The influence of blend composition and filler on the microstructure, crystallization, and mechanical behavior of polymer blends with multilayered structures

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ABSTRACT

The preparation of multilayered structures has been thought as a complicated process until our recent study illustrating an effective method through high speed thin wall injection molding (HSTWIM) of polypropylene (PP) and polyethylene (PE) based blends. Current study investigates the effect of blends composition as well as the addition of carbon nanotubes (CNT) on the structure and properties of these blends. It is observed that a close ratio of high density polyethylene (HDPE) and impact copolymer polypropylene (ICP) triggers the formation of a multilayered structure. Meanwhile, PE is migrated into the rubber phase in ICP, leading to the distribution of some rubber phase on the interface between PP and PE, which is thought as beneficial for the interfacial interaction. Meanwhile, epitaxial growth of PE crystals on PP substrate is also observed. The presence of rubber phase on the interface, multilayered structure and epitaxial growth of PE crystals on PP are thought to be responsible for the observed mechanical enhancement in tensile strength as well as strain at break. Furthermore, the addition of CNTs leads to enhanced strength, reduced strain at break and anisotropic conductive network.

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1. Introduction

In nature, there are many interesting structures which endow various materials with interesting and useful properties, the multilayered structure, observed in wood, shells, wings of the butterfly, etc. is one of them. More and more attention has been focused on this structure, which can lead to the fabrication of various functional materials, such as anisotropic conductive materials [1–4], barrier materials [5], dielectric materials [6], flame-resistant materials [7], robust mechanical properties [8–10] and so on. A number of methods [11,12], such as layer by layer spraying [13–15], layer-by-layer assembly [16,17], layer multiplying coextrusion
[18–21], pressure-induced flow (PIF) processing [22], uncontrolled casting of polymer/clay mixtures [23–25], ice-templating and sintering of ceramics [26,27], bidirectional freezing [28], etc. have been proposed to prepare materials with such multilayered structure. However, the application of these methods was hindered by the complex preparation procedure, or low production efficiency, etc.

In our recent works, the multilayered structure was fabricated through high speed thin-wall injection molding (HSTWIM) using polymer blends based on polyethylene (PE) and polypropylene (PP) [29]. PE phase and PP phase is stretched and deform to fibers or lamellae under strong shear action, and then these fibers or lamellae overlap to layers, finally form the alternating multilayer structure. Thanks to the fast cooling rate this multilayer structure is froze immediately. It was demonstrated that the microstructure of these injection molded products was not only influenced by thermodynamic factors [30], such as viscosity, melt elasticity, and interfacial interaction, but also kinetic factors [31] injection speed, mold temperature and mold thickness. Based on above studies, various functional materials, like anisotropic conductive materials [1] and barrier materials [5], could be fabricated by selective dispersing fillers into one of the polymer layers.

As well known, the composition ratio is also a key issue for the fabrication of multilayered structures, because it can largely effect the microstructure and properties of these materials. Meanwhile, the addition of fillers can also influence the structure of these materials and bring interesting functionalities to the final product [32–37]. Hence, current investigation is focused on the influence of blends composition ratio and the addition of fillers on the formation of multilayered structures. The high density polyethylene (HDPE), impact copolymer polypropylene (ICP), containing 21% rubber [ethylene-propylene rubber (EPR)] content, and carbon nanotubes (CNT) were used to study the influence of composition ratio and filler on the microstructure, crystallization behavior, and mechanical behavior.

2. Experimental

2.1. Materials

The melt flow rate of HDPE and ICP, used in this study, are 20 g/10 min (190 °C, 2.16 kg) and 20 g/10 min (230 °C, 2.16 kg), and the density of above materials are 0.956 g/cm³ and 0.9 g/cm³, respectively. According to the supplier, ICP has 21% rubber content. Carbon nanotubes (CNT) are provide by Nanocyl S. A. (NC 7000). It has an average diameter of 9.5 nanometers, an average length of 1.5 microns, and surface area of 250–300 m²/g according to the producer.

2.2. Sample preparation

HDPE and ICP were mixed with different composition ratios using twin-screw extruder with barrel temperature of 200 °C and screw speed of 150 rpm. After that, these blends were processed by high speed thin-wall injection molding (HSTWIM) and compression molding (CM), respectively. Meanwhile, CNT was added into HDPE before blending with ICP to fabricate HDPE-CNT/ICP composites. Subsequently, these composites were processed with HSTWIM.

2.2.1. High speed thin-wall injection molding (HSTWIM)

Supplementary Information Figure S1 shows the schematic diagram of thin wall parts which is a cuboid shape with a size of 80 × 60 × 0.4 mm. A larger thickness cavity was attached to the end of cuboid to allow high injection speed before polymer melt fills the mold completely. All samples were processed under an injection speed of 600 mm/s, injection distance of 50 mm and mold temperature of room temperature without any holding pressure. All injection parameters are set values. In addition, the barrel temperature is 160–200 °C, and the screw diameter is 25 mm.

2.2.2. Compression molding (CM)

The materials were pre-heated at 200 °C for 15 min, and then hot pressed at 2 MPa for 3 min, 5 MPa for 2 min, 10 MPa for 3 min, finally cold pressed at 10 MPa for 5 min.

2.3. Tensile testing

Tensile tests were performed with a crosshead of 20 mm/min at temperature of 25 °C on a SANS universal testing machine. The results are mean values of six specimens for each composition ratio.

2.4. Atomic force microscopy (AFM)

The microstructure was investigated under AFM (Bruker Dimension ICON) with tapping mode. The resonance frequency of the cantilever is 200 kHz, and the scan rate is 1 Hz.

2.5. Scanning electron microscopy (SEM)

The microstructure observation was also performed on SEM (FEI Inspect F) with a voltage of 20 kV.
These samples were fractured after being immersed in liquid nitrogen for 2 h. After that, they were chemically etched in mixed acid (concentrated sulfuric acid: 85% orthophosphoric acid = 2:1) which contain 3% potassium permanganate. Finally, they were washed, dried, gold-coated and observed with SEM.

2.6. Two dimension wide angle X-ray diffraction (2D-WAXD)

2D-WAXD measurement was performed on a Bruker DISCOVER D8 diffractometer at ambient temperature. And XRD data were collected using Cu-Kα radiation with 900 s exposure time. The full width at half maximum (FWHM) was calculated using the (040) reflection of WAXD for PP and the (110) for PE to assess the molecular orientation.

2.7. Different scanning calorimeter (DSC)

Thermal analysis was carried out on a Perkin–Elmer DSC Pyris-1, indium calibrated. Melt endothermic curves were obtained at 10 °C/min with 4–7 mg sample in nitrogen atmosphere. To compare with pure polymer, the crystallinity $X_c$ of component $i$ in the blends is normalized by following equation:

$$X_c = \frac{\Delta H_i}{\Delta H_i^{m} \phi_i}$$

where $\Delta H_i$, $\Delta H_i^{m}$ and $\phi_i$ are the enthalpy of fusion of component $i$ (directly obtained from DSC), the enthalpy of fusion of pure polymer $i$ and the mass fraction of component $i$ in the blend, respectively. The $\Delta H_i^{m}$ of 100% crystalline polymer is 293 and 177 J/g for HDPE and $\alpha$ phase of PP, respectively [38].

2.8. Conductivity tests

The samples were cut to cuboid and then coated with silver at two sides. After that, the resistance of samples were measured using an electrometer (Keithley6487) in two-wire resistance measurement configuration. Thus, the conductivity could be calculated with the equation as follow:

$$\sigma = \frac{1}{RS}$$

where $\sigma$ represents conductivity, $R$ represents resistance, $l$ represents the length between two sides of cuboid without silver, and $S$ represents the cross-section area.

3. Results and discussion

To study the influence of composition ratio on phase morphology, crystallization and mechanical behavior of polymer blends, HDPE/ICP blends with different composition ratios were processed by two different methods: CM and HSTWIM. The phase morphology of HDPE/ICP blends were observed with AFM and SEM. As shown in Figure 1, AFM images demonstrate that HDPE is the pure phase, while rubber phase is observed in ICP. It should be noted that the rubber phases are migrated from PP to PE phase (or PE phase is distributed into rubber phase for relative low PE content) in the blend. It is especially obvious when Figure 1(f) is compared
with Figure 1(g). There are some 'phase in phase' phenomena visible as the PE phases appear in rubber phases when the rubber phases is dispersed in PP phase (as noted in Figure 1(g)). When ICP and HDPE were mixed through twin-screw extrusion, the PE phase would migrate into the rubber phase in ICP, ending up at the interface between PE and PP phase for rather low PE content. Such migration should be caused by the rather large PE content in the rubbery intermediate layers of these rubber phases as demonstrated by Su et al. [39]. These rubber phases at the interface could strengthen the interfacial interaction between different layers. When ICP content reaches 70%, the PE phase is dispersed in PP phase and illustrate a fibrous structure, and the dispersed phases (PE) are deformed and oriented in shear direction. While HDPE content reaches 70%, PP phase is deformed into fibers, and is hard to be observed from shear direction owing to the small diameter of the fibers as shown in Figures 1 and 2 and Supplementary Information Figure S2. When PE content is close to PP content, the alternating multilayered structure is observed with some of these rubber phases located at the interface. Therefore, HDPE/ICP blends (50:50) have the most regular multilayered structure.

From Figure 2 and Supplementary Information Figure S2, it is observed that the phase morphology in surface MD (machine direction) × ND (normal direction) changes from discontinuous fibers to regular continuous layers and then to irregular lamella with increasing PP content, with 50:50 blends having the most regular layered structure. Continuous layers are observed when minority phase increases to 40%. The phase morphology of other surface TD (transverse direction) × ND changes from "sea-island" structure to multilayered structure and then back to 'sea-island' structure with different ratios between HDPE and ICP. The similarity with the surface MD × ND is the presence of a continuous layered structure while the minority phase increases to 40%. As discussed above, it can be inferred that the alternating multilayered structure which is parallel to surface MD × TD is fabricated when the minority phase content is >40%, and the most regular multi-layered structure is observed for HDPE/ICP (50:50). This agrees with AFM results. As shown in Supplementary Information Figure S3, 'sea-island' structure is observed for CM samples. For PP content below 40%, the quantity of dispersed phase increases and the size changes little with increasing PP content. With further increasing PP content, not only the quantity of dispersed phase increases, but also the size increases. Then, the structure is changed to continuous structure when PP content increases to 60%. The phase inversion is completed with further increasing PP content, while PE phase becomes
dispersed phase. After that, the quantity of dispersed phase and the size decreases with further increasing PP content.

With the addition of CNT, the phase morphology of HDPE-CNT/ICP composites is different from that of HDPE/ICP. A layer-like structure is observed for blend 50:50, while an ‘island-sea’ structure is observed for samples with ratio of 30:70 and 20:80, as shown in Figure 3 and Supplementary Information Figure S4. As to other blends, the detail phase morphology can not be observed clearly thanks to a mass of CNTs on etched fracture surface. In general, the addition of CNT damages such layer structure. It is thought that the HDPE-CNT phase is easier to form a continuous phase thanks to entanglements between CNTs, with these CNTs distributed as oriented bundles. While PP phase is more difficult to form a layered structure under the influence of entangled CNTs networks.

To understand the crystallization behavior of these blends, these materials were characterized with DSC, 2D-WAXD and 2D-SAXS. As shown in Figure 4 and Supplementary Information Figure S5, the crystallinity ($X_c$) and crystallization temperature ($T_c$) were collected from the DSC result. Figure 4(a) and Supplementary Information Figure S5 illustrate that the crystallinity of PE in HSTWIM samples are about 50%, and that of PE in CM samples with PE content more than 50% are about 55%. The crystallinity of PE in CM samples is higher than that in

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**Figure 3.** SEM micrographs in the core layer of HDPE-CNT/ICP blends with different composition ratios: (a, d) H/I 80:20, (b, e) H/I 50:50, (c, f) H/I 20:80, respectively. SEM images in Up column are observed from ND, and SEM images in down column are observed from MD.

**Figure 4.** The crystallinity ($X_c$) and crystallization temperature ($T_c$) of PE and PP calculated with DSC results: (a) crystallinity and (b) crystallization temperature.
HSTWIM samples with PE content more than 50%. While PE content is less or equal to 50%, the crystallinity of PE in CM samples is about 45% which is lower than that in HSTWIM samples. The crystallinity of PE in HDPE-CNT/ICP increases from about 42% to about 54% with increasing PE content. And the crystallinity of PE in HDPE-CNT/ICP composites is lower than HDPE/ICP blends in general. PE content of 50% is the cross-over point where a relative magnitude of PE crystallinity changes in HDPE/ICP blends and HDPE-CNT/ICP composites. The shear induces crystallization of PE, thus, the crystallinity of PE in HSTWIM samples is higher than that in CM samples. After adding CNT, the crystallinity of PE increases with increasing PE content. It is lower than that in HSTWIM samples without CNT having low PE content, and is higher in high PE content HSTWIM sample. The mechanism might be caused by the complex interaction between CNT, PE and PP phase on the crystallization behavior. Detailed mechanism needs further investigation. As to the crystallinity of PP, HSTWIM samples are higher than CM samples for PE content above 30%. While PE content is more than 70%, the HSTWIM samples are equal to CM samples. With increasing PE content, the crystallinity of PP in HSTWIM samples decreases from about 35% to about 25%, and the crystallinity of PP in CM samples decreases from about 30% to about 20% and then increases to 25%. The crystallinity of PP in HDPE-CNT/ICP decrease from about 36 to 30% with increasing PE content. Similar with PE phase, shear benefits the crystallization of PP, and CNT at the interface could induce the crystallization of PP. Thus, the crystallinity of PE in HDPE-CNT/ICP samples is higher than that in HSTWIM samples and then higher than that of CM samples. It is shown in Figure 4(b) and Supplementary Information Figure S5 that the crystallization temperature of PP in HSTWIM samples is about 164°C which is higher than that in CM samples (about 159°C) and HDPE-CNT/ICP composites (162°C). The crystallization temperature of PE in HSTWIM samples is 127°C which is also higher than that of CM samples (about 123°C) and HDPE-CNT/ICP composites (124°C). In summary, the crystallization temperature of all samples have little change with increasing PE content.

The crystal orientation of these samples was studied with 2D-WAXD, as shown in Figure 5. Through azimuthal scanning of (040) plane of iPP and the analysis of the diffraction peak full width at half maximum (FWHM), it is demonstrated that the orientation of PP in these blends are similar except for H/I 40:60, where the highest orientation is illustrated. Most of these blends have higher orientation in PP than neat ICP does. Moreover, the orientation of PP in HDPE-CNT/ICP composites is generally lower than that in HDPE/ICP blends. HDPE-CNT/ICP 30:70 illustrates the strongest orientation among HDPE-CNT/ICP composites. Overall, the composition ratio has little influence on the orientation of PP in these samples, and the addition of CNT reduces such orientation slightly. Supplementary Information Figure S6 shows the 2D-WAXD pattern of HDPE/ICP blends with different composition. The diffraction pattern at (110) plane changes from two large diffraction arcs at 0° and 180° (meridian line) to six diffraction arcs at 0°, 40°, 140°, 180°, 220° and 320° while PP content increases. The two diffraction arcs at 0° and 180° represent the ontology crystallization of PE, and the other four diffraction arcs may belong to the (111) of PE epitaxial crystallization or the (−131), (111) of PP. The 2D-WAXD pattern of CM samples shown in Supplementary Information Figure S7 are composed by several full diffraction rings which indicate that CM samples are isotropic without any orientation. The 2D-WAXD pattern of HDPE-CNT/ICP composites is
similar to that of HDPE/ICP blends, as shown in Supplementary Information Figure S8. Hence, there is little difference on crystal form between HDPE/ICP blends and HDPE-CNT/ICP composites.

The crystallization behavior was further studied with SAXS as shown in Figure 6. It is noted that the pattern of HDPE has two scatter arcs at the meridian line, and the four scatter arcs which are tilted by 45° to the meridian start to appear and their strength is gradually enhanced till PE content reaches 50% and then gradually weakens with further increasing PE content. These four scatter arcs indicate the epitaxial crystal growth on PP crystal substrate. At the same time, the two scatter arcs at meridian line gradually become long and narrow and move to the circle with larger radius. With increasing PE content, the absolute crystallinity of PE for ontology crystallization increases, and PE starts to crystallize on the surface of the PP substrate along the (010)$_{PP}$, with the chains of PE apart ± 50° from chains of PP. For PE content above 50%, the epitaxial crystallization of PE decreases owing to less and less PP substrate. Such epitaxial crystallization is thought to be able to enhance the interfacial interaction between PP and PE layers [8].

Figure 7 shows the tensile behavior of HSTWIM HDPE/ICP blends with different composition ratios. For MD of HSTWIM samples, the elongation at break increases from about 70% to maximum (about 300%) while PE content increases to 50%, and then decreases to about 40% with further increasing PE content, as shown in Figure 7(a). The elongation of H/I 50:50 enhances to about 4 times than that of ICP and 8 times than that of HDPE. Meanwhile, tensile modulus decreases from about 750 MPa to a minimum value (about 450 MPa) when PE content increases to 60%, and then increases to 660 MPa. It achieves the relative maximum value when PE content is 30% (996 MPa) and 70% (705 MPa). Tensile strength decreases from 33 MPa to the minimum value
when PE content increases to 80%, and then increases to 28 MPa. As to TD of HSTWIM samples, Supplementary Information Figure S9(a) shows that the elongation at break increases from 50 to 950% and then decreases to 340% with increasing PE content. Neat HDPE and ICP have relatively higher elongation at break (870 and 490%) than these blends, except for those blends with 40 to 60% PE content. For tensile modulus, it is shown in Supplementary Information Table S1 that it fluctuates around 620–770 MPa for various PE/ICP blends with increasing PE content. Moreover, the tensile strength in TD fluctuates at 20 MPa with increasing PP content. Neat ICP have higher Young’s modulus than neat PE. When CNT was added to HDPE, different mechanical behaviors are illustrated as shown in Figure 7(c,d) and Supplementary Information Table S2. The composites with no less than 60% PP content illustrate higher tensile strength (about 43 MPa) than the other composites (about 35 MPa) in MD. Moreover, the tensile strength in TD fluctuates between 24 and 27 MPa with increasing PP content. Neat ICP have higher Young’s modulus than neat PE. When CNT was added to HDPE, different mechanical behaviors are illustrated as shown in Figure 7(c,d) and Supplementary Information Table S2. The composites with no less than 60% PP content illustrate higher tensile strength (about 43 MPa) than the other composites (about 35 MPa) in MD. Moreover, the tensile strength in TD fluctuates between 24 and 27 MPa with increasing PP content. This tensile strength of HDPE-CNT/ICP composites is about 10 MPa higher than that of HDPE/ICP blends. The Young’s modulus of the composites with no less than 50% PE content (about 1800 MPa in MD, about 1600 MPa in TD) is much higher than that of other composites (about 1250 MPa in MD, about 900 MPa in TD) in two directions. As to elongation at break, it decreases from about 120 to 90% and then back to 120% in MD, while it increases from about 260 to 530% and then decrease to 130% in TD. From Supplementary Information Figure S9, it can be observed that elongation at break of HDPE/ICP blends via CM decrease from about 100 to 12%, and then increases to 60%. The minimum value is achieved at 40%. Moreover, CM neat HDPE has a quite large elongation at break. In Supplementary Information Table S1, it is listed that the tensile strength of CM samples decreases from about 16 MPa to a minimum value of around 8 MPa, and then increases to about 22 MPa. The tensile modulus of CM samples decreases from about 1040 to 680 MPa and then increase to about 1500 MPa with increasing PE content. The minimum value is achieved at 60% PE content.

To further study the tensile behavior of HDPE/ICP blends and HDPE-CNT/ICP composites with different composition ratios, the strain energy can be calculated with these tensile curves. As shown in Table 1, the strain energy of HDPE/ICP blends via HSTWIM increases from 2130 N/m² to 4930 N/m² and then decreases to 730 N/m² with increasing PE content in MD, and the maximum value is achieved at 50% PE content. As to HDPE/ICP blends via HSTWIM in TD, the strain energy decreases from 7440 to 340 N/m² and then increases to 14,820 N/m², after that, decreases to 2720 N/m², finally increases to 8750 N/m². The maximum value is achieved at 40% PE content, and the relative minimum values are achieved at 20 and 80%, respectively. For HSTWIM samples, the strain energy of blend (50:50) enhances about 572% than pure

|                | HDPE | H/I 90:10 | H/I 80:20 | H/I 70:30 | H/I 60:40 | H/I 50:50 | H/I 40:60 | H/I 30:70 | H/I 20:80 | H/I 10:90 | ICP |
|----------------|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----|
| HSTWIM, MD     | 73,330 | 820     | 1850     | 4220     | 3590     | 4930     | 3220     | 3100     | 2700     | 2260     | 2130 |
| HSTWIM, TD     | 8750 | 4660     | 2720     | 5420     | 10,680   | 14,440   | 14,820   | 8870     | 340      | 760      | 7440 |
| CNT, MD        | 1080 | 2310     | 4700     | 3030     | 3560     | 3520     | 5000     | 5710     | 5250     |          |     |
| CNT, TD        | 6220 | 12,200   | 6700     | 9690     | 12,610   | 12,050   | 8660     | 3790     | 3350     |          |     |
| CM             | 19,620 | 500     | 980      | 300      | 490      | 70       | 140      | 410      | 570      | 1330     | 920  |

Table 1. The strain energy (N/m²) of HDPE/ICP blends.
HDPE and 131% than pure ICP in MD, and enhances 65% than pure HDPE and 94% than pure ICP in TD, respectively. Moreover, the strain energy of HDPE-CNT/ICP composites increases from 1080 to 5710 N/m² with increasing PP content in MD, and increases from 6220 to 12,610 N/m² and then decreases to 3350 N/m² in TD. Specially, some of these data deviate from the increasing trend with a strain energy of 4700 N/m² for HDPE-CNT/ICP 70:30 in MD and 12,200 N/m² for HDPE-CNT/ICP 80:20 in TD. On the contrary, the strain energy of CM samples decreases from 1330 to 30 N/m², and then increases to 980 N/m² with increasing PE content. The CM neat HDPE has the highest strain energy of 19,620 N/m².

As above study on phase morphology and mechanical behavior has shown the continuous phase changes from the PP to the PE with increasing PE content, and with the continuous phase provides basic and main mechanical properties to these...
materials. Thus, the tensile strength and Young’s modulus are sharply improved when ICP content is over 70%. When ICP is mixed with HDPE, the rubber phase will immigrate from PP phase to PE phase, as shown in Figures 1 and 8. When PE content is <20%, the PE phase could not form orient structures, as shown in Figure 8(b). Under external force, the cracking and crazing will start at the interface between PP and PE, causing rather low strain at break. When PE content increases to 30%, the rubber phase could be confined to the surrounding PE phase, while the dispersed phase deforms to an oriented layered structure. Some rubber phases dispersed at interface can enhance the interfacial interaction, and this oriented layered structure could enhance tensile strength and Young’s modulus. Thus, the relative maximum of tensile strength and Young’s modulus is achieved when the PE content is 30%. When PE content is between 40 and 60%, the alternating multilayer structure is formed. When these materials were under external stress, the multilayer structure could uniformly transfer the external force and the rubber phase could absorb the energy and enhance the interfacial interaction as shown in Figure 8(c). Thus, those blends have a rather large strain at break. With further increasing PE content, the continuous phase shifts to the PE phase. The rubber phase immigrates to the PE phase, and no rubber phase is located at the interface due to the abundant amount of PE, as shown in Figure 8(d). The rather poor interfacial interaction between PE and PP will negatively affect the mechanical property. Thus, the tensile property sharply decreases. Meanwhile, it is well known that rigid nanofillers can enhance the stiffness and reduce the toughness of materials. When CNT was added into PE phase, HDPE-CNT/ICP illustrate higher tensile strength and Young’s modulus than HDPE/ICP blends. Meanwhile, the elongation at break of composites is lower than that of neat blends. When PE content is over 60%, the continuous phase becomes the PE phase, and the Young’s modulus sharply increases because the continuous PE-CNT phase has a higher rigidity than ICP. As to CM samples, the dispersed phase is so large that they provide little contribution to the energy absorption and prohibiting the deformation and destruction of materials under external force. Thus, the CM samples illustrate rather poor mechanical property in term of low strain at break and low tensile strength.

To understand the influence of above issues on anisotropic conductivity, the conductivity of these samples is characterized at three different directions. As shown in Figure 9, it is observed that the conductivity of HDPE-CNT/ICP composites decreases from $10^{-3}$s to $10^{-4}$s and then increase $10^{-3}$s, finally, decreasing to $10^{-7}$s in MD and TD with increasing PE content. Similar trend is observed at both MD and TD directions. The conductivity of composites increases from $10^{-10}$s to $10^{-9}$s and then decreases to $10^{-12}$s in ND. In addition, those composites are almost insulating when PE content is <40%. As above, these composites show conspicuous anisotropic conductive behavior, and the change in trend of conductivity in MD and TD indicates that the continuous layered or fiber structure is beneficial for the establishment of conductive networks.

Through above study on phase morphology, crystallization behavior, tensile behavior and conductivity, it is observed that composition ratio greatly affect the phase morphology and various properties. For CM samples, there are some globules at the fracture surface of H/I 50:50, this indicates that they are almost not deformed and have little contribution to absorbing energy when these specimens are under external force. This should be owing to the poor interfacial interaction and large phase size. Thus, the dispersed phase has little contribution on stopping the development of crazing and cracking under external force. Moderate PE (<20%) could enhance the toughness of PP, while moderate PP (<20%) could enhance the strength of PE. Comparison with CM samples reveals an alternating structure of HSTWIM samples which greatly enhances the mechanical property. When these materials were injected into a thin mold with high injection speed, the melt was stretched and deformed under strong shear and confined flow. Thus, the dispersed phase was deformed from droplet into small thin lamella or fibres. With increasing dispersed phase content, these small lamelae or fibres would coalesce and become larger, finally becoming layers. When these materials were under external stress, the multilayer structure can uniformly transfer the external force and the rubber phase could absorb energy and enhance the interfacial interaction. Thus, the specimens (H/I 40:60, H/I 50:50, H/I 60:40) with alternating multilayer structure have rather good mechanical performance. Moreover, CNT acts as rigid particles, which enhance the rigidity and reduce the toughness of these composites. Hence, higher tensile strength and Young’s modulus, and lower strain energy and elongation at break are observed for HDPE-CNT/ICP composites.

4. Conclusion

Current study investigates the effect of composition ratio as well as addition of CNTs on the structure and properties of PE/ICP polymer blends through HSTWIM. With the addition of PE in ICP, it is noted that PE is migrated into the rubber phase in
ICP, leading to the distribution of rubber phase on the interface between PP and PE, especially at rather low PE content. With increasing PE content, it is observed that moderate composition ratio is essential to fabricate alternating multilayer structures, with only part of the rubber phase distributed at the interface. With further increasing PE content, ICP is observed as dispersed phase in PP without any rubber phase at the interface. HSTWIM process is beneficial for epitaxial crystallization and can enhance the crystallization temperature and crystallinity. Similar content of PE and ICP phase gives rather poor mechanical behavior to CM samples and excellent mechanical behavior to HSTWIM samples, respectively. Such improvement in mechanical performance through HSTWIM is caused by the formation of an alternating multilayer structure, epitaxial crystallization of PE onto PP and selective distribution of some of the rubber phase at the interface. Furthermore, the addition of CNT enhances the strength and modulus of these blends, while also giving rise to anisotropic electrical conductive networks. This study could provide some useful guidelines for preparing multi-phase functional materials.

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