivity is then written as

$$\alpha = \frac{(\Delta x)^2}{2\Delta t \ln \frac{A_1}{A_2}}$$

Given the heat capacity (1.8 J/gK) and density (0.98 g/cm^3) of films, thermal conductivity is calculated. The set-up for thermal conductivity measurement is calibrated by reference material glass coverslip and plastic wrap film made of low density polyethylene. The thermal conductivity of several films with different draw ratios are shown in Table 2.

Table 2. Thermal conductivity of UHMWPE films

Sample	Thermal conductivity (Wm^{-1}K^{-1})±10%
1wt%, DR~1	0.36
1wt%, DR~108	3.4
1wt%, DR~432	10.1
3wt%, DR~1	0.4
3wt%, DR~25	11.66
3wt%, DR~125	16.38

measured by Angstrom method

CONCLUSIONS

High thermal conductivity UHMWPE thin films are developed by sol-gel process followed by the drawing process. With an automated drawing platform uniaxial stretching up to 400 draw ratio is achieved. The structural characterization of the fabricated films shows aligned polyethylene structure with 99% crystallinity. The thermal conductivity of these films are measured by Angstrom method which indicated a value of 16.4 Wm^{-1}K^{-1} at draw ratio of 125. Further optimization of the platform is in progress to achieve UHMWPE polyethylene sheets with higher thermal conductivities. This work opens a new avenue for fabrication of high thermal conductivity polymers for heat transfer applications (e,g. heat exchangers and heat spreaders).

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