Supporting information

Crystallization of Linear Low Density Polyethylene on In Situ Oriented Isotactic Polypropylene Substrate Manipulated by Extensional Flow Field

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Fig. S1 (a) 1D-WAXD curve and (b) DSC melting curve of LLDPE/iPP pellet obtained by twin-screw extrusion, showing the crystalline structure and crystallinity of LLDPE/iPP pellet respectively. (The 2D-WAXD pattern is inserted in Figure S1a)
Fig. S2 Schematic diagram of “extrusion-hot stretching-quenching” process.

To confirm whether the crystallites in LLDPE/iPP pellets will be completely melted or not before hot stretching, the staying time of the pellets in the single screw extruder was tested to be about 95 s, and the heating rate of the pellets from room temperature to 180 °C was calculated to be 88.4 °C/min. Herein, DSC and online FTIR were applied to simulate the melting behavior of the pellets in the single screw extruder. As shown in Figure S3a, under the rapid heating rate of 88.4 °C/min, the melting peak temperature for LLDPE and iPP is 127.6 and 163.6 °C respectively, and no obvious melting peak was observed when further heating from 180 to 200 °C, indicating that no crystallites still exist. The same conclusion can be reached by online FTIR. Figure S3b presents the temperature dependent FTIR spectra of the pellets during rapid heating of 88.4 °C/min. It can be clearly seen that the band at 730 cm\(^{-1}\) and bands at 808, 841, 900, 998 and 1167 cm\(^{-1}\) disappear totally at 136.4 and 182.8 °C, respectively. Since the band at 730 cm\(^{-1}\) is associated with crystalline a-axis of PE\(^{1,2}\) and the bands at 808, 841, 900, 998 and 1167 cm\(^{-1}\) belong to 3/1 helical structure of iPP\(^{3,4}\) it can be definitely concluded that all the
crystallites in pellets are completely melted at 180 °C, which is consistent with the results of DSC.

Fig. S3 (a) DSC melting curve of LLDPE/iPP pellet and (b) the development of FTIR curves for LLDPE/iPP pellet during heating from 90.0 °C to 200 °C. (Note that the heating rates for DSC and FTIR are both 88.4 °C/min)
Scanning electron microscopy (SEM) was utilized to observe the phase morphology of LLDPE/iPP common blend and stretched blend. The test specimens were cryogenically fractured in liquid nitrogen along the stretching direction. Then the fractured surface was sputter-coated with a thin layer of gold and observed by a field-emission SEM (Inspect F, FEI, Finland) operating at 20 kV.

As revealed by Fig. S4, for LLDPE/iPP common blend, discrete droplets of iPP phase are dispersed in the LLDPE matrix, showing the classic “sea-island” structure. In clear contrast, after the application of extensional flow field by hot stretching iPP phase shows a microfibrillar morphology, evidencing the transition of iPP particles to microfibrils along the stretching direction. Nevertheless, compared with other in situ microfibrillar blend systems, such as poly (ethylene terephthalate) (PET)/iPP, poly (butylene succinate)/poly (lactic acid), polyethylene/polyamide (PA), etc., the length-diameter ratio of iPP microfibrils in this work is relatively small, representing a range from 5 to 10.

The limited deformation of iPP phase in this work, in principle, lies in the high viscosity ratio of iPP to that of LLDPE. According to the melt flow rate (MFR) of iPP and LLDPE in this work, under load of 2.16 Kg, MFR of LLDPE is 20 g/10min at 190 ºC, while that of iPP shows only 3 g/10min at 230 ºC, thus it can be concluded that the melt viscosity of LLDPE is much lower than that of iPP when stretching, finally leading to limited stress transfer efficiency from LLDPE matrix to iPP phase and serious coalescence of iPP phase during stretching. However, iPP chain is more flexible than PET as well as PA investigated before, thus the iPP substrate still has high molecular orientation to induce
the epitaxial crystallization of LLDPE as identified by FTIR and X-ray diffraction in our work, although the deformation of iPP phase is limited.

**Fig. S4** SEM images of LLDPE/iPP (a) common blend; (b) stretched blend. (The stretching direction is horizontal)

**Fig. S5** 2D-SAXS pattern of LLDPE/iPP stretched blend with the HSR of 17.1, showing the structure of shish-kebab. Note that the signal of shish is relatively too weak to clearly detect, which is mainly due to its low concentration.\textsuperscript{10,11}
Fig. S6 Azimuthal scan of LLDPE (200) plane in 2D-WAXD pattern of LLDPE/iPP stretched blend.

Notes and references


