Supplementary Information

Enhanced Strength and Foamability of High-Density Polyethylene Prepared by Pressure-Induced Flow and Low-Temperature Crosslinking

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1. Materials

HDPE powder (SL series, density: 0.95 g/cm^3, melting temperature: 132-135°C, MFI: 8) was provided by National Institute of Clean and Low-Carbon Energy (Beijing, China). 3-Chloroperbenzoic acid (mCPBA, density: 1.482 g/cm^3, melting temperature: 92-94°C, boiling temperature: 302.76^{o}C), ethanol and xylene were purchased from Sigma-Aldrich (USA). All chemicals were used as received.

2. Experimental Process

2.1 Combine Pressure-Induced Flow Process with Low-Temperature Crosslink

The HDPE powder was placed in a press to form a circle sample (diameter: 5 cm, thickness: 5 mm). The circle sample was cut into the required rectangular plate (eg. 25mm×12mm×5mm) to fit the used mold. Then, the sample was put into the middle of the designed mold (as shown in Scheme 1a) in order to make it sufficient flow. Afterwards, the whole mold was placed into a vulcanizing press machine and pre-heated up to the certain temperature (110°C). The sample was forced to flow by applying enough pressure (450 MPa) on the top of the mold. Finally, after a short time (5min), the mold was removed from the press and cooled into the room temperature. Above process called pressure-induced flow (PIF) process.

We next introduced the properly crosslinking effect into the PIF processing. The rectangular HDPE plate, ie. 25mm×12mm×5mm, with lower crosslinking temperature was placed into the middle of the mold, and then put into the vulcanizing press machine.

The mold was pre-heated into the PIF temperature (110°C) and the desired pressure (450 MPa) was applied on the mold. After enough time (1 hour) for crosslinking and deformation, the mold was removed from the machine and cooled to the room temperature. The sample, which combined PIF processing with crosslinking, was obtained.

2.2 Supercritical CO_2 (scCO_2) Foaming Process

Various HDPE samples were foamed in a typical solid-state foaming process. Samples were placed in a high-pressure autoclave, injected CO_2 gas (purity 99.9%) and saturated at 120°C, 20 MPa for 1 day in order to reach complete saturation. After saturation, the high-pressure autoclave was rapidly depressurized to atmospheric pressure, and then cooled to the room temperature. After scCO_2 foaming process, the relative density of the samples was also measured.

3. Characterization

3.1 X-ray Diffraction (XRD)

XRD analysis was performed with a Bruker D8 Advance X-ray diffractometer (USA) machine using Cu Kα (k = 0.154056 nm) radiation at a scanning rate of 4°/min and scattering range of (2ϑ) 5-45° with the rotation speed of 30 rpm. The average crystallite sizes can be calculated from the integrated XRD patterns by using the Scherrer formula as follows:

$$D = \frac{K^* \lambda}{\beta \cos \theta} \qquad (1)$$

Where ϑ is Bragg angle, β is half-peak breadth, D is crystallite size (nm), λ= 0.154056 nm and K= 0.9.

3.2 Differential Scanning Calorimetry (DSC)

DSC tests were carried out under nitrogen atmosphere to investigate the crystallization capacity with a DSC Q200 instrument (TA, USA). The neat PE samples were first heated to 200°C at a heating rate of 10°C/min and kept isothermal for 3 min to eliminate thermal history, then cooled to 20°C at a cooling rate of 10°C/min and subsequently scanned to 200°C at the same rate. The PIF samples were just heated to 200°C at a heating rate of 10°C/min in order to avoid melting the "brick and concrete" structure. The degree of crystallinity (X_c) of the polymer can be calculated using the equation as follows:

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \qquad\qquad (2)$$

Where, ΔH_m is the melting enthalpy obtained by the DSC curves, ΔH_m^0 is the enthalpy of 100% crystalline HDPE sample, which is 288 J/g for the HDPE used in this study.

3.3 Dynamic Mechanical Analysis (DMA)

DMA test was conducted by using a dynamic mechanical analyzer (Netzsch DMA242, German) in dynamic creep mode (110°C) and single cantilever mode (strain amplitude of 50 μm, oscillatory frequency of 1 Hz, temperature range of -100 to 100 °C and at a heating rate of 3°C/min), respectively.

3.4 Gel content Determination

The determination of gel content was conducted according to ISO/DIS 17278:2012. Before the determination, the neat PE samples was weighed as m_0 and then placed into an oven at 110°C for 0.5h, 1.0h, 1.5h, 3h, respectively. The as-prepared samples were wrapped in a stainless steel cage(each samples were weighed as m1) and extracted by using boiling xylene for 24h. After extraction, the samples were removed from the tube and dried in vacuum oven to completely remove the residual solvents. The samples were recorded as m_2 after completely remove xylene. The gel content can be determined by using the equation as follows:

$$Gel\ content(\%) = \frac{m_2 - m_1}{m_0} \tag{3}$$

The XLPE, PIF PE and PIF XLPE samples were determined by using the same method as above.

3.5 Mechanical Properties

The tensile strength and flexural strength were tested to investigate the effects of PIF and crosslinking on the mechanical properties of PE, and the compressive strength was used to characterized the mechanical property of the foamed samples. Tensile and compressive tests were performed on a universal testing machine (Instron 5566, USA) at room temperature with a 50 kN load cell, and flexural test was conducted using the same machine with a 5 kN load cell. Five specimens were tested for each sample.

3.6 Scanning Electron Microscopy (SEM)

The microstructure of neat PE, PIF PE and PIF XLPE samples and the cross-section views

of foamed neat PE, PIF PE and PIF XLPE samples were examined using a field emission scanning electron microscope (SEM), Hitachi S-4300 (Tokyo, Japan). The samples were coated with gold for 5 min prior to observation. The average cell size was determined by analyzing SEM micrographs using Image-pro Plus Software. The cell density (N_o) was calculated by the following equation:

$$N_o = \left[\frac{N}{A} \right]^{\frac{3}{2}} \qquad\qquad (4)$$

Where N is the number of pores in the SEM micrograph, A is the area of the picture (cm²).
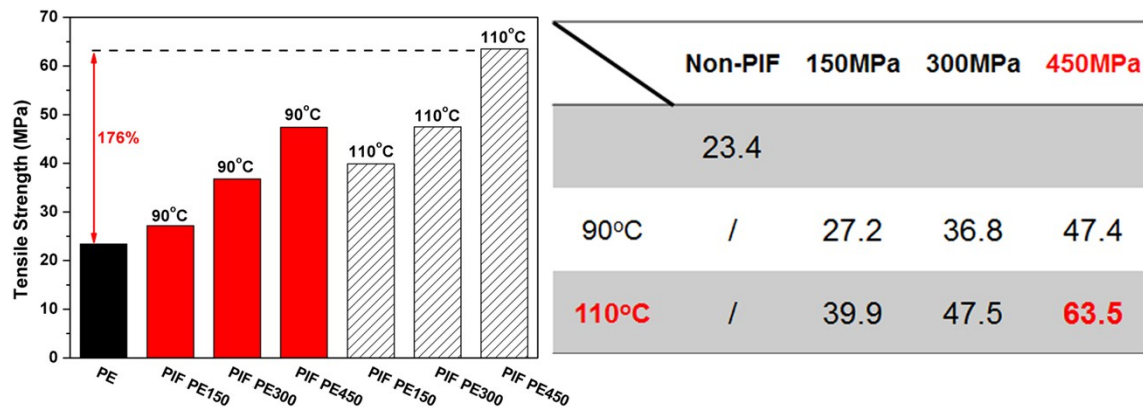
4. Optimal PIF Processing Condition

Figure S1. Tensile strengths of HDPE samples by the PIF process with different conditions.

We tested different PIF conditions of HDPE and compared their tensile strengths. As shown in Figure S1, higher the pressure and temperature, larger the tensile strength of HDPE by the PIF process. The optimal conditions were selected as 450 MPa and 110°C.

5. DSC Results of Neat PE, PIF PE and PIF XLPE Samples

Table S1. The DSC results of investigated samples.

Samples	T_m (°C)	ΔH_m (J/g)	X (%)
Neat PE	132.3	165.0	57.3
XLPE	136.5	171.1	59.4
PIF PE	137.2	181.2	62.9
PIF XLPE	144.2	195.8	67.9

6. Gel Contents of XLPE Samples with Various Crosslinking Times
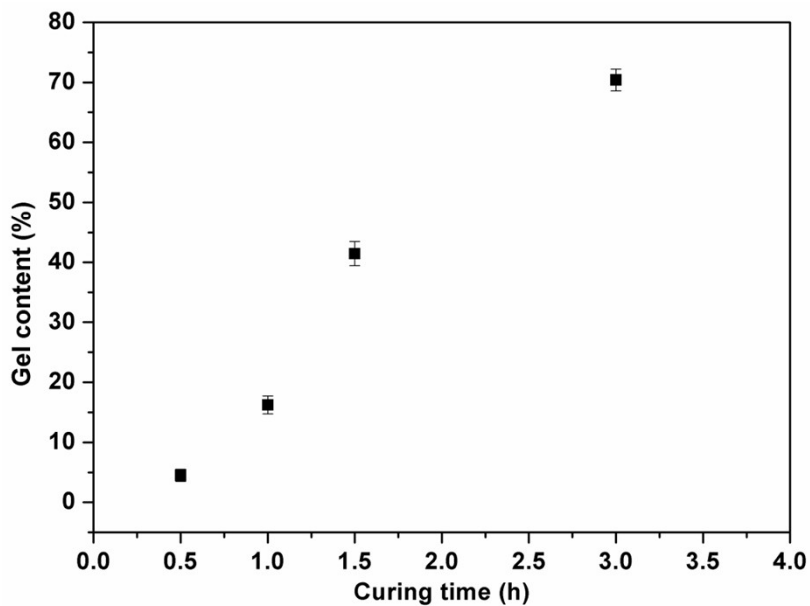
Figure S2. Gel contents of XLPE with various curing times at 110°C.

When increasing the crosslinking times, the gel content of XLPE samples is inceased as a

S-type trend (Figure S3). Such very high gel content (>70%) can be reached after 3 h of

curing times at 110°C. However, excessive crosslink helps not to improved the tenstile strengths of XLPE samples.

7. Tensile Strength of HDPE by the PIF Process with Various Crosslinking Times
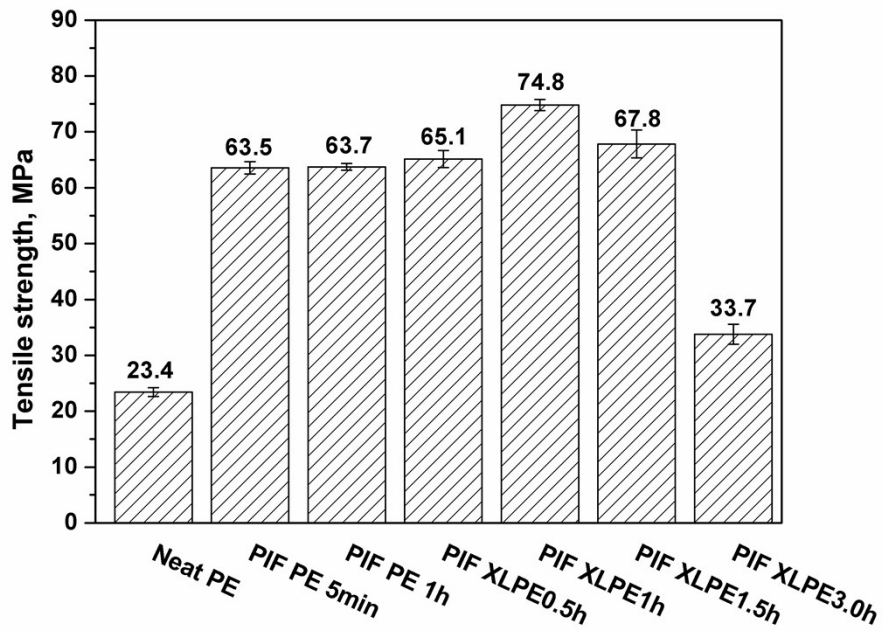

Figure S3. Tensile strengths of neat PE, PIF PE and PIF XLPE with various processing times.

To optimize the crosslinking time, samples with various processing times were prepared and tested. As shown in Figure S4, the PIF XLPE sample has a maximum tensile strength when take 1h for PIF and crosslink process. Excessive crosslink shows rigid and declined tensile strength.

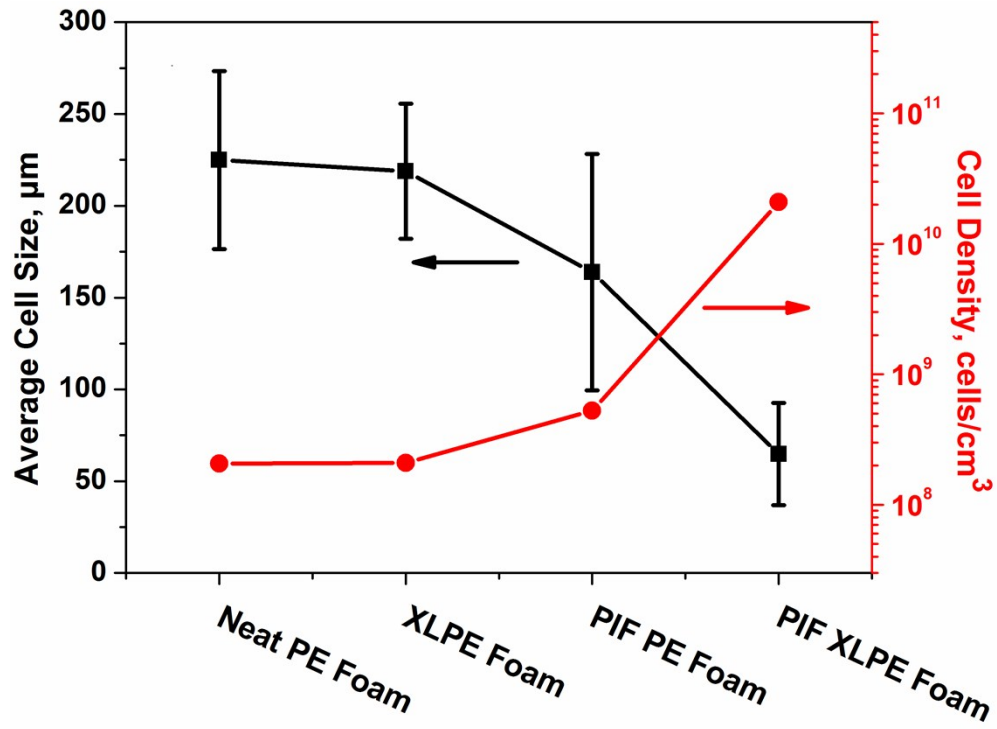**8. Average cell size and cell density of the foams**

Figure S4. Average cell size and cell density of foams

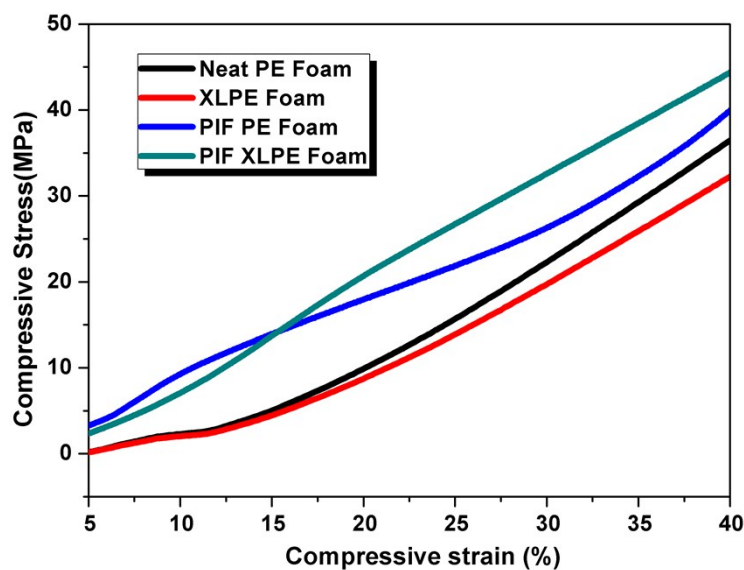## 9. Compressive Stress-Strain Curves of Foamed Samples

Figure S5. Compressive stress-strain curves of various PE foamed samples.

The original compressive strengths of foamed samples are shown in Figure S5. After the

$scCO_2$ foaming process, PIF PE and PIF XLPE samples shows better compressive strengths

than them of neat PE and XLPE samples.

10. DSC Results of Foamed Samples

Table S2. The DSC results of various HDPE foamed samples.

Samples	T_m (°C)	$\varDelta H_m$(J/g)	X (%)
Neat PE	139.3	191.8	66.6
XLPE	140.1	196.6	68.3
PIF PE	141.0	204.8	71.1
PIF XLPE	144.8	210.8	73.2