

Unique impact behavior and toughening mechanism of the polypropylene and poly(ethylene-co-octene) alternating multilayered blends with superior toughness

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Supplementary Information

DSC, WAXD and Polarized FTIR measurements, the melt behaviors of the multilayered PP/POE blends and conventional blends and neat PP, the 1D-WAXD curves and 2D-WAXD patterns of neat PP and PP/POE multilayered blends, and a typical part of polarized FTIR spectra absorbance in the parallel and vertical to the flow direction for neat PP and PP/POE multilayered blends are provided.

EXPERIMENTAL

Differential scanning calorimetry (DSC) measurement

The thermal analysis of the some heat treated samples were conducted with the instrument (Q20, TA Instrument), calibrated by indium. The mass of tested samples was about 8 mg and the thermal treated samples were directly heated from 23°C to 200°C with a rate of 10 °C/min. The degree of crystallinity was calculated from heat of fusion according to following formula:

$$X = \frac{\Delta H}{\Delta H^o} \quad (2)$$

where ΔH is the calibrated specific fusion heat of the samples by integrating area of the melting peak, and ΔH^o is the standard fusion heat of 100% crystalline PP, 209 J/g [1].

2D wide-angle X-ray scattering

The 2D wide-angle X-ray scattering (2D WAXS) experiments were conducted on a German Bruker (D8 Discover) diffractometer. The wavelength of the monochromated X-ray from Cu Ka radiation was 0.154 nm and the transmission mode was used. The samples were placed with the orientation (flow direction) perpendicular to the beams. The spectra were recorded in the diffraction angle (2θ) range of 5° ~ 35° at 40 kV and 40 mA. The overall crystallinity, X_c , was calculated according to the following equation:

$$X_C = \frac{\sum A_{cryst}}{\sum A_{cryst} + \sum A_{amorp}} \quad (3)$$

where *A_{cryst}* and *A_{amorp}* are the fitted areas of crystal and amorphous region, respectively.

Polarized FTIR measurement

The molecular orientation of PP phase in different samples was measured by a Thermo Nicolet iS10 FTIR spectrometer with a resolution of 2cm⁻¹ and an accumulation of 64 scans. The test slice samples with thickness about 20 μm were cut by a rotary Microtome (YD-2508B) along the flow direction from the centre of heat treatment and virgin samples, respectively. Polarized infrared spectra, both parallel and perpendicular to the flow direction, were collected by rotating a ZnSe polarizer. The orientation function *f*, dichroic ratio *R* and structural absorbance *A* of the desired absorption band are deduced by using the following relations [2]:

$$f = \frac{(R-1)/R+2}{(3\cos^2\alpha-1)/2} \quad (4)$$

$$R = A_{\parallel}/A_{\perp} \quad (5)$$

where *A_∥* and *A_⊥* are the parallel and perpendicular absorbance at the same positions, respectively, and *α* is the angle that the transition moment makes with the polymer chain axis, which was taken to be equal to 18°, as mentioned in ref. [2].

For PP, the absorption at a wave number of 998 cm⁻¹ is attributed to

the crystalline phase (c axis), whereas the absorption at a wave number of 972 cm^{-1} is due to the contributions of both the crystalline and amorphous phases. From the former absorption, the orientation of the crystalline phase (f_c) is determined, whereas from the latter, the average orientation function (f_{avg}) is obtained [3]. Generally, higher values of dichroic ratio R always indicate obvious orientation of the materials. There is hardly any orientation in materials in the case that the value of the R is close to 1.

RESULTS AND DISCUSSION

The DSC melting curves are used to investigate the influences of the same heat treatment on the crystalline structure of PP, and the first heating curves are presented in Figure. S1. As expected, it's no distinct thermal difference between the multilayered and conventional samples after heat treatment, while the melting point of the multilayered samples is slightly higher than that of the conventional blending samples. Moreover, there is almost no difference in the multilayered samples with different layers, and both the multilayered and conventional samples have close crystallinity. Additionally, the incorporation of POE seems to have negligible effects on the melting curves of the PP phase in both the multilayered and conventional blends. It's difficult to recognize the POE

melting peak in all samples since both the crystallinity of neat POE and the POE content are low.

To further obtain crystalline information, the representative virgin and heat treated samples were investigated by 2D-WAXD, and the results are shown in Figure. S2. Clearly, the diffraction intensity distribution basically consists of four diffraction circles associated with different lattice planes of PP, including (110), (040), (130), and ((131), (041)), which are typical of α -crystals. Molecules tend to orient along the flow direction, and this can be well observed from the virgin C0-128 2D-WAXD diffraction pattern. Four arches are formed in the diffraction circles for the (110) and ((131), (041)) lattice planes while only two sharp spots are observed along the meridian in those for the (040) and (130) lattice planes. All these characteristics indicate the high molecular chain orientation in C0-128 along the flow direction. As expected, all 2D-WAXD patterns of the heat treated samples show four perfect diffraction circles, indicating that the molecular orientation of the heat treated samples had been really eliminated. After circularly integrating intensities of WAXD patterns, one-dimensional wide-angle X-ray diffraction (1D-WAXD) curves are shown in the Figure. S3. It is clearly that all diffraction peaks of the samples present the same location, and the crystallinity of PP phase in all heat treatment samples calculated according to the equation (3) are almost invariable, both indicate that the

addition of POE into PP has little effects on the crystalline structure of PP, which is consistent with the DSC results.

The orientation of the PP molecular chains is also studied through the polarized FTIR. A typical part of FTIR spectra absorbance in the parallel and perpendicular to flow direction for neat PP and PP/POE multilayered blends is shown in Figure. S4. The dichroic ratio R of the virgin C0-128 is much higher than that of the other heat treated samples, indicating higher orientation of PP molecules chains in the virgin C0-128. As for the heat treated samples, the value of R is close to 1, indicating the orientation of PP molecules has been removed. Therefore, it can be concluded that the heat treatment condition, which under 10 MPa for 10 min at 200 °C, indeed removed the shear and thermal history.

REFERENCES

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- (3) S. H. Tabatabaei, P. J Carreau and A. Ajji, J. Membr. Sci. 2009, 345, 148-159.

Illustration for the numbered graphics of the supplementary information

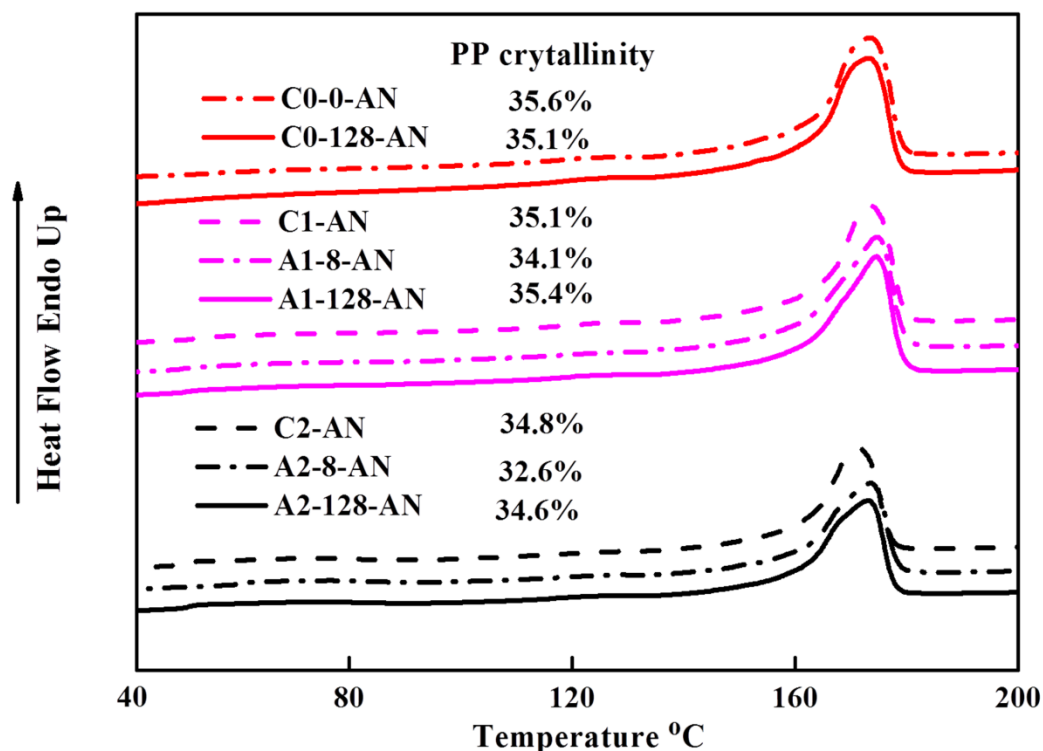


Figure S1. First DSC heating curves of the PP/POE multilayered and conventional blends and neat PP, The values of PP crystallinity calculated from the curves are given in the profile. (suffix “AN” means the samples have been thermally treated)

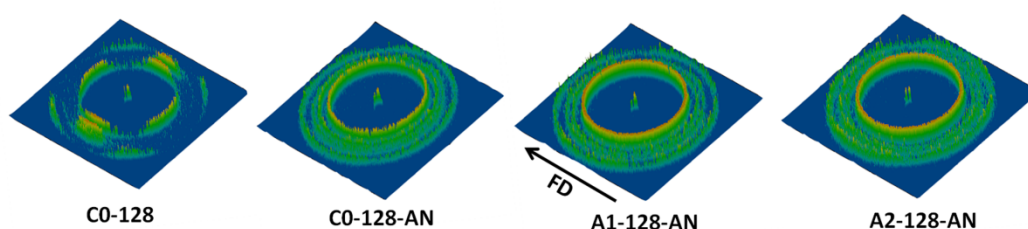


Figure S2. 2D-WAXD patterns of neat PP and PP/POE multilayered blends (C0-128: without heat treatment; C0-128-AN, A1-128-AN and A2-128-AN: heat treatment)

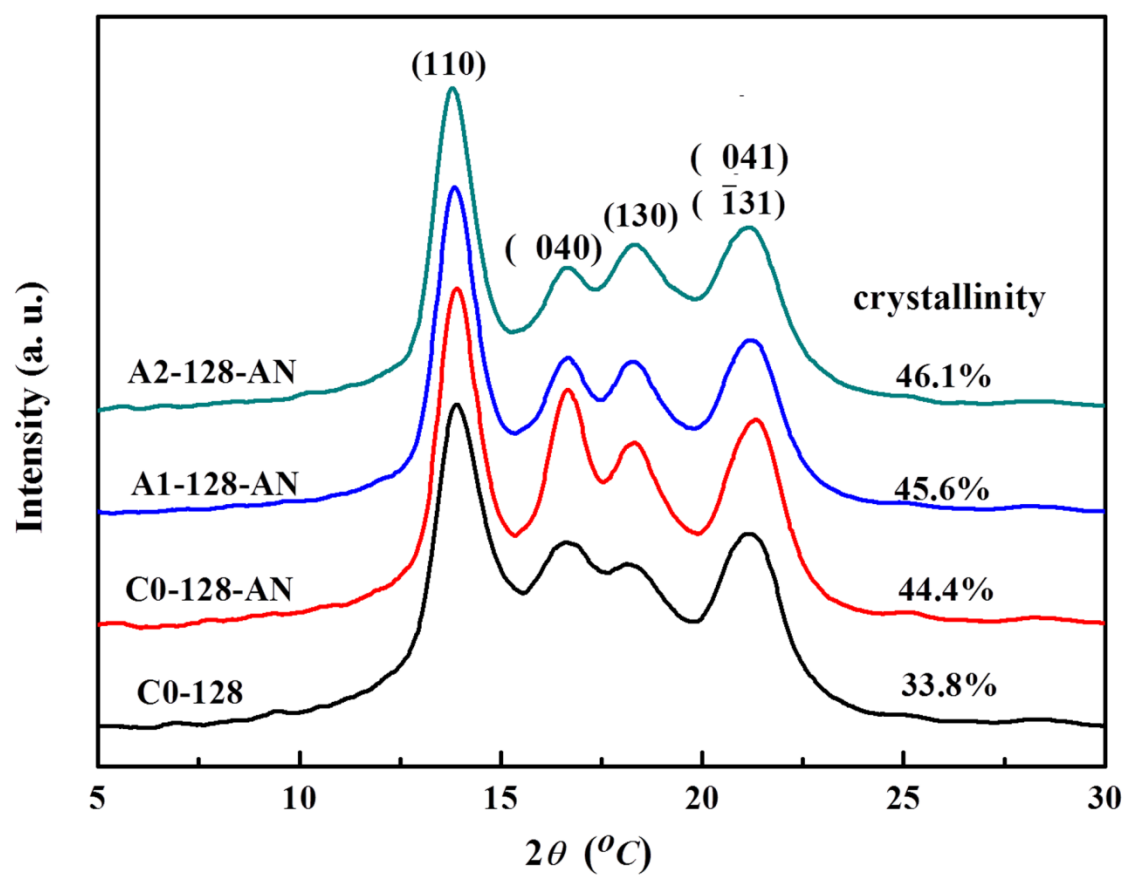


Figure S3. 1D-WAXD curves of neat PP and PP/POE multilayered blends (C0-128: without heat treatment; C0-128-AN, A1-128-AN and A2-128-AN: heat treatment)

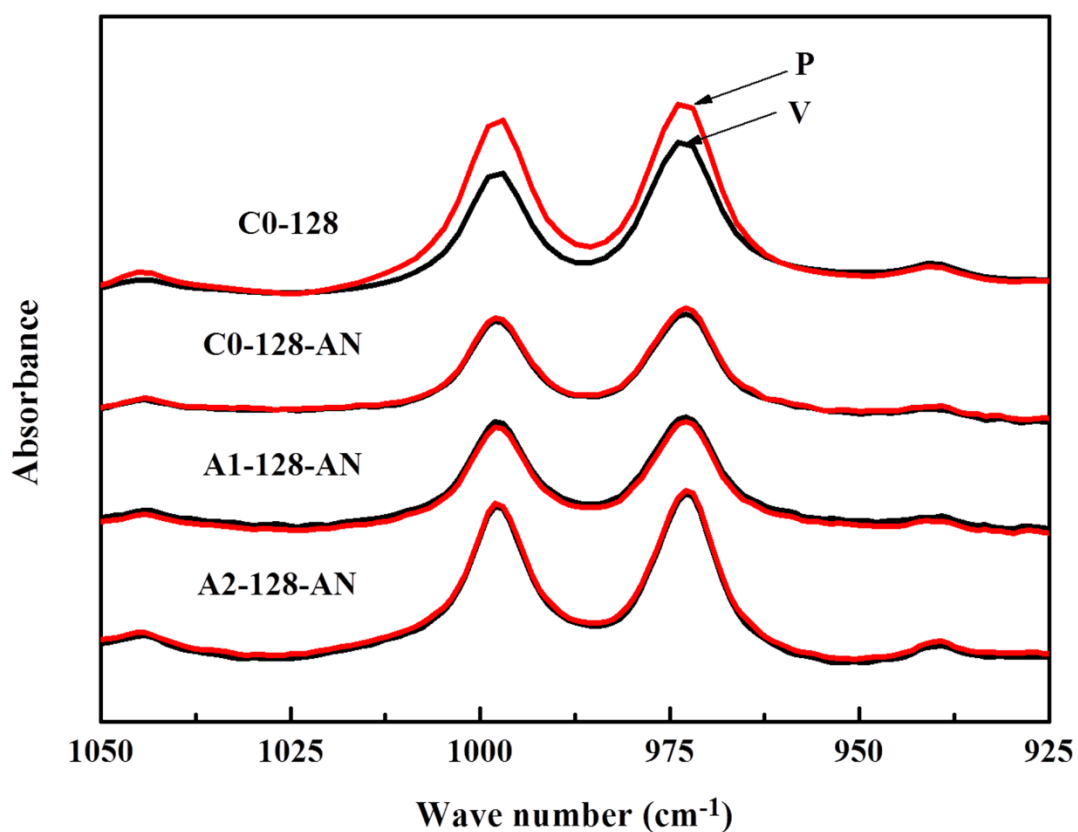


Figure S4. A typical part of FTIR spectra absorbance in the parallel and vertical to the flow direction for neat PP and PP/POE multilayered blends (C0-128: without heat treatment; C0-128-AN, A1-128-AN and A2-128-AN: heat treatment)