

Electronic Supplementary Information (ESI)

Self-Reinforced Polyethylene Blend for Artificial Joint Application

Yan-Fei Huang,^a Jia-Zhuang Xu,^a Jun-Yi Xu,^a Zheng-Chi Zhang,^a Benjamin S. Hsiao,^c Ling Xu^{*b} and
5 Zhong-Ming Li^{*a}

^a College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, People's Republic of China. Fax: +86-28-85401988; Tel: +86-28-85406866; E-mail: zmli@scu.edu.cn (Z.M. Li)

^b State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, People's Republic of China. Tel: +86-28-85405731; E-mail: xulingshannon@gmail.com (L. Xu)

^c Department of Chemistry, Stony Brook University, Stony Brook, New York 11794-3400, United States

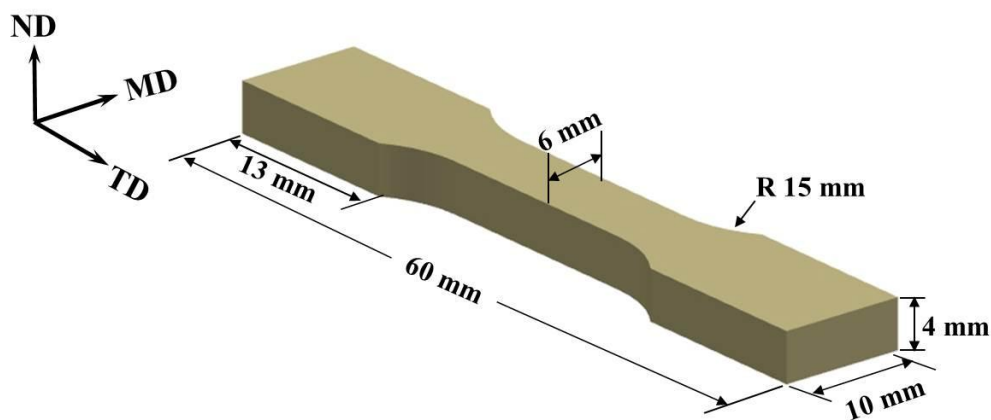


Fig. S1 Detailed dimensions of tensile test specimen.

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Table S1 Mechanical properties of the 40 wt% cross-linked UHMWPE/ 60 wt% LMWPE blend.

Ultimate tensile strength/ MPa)	Impact strength/ kJ m ⁻²
72.1 ± 0.6	29.7 ± 2.3

Table S1 shows the mechanical properties of the 40 wt% cross-linked UHMWPE/ 60 wt% LMWPE blend. The ultimate tensile and
20 impact strength are 72.1 MPa and 29.7 kJ m⁻², respectively.

Table S2 Mechanical properties, wear rate, and fatigue strength of neat LMWPE fabricated by oscillatory shear injection molding.

Ultimate tensile strength/ MPa	Young's modulus/ GPa	Impact strength/ kJ m ⁻²	Wear rate/ mg MC ⁻¹	Fatigue strength (%)
38.7 ± 0.9	1.07 ± 0.2	15.8 ± 3.7	17.3 ± 1.2	79 ± 3.0

Table S2 shows the mechanical properties, wear rate and fatigue strength of neat LMWPE fabricated by shear oscillatory injection molding under the same processing conditions. The ultimate tensile strength and Young's modulus of neat LMWPE are 38.7 MPa and 1.07 GPa, respectively, which are inferior to that of xUHPE blend (81.2 MPa and 1.98 GPa). The impact strength decreases from 35.2 kJ m⁻² for xUHPE to 15.8 kJ m⁻² for neat LMWPE. The wear rate and fatigue strength of neat LMWPE are 17.3 mg MC⁻¹ and 79 %, respectively, indicating inferior wear and fatigue resistance compared with the xUHPE blend (5.3 mg MC⁻¹ and 85.0 %).

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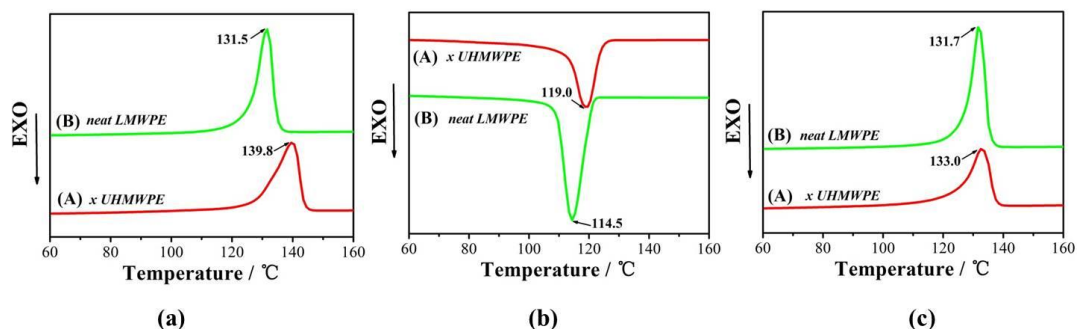


Fig. S2 DSC curves of xUHMWPE (A) and neat LMWPE (B): (a) the 1st heating thermograms; (b) the 1st cooling thermograms and (c) the 2nd heating thermograms.

15 The thermal behavior of 40 kGy-irradiated UHMWPE powder (xUHMWPE) and neat LMWPE was examined by a Perkin-Elmer diamond-II differential scanning calorimetry (DSC). Samples (3 ~ 5 mg) were firstly heated from 40 to 180 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere, and then held at 180 °C for 5 min. After that the samples were cooled from 180 to 40 °C at a rate of -10 °C min⁻¹, and again heated from 40 to 180 °C at a heating rate of 10 °C min⁻¹.

The melting temperature of xUHMWPE (139.8 °C) is higher than that of neat LMWPE (131.5 °C) in the first heating thermogram (Fig. S2a). The crystallization behavior of xUHMWPE and neat LMWPE is also shown in Fig. S2b, and the crystallization temperature of xUHMWPE and LMWPE is 119.0 and 114.5 °C, respectively. The thermograms of the second heating cycle showed the melting temperature of the remelted xUHMWPE and LMWPE is 133.0 and 131.7 °C, respectively. Considering the DSC data reported in the manuscript, the lower temperature at 133.9 °C (Fig. 7, curve A1) can be ascribed to the remelting of cross-linked UHMWPE and LMWPE.

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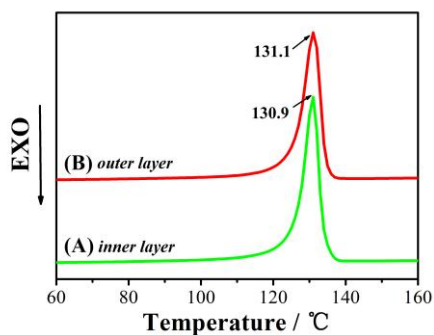


Fig. S3 DSC curves of oscillatory shear injection molded neat LMWPE from inner (A) to outer layer (B).

5 Fig. S3 shows the melting curves of oscillatory shear injection molded neat LMWPE. Only one melting peak around 131 °C appears in both outer and inner layers, indicating that only one type of crystalline structure exists in the whole sample.

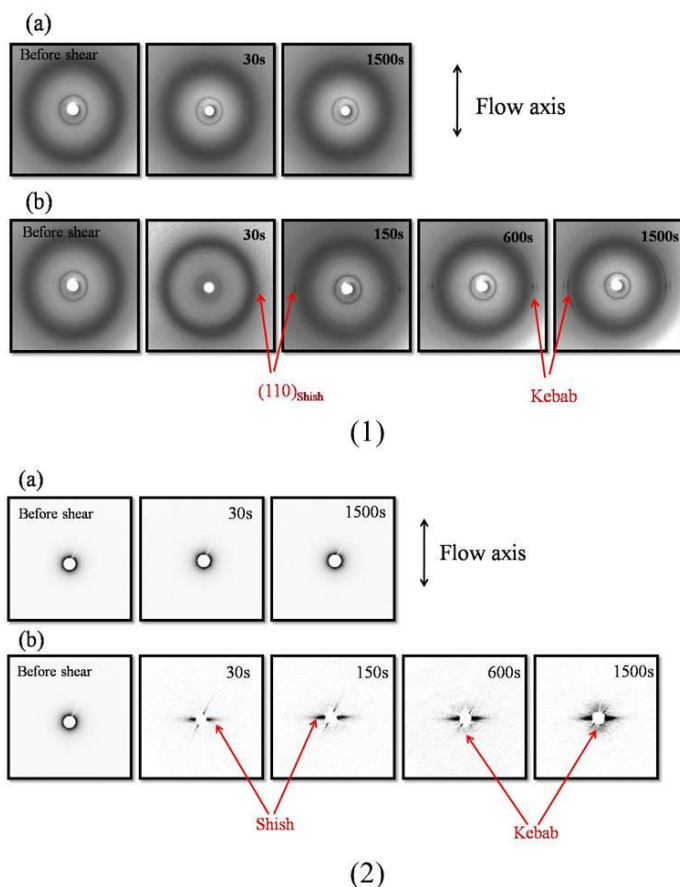


Fig. S4 Selected rheo-WAXD patterns (1) and rheo-SAXS patterns (2) of (a) neat LMWPE, (b) 2/98 wt % UHMWPE/LMWPE blend

10 obtained before and after the step shear at 138 °C ($\dot{\gamma} = 60 \text{ s}^{-1}$ and $t_s = 5 \text{ s}$)

The purpose of incorporating 2 wt% UHMWPE into LMWPE is to effectively induce the formation of shish-kebab. The background theoretical reason is: high-molecular-weight species (such as UHMWPE) facilitate the formation of shish-kebabs in the entangled melt under a given flow condition¹⁻³. The estimated overlap concentration of UHMWPE is deduced to be ~0.2 wt%⁴. In order to amplify the role of long molecular chains in inducing the shish-kebabs, a significantly higher concentration of UHMWPE (2 wt%) in LMWPE was used in this current work.

To verify our hypotheses, we measured the crystallization kinetics of neat LMWPE and 2/98 wt % UHMWPE/LMWPE blend after shear flow by in-situ WAXS and SAXS, which were carried out at the Advanced Polymers Beam-line (X27C, wavelength $\lambda = 0.137$ nm) with a Mar CCD (MARUSE) as detector in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The chosen temperature protocol was as follows: (a) heat the polymer sample from room temperature to 180 °C at a rate of 30 °C/min; (b) erase the thermal history of the polymer by holding the temperature at 180°C for 5 min; (c) cool down to 138 °C at a rate of 30 °C/min. Polymer melt was subjected to short-time shear (Linkam CSS-450 high-temperature shear stage) of 5 s with the shear rate of 60 s⁻¹. The entire crystallization process was monitored in real time. Two-dimensional X-ray images (SAXS and WAXD) were recorded before and after shear. The data acquisition time for each scattering pattern (image) was 15 s, with a pause time of 5 s between adjacent images.

Fig. S4 shows the selected rheo-WAXD and rheo-SAXS patterns, from which we know that signal of shish-kebab structure is observed in the system containing 2 wt% UHMWPE, but is not detected in the system without the initial UHMWPE. This result confirmed that incorporation of a small amount of UHMWPE effectively induced the formation of shish-kebab structures.

We also compared the mechanical properties of the xUHPE with (Fig. 2) and without 2 wt% UHMWPE (Table S3), and found that addition of 2 wt% did increase the mechanical properties.

Table S3 Mechanical properties of the blend of 50 wt% cross-linked UHMWPE and 50 wt% neat LMWPE

Ultimate tensile strength/ MPa	Impact strength/ kJ m ⁻²
67.5 ± 0.7	31.2 ± 1.8

Reference

- 1 F. Zuo, J. K. Keum, L. Yang, R. H. Somani and B. S. Hsiao, *Macromolecules*, 2006, **39**, 2209-2218.
- 2 M. Seki, D. W. Thurman, J. P. Oberhauser and J. A. Kornfield, *Macromolecules*, 2002, **35**, 2583-2594.
- 3 R. H. Somani, B. S. Hsiao and A. Nogales, *Macromolecules*, 2000, **33**, 9385-9394.
- 4 J. K. Keum, F. Zuo and B. S. Hsiao, *Macromolecules*, 2008, **41**, 4766-4776.