Regulating the Microstructure of Intumescent Flame-Retardant Linear Low-Density Polyethylene/Nylon Six Blends for Simultaneously Improving the Flame Retardancy, Mechanical Properties, and Water Resistance

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ABSTRACT: A compatibilizer was melt-blended with intumescent flame-retardant linear low-density polyethylene/nylon six blends (LLDPE/PA6/IFR) by different methods, and the effect of microstructure on the flame retardancy, mechanical properties, and water resistance was investigated. Melt-blending compatibilizers with LLDPE/PA6/IFR above the polyanime-6 (PA6) melt temperature formed the microstructure with IFR dispersion in the LLDPE matrix and good interphase adhesion between the PA6 phase and the matrix. Compared with the blends with the lack of compatibilizers, although good interphase adhesion improved the mechanical properties and water resistance, IFR dispersion in the LLDPE matrix reduced the flame retardancy sharply. To obtain the microstructure with IFR dispersion in the PA6 phase and strong interface adhesion of the PA6 phase with a matrix, a novel method in which a compatibilizer was melt-blended with LLDPE/PA6/IFR between the melt temperatures of LLDPE and PA6 was employed. The results showed that the flame retardancy, mechanical properties, and water resistance were improved simultaneously.

1. INTRODUCTION

Intumescent flame retardants are now being used more and more in polymer flame retardants because they are more environmentally friendly than traditional halogen-containing flame retardants. The characteristic of intumescent flame retardants is that the combustion chamber can form a honeycomb expansion carbon layer, which reduces the mass transfer and heat transfer between the gas phase and the solidification phase.1−3 Acid source, carbon source, and blowing agent are the three elements of chemically intumescent flame retardants.4−6 In general, ammonium polyphosphate (APP as the acid source and blowing agent), pentaerythritol (PER as the charring agent) and melamine (as the blowing agent) form a traditional IFR system together.

However, IFR has poor water resistance and compatibility with many polymer matrices, resulting in the decrease of flame retardancy and the damage to the mechanical properties of polymer composites. These drawbacks will restrict their wide industrial applications. Microencapsulation of IFR is regarded as an efficient method to get rid of these drawbacks mentioned above.7−11 The microencapsulated IFR particles have a core−shell structure, which allows the isolation of encapsulated substances from the surrounding and thus improves their compatibility with the polymer matrix and the water resistance. In general, the encapsulating shell, such as polyurethane (PU), melamine−formaldehyde, melamine, silicon resin, or urea−melamine−formaldehyde, was prepared by the in situ polymerization method.12−17

Physics encapsulation technology was also employed to prepare microencapsulated IFR particles. Wang18,19 provided a novel method of preparing microencapsulated IFR by the extrusion of melamine phosphate and PER, together with a polypropylene (PP) carrier. The results showed that the IFR encapsulated by the PP carrier improved flame retardancy and water resistance. Zeng20 used PU as a carrier resin to encapsulate melamine pyrophosphate/PER through melt blending, and encapsulated IFR was adopted to flame-retard PP. The results showed that encapsulated IFR endowed PP with better flame retardancy, water resistance, and mechanical properties. Compared with the in situ polymerization method, physics encapsulation technology has the advantages of a simple process and less environmental problems.

Polymer blending has gained considerable interest as a suitable way to tailor the properties of polymeric materials without investing in new chemistry.21 However, the flame retardancy of polymer blends is more complex than that of pure polymers because of the complicated microstructure caused by the dispersion of IFR and their synergists in the
Lu26,27 found that blends with organic montmorillonite and APP, respectively, distributed in the phase interface and PA6 phase have better flame retardancy than that of the blends with the sea-island structure. For the blends of PS/PA6 and acrylonitrile–butadiene–styrene/PA6 with sea-island morphology, Lu26,27 found that blends with organic montmorillonite and APP, respectively, distributed in the phase interface and PA6 phase have better flame retardancy than that of the blends with clay and APP dispersed in the PA6 phase. Jin28 employed the compatibilizer to adjust the microstructure for improving the mechanical properties and flame retardancy of PP/ethylene-octene copolymer/IFR. Along with the increase of compatibilizer content, the blends exhibited different microstructures. The addition of compatibilizers in a proper range caused the simultaneous improvement on mechanical properties and flame retardancy.

IFR for flame-retardant polymer blends also encounters the challenges of poor water resistance and damage on mechanical properties. Although the microstructure of polymer blends contributes to the improvement of the flame retardancy to a great extent, improving IFR water resistance and decreasing its damage on mechanical properties with resorting to regulating the microstructure have not been studied systematically. In this paper, we attempted to regulate the microstructure of polymer blends for the purpose of overcoming these disadvantages. The microstructure in which IFR localizes in the dispersed phase can be regarded as the microencapsulated IFR in which dispersed phase as the shell encapsulates IFR to improve water resistance.Compatibilizers can be employed to improve the compatibility. Moreover, char-forming polymers chosen as dispersed phase to encapsulate IFR particles could endow the blends with better flame retardancy.

The flammability of linear low-density polyethylene (LLDPE)/PA6 blends has limited its applications in packaging and automotive fields. In the LLDPE/PA6 blends, higher affinity of IFR for PA6 than for LLDPE should exhibit the dispersion of IFR in the PA6 phase. Furthermore, it was reported that PA6 acted as the charring agent of APP to enhance the charring performance, resulting in better flame retardancy.29–31 Therefore, the use of IFR as flame retardants was investigated for their potential in improving the fire-retardant behavior of LLDPE/PA6. The IFR system used consists of APP and PER. Meanwhile, maleic anhydride grafted with LLDPE (LLDPE-g-MAH) was chosen as a compatibilizer for enhancing the compatibility of LLDPE/PA6 blends. The compatibility of LLDPE-g-MAH may prohibit the dispersion of IFR in the PA6 phase, while LLDPE, PA6, and IFR are melt-blended with LLDPE-g-MAH simultaneously. In order to prepare the blends with IFR dispersion in the PA6 phase, a two-step processing method was employed: PA6, LLDPE, and IFR were melted above the melting temperatures of LLDPE and PA6 to first prepare blends of LLDPE/PA6/IFR, and then LLDPE-g-MAH was melt-blended with LLDPE/PA6/IFR between the melt temperatures of LLDPE and PA6. The effects of the microstructure on the flame retardancy, mechanical properties, and water resistance were investigated.

2. RESULTS AND DISCUSSION

2.1. Dispersion of APP and PER in LLDPE/PA6 Blends and Their Microstructure. In order to investigate the spontaneous dispersion of APP or PER in the blends of LLDPE/PA6, PA6/LLDPE/APP or PA6/LLDPE/PER prepared by method one was investigated by Fourier transform infrared (FTIR) spectra, respectively. Figure 1 shows the FTIR spectra of the remaining parts of the PA6/LLDPE/IFR or PA6/LLDPE/PER extracted by formic acid or formic acid and ethyl alcohol, respectively. The –CH3– asymmetric stretching (2919 cm−1), symmetric stretching (2849.5 cm−1), bending vibrations (1469 cm−1), and the wagging vibration of C–H (719.4 cm−1) were observed, indicating that the remaining parts consisted of PE. In these blends, PA6 formed a continuous phase because of high PA6 content. The absence of PA6 in the remaining parts indicated that continuous PA6 phase was completely extracted by formic acid. The absence of APP or PER in the remaining parts showed that APP or PER was also completely extracted by formic acid or ethyl alcohol, respectively. If APP or PER was localized in the LLDPE phase of blends, they could not be extracted by formic acid or ethyl alcohol, with the result that APP or PER could be detected in the remaining parts. Therefore, the results that APP or PER was not detected in the remaining parts indicated that APP or PER was localized in the PA6 phase. In the blends tested by FTIR, APP or PER should disperse spontaneously in the polymer with high affinity, due to which the processing temperature was higher than the melting temperature of LLDPE and PA6. Therefore, the localization of APP or PER in the PA6 phase indicated that the affinity of APP or PER is higher for PA6 than for LLDPE because of similar polarity between PA6 and IFR.

Scanning electron microscopy-energy-dispersive spectroscopy (SEM–EDS) was employed to characterize the dispersion of IFR in the blends and the microstructure of the blends, as shown in Figure 2. SEM results showed that APP and PER were irregular particles. The spherical particles with a large dimension were observed in the matrix of C-0. The results of FTIR showed that IFR is spontaneously distributed in the PA6 phase. Therefore, IFR particles were coated by the PA6 phase to form the spherical particles. The EDS results showed that the P content was 1.83 wt %. Generally, the detected depth for the EDS measurement is about 1000 nm, so small amounts of elemental P dispersed in the PA6 phase were detected. Some cavities were seen on the surface of C-0, and there were clear interfaces between PA6 particles and LLDPE, indicating poor compatibility between PA6 and LLDPE, which
is due to the different polarity between PA6 and LLDPE, exhibiting a weak interfacial adhesion. The results showed that C-0 formed sea-island morphology in which IFR localized in the dispersed PA6 phase and the LLDPE matrix exhibited poor interface adhesion. Meanwhile, strong interfacial adhesion between PA6 particles and the LLDPE matrix was observed because of vague interface. The results indicated that the compatibilizer improved the interfacial adhesion between the PA6 phase and the LLDPE matrix. The different polarity between IFR and LLDPE caused a weak interfacial adhesion. The SEM−EDS results showed that LLDPE/PA6/IFR/LLDPE-g-MAH blends prepared by method one formed the sea-island morphology such that both IFR and PA6 localized in the LLDPE matrix and LLDPE-g-MAH improved the interfacial adhesion of the PA6 phase and the LLDPE matrix.

Interfacial tensions between the filler and each polymer determine the filler distribution in the filler-filled polymer blends. In the uncompatibilized blends, IFR dispersion in the PA6 phase rather than in the LLDPE phase indicated that the interfacial tension between IFR and PA6 was lower than that of IFR and LLDPE. When LLDPE-g-MAH was melt-blended with LLDPE/PA6/IFR, LLDPE-g-MAH was reacted with PA6 to form a copolymer. The copolymer should migrate to the interface of PA6 and LLDPE to reduce the interfacial tension and phase size, indicating that the interfacial tension between LLDPE and PA6 was lower than that of IFR and PA6. As a result, IFR particles were found to localize in the LLDPE matrix rather than in the PA6 phase.

The blends of C2-M2 and C8-M2 were prepared via a two-step process. At the first step, IFR should disperse in the PA6 phase because of similar polarity between PA6 and IFR. When LLDPE-g-MAH was melt-blended with LLDPE/PA6/IFR at the second step, LLDPE-g-MAH should not change the dispersion of IFR, due to which the PA6 phase remained solid, exhibiting IFR dispersion in the PA6 phase. The typical empty holes and the exfoliation phenomenon that appeared in C-0, C2-M1, and C8-M1 almost vanished, which suggested good interfacial adhesion. The results indicated that LLDPE-g-MAH improved the compatibility between PA6 and LLDPE. The PA6 phase remained solid when LLDPE-g-MAH was melt-blended with LLDPE/PA6/IFR. Therefore, the improvement of interfacial adhesion and compatibility between PA6 particles and LLDPE should be attributed to the reaction between the maleic anhydride group in the LLDPE-g-MAH melt and the amidogen on the surface of solid PA6 particles. The EDS results showed that the percentages of elemental P and O in C2-M2 and C8-M2, respectively, were lower than that of C-0, indicating that LLDPE-g-MAH encapsulated the PA6 phase, demonstrating that IFR dispersed in the PA6 phase was hard to be detected by EDS. As the content of LLDPE-g-MAH increased from 2 to 8 wt %, the coating thickness of LLDPE-g-MAH on the surface was also increased, causing the percentages of P and O to decrease from 14.88 and 1.03 to 14.12 and 0.6%, respectively. Therefore, the sea-island morphology in which IFR localized in the dispersed PA6 phase and LLDPE-g-MAH improved the compatibility of the PA6 phase and the LLDPE matrix was formed in LLDPE/PA6/IFR/LLDPE-g-MAH blends prepared by method 2.

Figure 2. SEM−EDS of IFR and blends prepared by different methods.
In order to confirm the reaction between LLDPE-g-MAH and PA6 in the blends prepared by method 2, the blends of LLDPE/PA6 (85/15) or LLDPE/PA6/LLDPE-g-MAH (80/15/5) were extracted by dimethylbenzene to remove LLDPE and LLDPE-g-MAH and the remaining part were tested by FTIR, as shown in Figure 3. The blend of LLDPE/PA6 was melt-blended above the melting temperature of LLDPE and PA6. LLDPE/PA6/LLDPE-g-MAH blend was prepared by method 2. The typical infrared spectra of PA6 were shown, and no characteristic peaks of LLDPE were found in the remaining part of LLDPE/PA6, indicating that whole LLDPE was dissolved by dimethylbenzene and the remaining part consisted of PA6. For the remaining part of LLDPE/PA6/LLDPE-g-MAH prepared by method 2, the peaks at 2934 and 2968 cm\(^{-1}\) shown in LLDPE/PA6/PA6 were replaced by 2918 and 2850 cm\(^{-1}\), respectively. The peaks at 2934, 2968 cm\(^{-1}\) in the remaining part of LLDPE/PA6 were the \(-\text{CH}_3\text{−}\) asymmetric stretching and symmetric stretching of PA6, respectively. From Figure 1, it was observed that the peaks at 2918 and 2850 cm\(^{-1}\) were the \(-\text{CH}_3\text{−}\) asymmetric stretching and symmetric stretching of LLDPE. The results indicated that the remaining part of LLDPE/PA6/LLDPE-g-MAH contained LLDPE or LLDPE-g-MAH. LLDPE or unreacted LLDPE-g-MAH can be extracted by dimethylbenzene, but LLDPE-g-MAH reacted with PA6 should not dissolve in dimethylbenzene. Therefore, it can be concluded that the maleic anhydride group in the LLDPE-g-MAH melt can react with the amidogen on the surface of solid PA6 particles in the blends prepared by method 2.

2.2. Flame Retardancy. The flame retardancy of LLDPE/PA6/IFR and LLDPE/PA6/IFR/LLDPE-g-MAH prepared by different methods was investigated by limiting oxygen index (LOI) and UL-94 test, as shown in Table 1. For C-0, the LOI value was 29.7, and the samples achieved a V-2 rating in UL94 testing because of the melt dripping during combustion. Processing methods showed a remarkable influence on the flame retardancy. Blends of LLDPE/PA6/IFR/LLDPE-g-MAH prepared by method 1 exhibited poor flame retardancy, and the LLDPE-g-MAH content showed weak influence on the flame retardancy. The LOI values of C-2-M2 and C5-M2 were both 28.6 and the samples passed the UL-94 V-2 rating, indicating that their flame retardancy was close to C-0. The best flame retardancy was exhibited in C8-M2. The LOI value reached 30.0%. The samples passed the UL-94 V-0 rating, indicating that the dripping properties exhibited in C-0, C2-M2, and C5-M2 were restrained in C8-M2.

The results showed that blends with IFR dispersion in the PA6 phase (C-0, C2-M2, C5-M2, and C8-M2) exhibited better flame retardancy than the blends with IFR dispersion in the LLDPE phase (C2-M1, C5-M1, and C8-M1). It was reported that PA6 can act as the charring agent of APP to enhance the charring performance and flame retardancy.\(^\text{29–31}\) Therefore, IFR dispersion in the PA6 phase was more beneficial for the reaction between APP and PA6, exhibiting better flame retardancy, compared with the blends with IFR dispersion in the LLDPE phase. C8-M2 samples had no melt dripping during combustion. The reason for this may be the case that LLDPE-g-MAH increases the viscosity of blends and enhances the antidripping property.

Melt flow index (MFI) can relate to viscosity indirectly, which indicates the dripping properties of flame-retardant LLDPE/PA6 blends. MFI experiments were used to test the flow rate of flame-retardant LLDPE/PA6 blends at different LLDPE-g-MAH contents, as shown in Table 2. The highest MFI value observed in C-0 indicated the lowest melt viscosity. Obviously, the melt dripping of C-0 should be attributed to the low melt viscosity. MFI values of the LLDPE/PA6/IFR/LLDPE-g-MAH blends prepared by method 1 were lower than that of C-0. Moreover, the increase of LLDPE-g-MAH contents caused a sharp reduction of MFI values. The results indicated that LLDPE-g-MAH increased the melt viscosity. The copolymer formed by the reaction of LLDPE-g-MAH and PA6 can entangle with PA6 and LLDPE molecular chains at the interface to increase the flow resistance of melt, resulting in high melt viscosity. The increase of LLDPE-g-MAH contents in the blends produced more copolymers, resulting in higher melt viscosity. For the LLDPE/PA6/IFR/LLDPE-g-MAH blends prepared by method 2, the MFI values were also lower than that of C-0 and the increase of LLDPE-g-MAH contents caused the reduction of MFI values. The MFI value of C8-M2 was about one-third of C-0, indicating a sharp increase of melt viscosity, resulting in the enhancement of antidripping property. The increase of melt viscosity can also be attributed to the copolymer formed by the reaction of LLDPE-g-MAH and PA6.

2.3. Cone Calorimeter Analysis. The cone calorimeter was also employed to evaluate the flame retardancy. Samples of C-0, C8-M1, and C8-M2 were chosen for testing by cone calorimeter. The heat release rate (HRR), total heat released (THR), and mass loss curves recorded during cone calorimeter

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**Table 1. Flammability Characteristics of Blends**

| sample code | LOI (%) | UL-94 rating |
|-------------|---------|--------------|
| C-0         | 29.7    | V-2          |
| C2-M1       | 24.0    | no rating    |
| C5-M1       | 24.0    | no rating    |
| C8-M1       | 24.7    | no rating    |
| C2-M2       | 28.6    | V-2          |
| C5-M2       | 28.6    | V-2          |
| C8-M2       | 30.0    | V-0          |
The peak HRR (PHRR) value of C8-M1 was higher than that of C-0 and C8-M2, indicating that the flame retardancy of C8-M1 was poorer than that of C-0 and C8-M2. The results showed that IFR dispersion in the PA6 phase enhanced flame retardancy in comparison with IFR dispersion in the LLDPE phase.

The HRR curves of C-0 and C8-M2 displayed two peaks: the first peak was assigned to the formation of expandable char layers and the second peak was assigned to the further decomposition of a carbonaceous residue. The first PHHR and the HRR values for the initial 250 s of C8-M2 were lower than that of C-0, indicating that the char layer of C8-M2 formed in the initial period can provide better protection against the combustion of the matrix than that of C-0. Combustion experiments performed in the UL94 or LOI test were similar to the scenario of cone calorimetry at the ignition stage. Therefore, the results that the LOI and the vertical combustion level of C8-M2 were better than that of C-0 can be due to reduced combustion intensity in the initial period. The second PHHR value of C8-M2 was higher than that of C-0, indicating that the stability of the carbonaceous residue in C8-M2 was poorer than that of C-0.

The THR of C-0 and C8-M2 was lower than that of C8-M1, and the mass loss curve showed that the char residue of C-0 and C8-M2 was higher than that of C-0, indicating that the dispersion of IFR in the PA6 phase was more favorable to the formation of a carbonaceous residue, resulting in the decrease of THR.

Fire performance index (FPI) is defined as the proportion of TTI and PHRR; fire growth index (FGI) is defined as the proportion of PHRR and time to PHRR; MARHE is the maximum of the average rate of heat emission. The values of MARHE, FPI, and FGI can evaluate the fire hazard. It can be seen from Table 1 that the highest MAHRE and FGI values or
the lowest FPI was observed in C8-M1, suggesting that C8-M1 possessed the strongest fire hazard in comparison with C-0 and C8-M2.

2.4. Characterizations of Residue Char. Figure 5 shows the residue of the blends at the end of the cone calorimeter test. Broken char residue was observed in C8-M1. C-0 and C8-M2 formed a coherent and dense char residue with high intumescence. The high FPI and char residue of C8-M1 were attributed to the different microstructures of the blends. The different morphologies of char residues should be attributed to the different dispersion of IFR in polymer blends. Compared with IFR dispersion in the LLDPE phase, IFR dispersion in the PA6 phase was beneficial for the reaction between APP and PA6, forming a high char residue, resulting in the formation of a continuous and compact char residue. However, IFR dispersion in the LLDPE phase was against the improvement of water resistance. Blends of LLDPE/PA6/IFR prepared by method 2, the sample of C-0 had the microstructure in which IFR dispersed in the dispersed PA6 phase and the interfacial adhesion between the PA6 phase and the LLDPE matrix was poor. Poor interfacial adhesion contained a number of microgaps, through which the water entered to dissolve IFR, resulting in poor water resistance. Blends of LLDPE/PA6/LLDPE-g-MAH/IFR prepared by method 1 possessed the microstructure in which IFR and PA6 phase both dispersed in the LLDPE matrix and the interfacial adhesion between the PA6 phase and the LLDPE matrix was strong or poor, respectively. Although the compatibilization of LLDPE-g-MAH on LLDPE/PA6 decreased the microgaps, the dispersion of IFR in the LLDPE phase and the interfacial adhesion between the PA6 phase and the LLDPE matrix was formed.

2.5. Water Resistance of Flame-Retardant LLDPE/PA6. Table 5 shows the mass loss percentages, LOI, and the UL-94 test results of flame-retardant LLDPE/PA6 after water immersion. The highest mass loss percentage was exhibited in C-0. Mass loss percentages of LLDPE/PA6/LLDPE-g-MAH/IFR blends prepared by method 1 were higher than that of blends prepared by method 2. The results indicated that LLDPE/PA6/LLDPE-g-MAH/IFR prepared by method 2 exhibited the best water resistance. The LOI and UL-94 test results were in accordance with the mass loss results. After water immersion, the LOI value of C-0 reduced from 29.7 to 24%, and the samples failed to pass the UL-94 test, indicating remarkable reduction in flame retardancy because of poor water resistance. Blends of C2-M1, C5-M1, and C8-M1 had poor flame retardancy before water immersion. Therefore, little change in flame retardancy was observed after water immersion. Good water resistance was exhibited in C2-M2, C5-M2, and C8-M2. After water immersion, the LOI values were reduced slightly, and UL-94 rating grades were unchanged.

The different water resistance exhibited in Table 4 should be attributed to different microstructures of the blends. The

| sample code | mass loss percentage (%) | LOI (%) | UL-94 rating |
|-------------|--------------------------|---------|--------------|
| C-0         | 3.2 ± 0.1                | 24      | failed       |
| C2-M1       | 1.7 ± 0.2                | 24      | failed       |
| C5-M1       | 1.9 ± 0.1                | 24.7    | failed       |
| C8-M1       | 1.6 ± 0.1                | 24      | failed       |
| C2-M2       | 0.9 ± 0.1                | 26.3    | V-2          |
| C5-M2       | 0.9 ± 0.1                | 27.1    | V-2          |
| C8-M2       | 0.7 ± 0.1                | 28.6    | V-0          |

Figure 6. SEM of intumescent char residues for blends prepared by different methods.
The mechanical properties of flame-retardant LLDPE/PA6 are compiled in Table 5. The tensile strength, elongation at break, and impact strength of C-0 were 7.1 MPa, 9.4%, and 3.0 kJ/m², respectively. Poor compatibility between PA6 and LLDPE should be responsible for the deteriorated mechanical properties. For the blends prepared by method 1, compatibilizer LLDPE-g-MAH improved the tensile strength and elongation at break. Introduction of LLDPE-g-MAH to C-0 through method 1 also improved the mechanical properties except for C2-M1. The mechanical properties of the blends prepared by method 2 were higher than that of C-0 and the blends prepared by method 1. This phenomenon should be attributed to different morphologies. For the blends prepared by method 1, PA6 phase and IFR were both dispersed in continuous LLDPE phase. The compatibilizer elevated the interphase adhesion of PA6 and LLDPE phases and decreased PA6 phase size. Therefore, the tensile strength and elongation at break were increased from 7.1 MPa and 9.4% for C-0 to 9.0 MPa and 23.4% for C5-M1, respectively. For the blends prepared by method 2, IFR was dispersed in the PA6 phase and the compatibilizer elevated the interphase adhesion between the PA6 phase and the matrix. Therefore, the tensile strength, elongation at break, and impact strength were increased about 60, 300, and 50% in comparison with C-0, respectively. It was observed that the compatibilizer contents exhibited a weak effect on the mechanical properties of LLDPE/PA6/LLDPE-g-MAH/IFR prepared by different methods, due to which the increase of compatibilizer contents caused little change of the mechanical properties. For the blends prepared by method 1, although the increase of LLDPE-g-MAH content reduced the PA6 phase size and contributed to the augment of the mechanical properties to a certain extent, the poor interphase adhesion between IFR and the LLDPE matrix showed a greatly negative impact on mechanical properties, indicating that the mechanical properties were not influenced remarkably along with the increase of LLDPE-g-MAH content. In the blends prepared by method 2, the PA6 phase remained solid when LLDPE-g-MAH was melt-blended with LLDPE/PA6/IFR. Therefore, LLDPE-g-MAH cannot reduce the PA6 phase size. The increase of LLDPE-g-MAH content increased the coating thickness of LLDPE-g-MAH on the PA6 particles surface rather than increasing the interfacial strength. Therefore, the poor effect of the compatibilizer contents on mechanical properties was exhibited.

3. CONCLUSIONS

Different processing methods were employed to prepare LLDPE/PA6/IFR blends with different microstructures, and the results showed that the microstructure affected the flame retardancy, mechanical properties, and water resistance greatly. Melt-blending IFR with LLDPE/PA6 simultaneously formed the microstructure in which IFR was selectively dispersed in the PA6 phase of LLDPE/PA6/IFR and the interphase adhesion between PA6 and the LLDPE matrix was poor. Although IFR dispersion in the PA6 phase was beneficial for the increase of flame retardancy, poor interphase adhesion deteriorated the mechanical properties and water resistance. When the compatibilizer LLDPE-g-MAH was melt-blended with LLDPE/PA6/IFR simultaneously, a microstructure was formed, indicating that IFR and PA6 particles were respectively dispersed in the LLDPE matrix and that LLDPE-g-MAH strengthened the interphase adhesion between the PA6 phase and the LLDPE matrix rather than IFR particles and the LLDPE matrix. The improvement of the interphase adhesion increased the mechanical properties and water resistance, but IFR dispersion in the LLDPE matrix decreased the flame retardancy sharply. A novel processing method that the IFR was first melt-blended with LLDPE/PA6 and then LLDPE-g-MAH was melt-blended with LLDPE/PA6/IFR between the melt temperatures of LLDPE and PA6 was employed to obtain the microstructure with the dispersion of IFR in the PA6 phase and strong interfacial adhesion of the PA6 phase with the matrix. The flame retardancy, mechanical properties, and water resistance were improved simultaneously. IFR dispersion in the PA6 phase and high viscosity caused by the compatibilization of LLDPE-g-MAH should be responsible for the improvement of flame retardancy. Strong interfacial adhesion of the PA6 phase with the matrix and IFR dispersion in the PA6 phase caused good water resistance. Moreover, good mechanical properties were attributed to the strong interfacial adhesion between the PA6 phase and the LLDPE matrix.

4. EXPERIMENTAL SECTION

4.1. Materials. The materials used in this study were LLDPE (LL6201XR, MI = 50 g/10 min, d = 0.926 g/cm³) supplied by ExxonMobil Corp. and PA6 (3350, relative viscosity of 3.50, d = 1.14 g/cm³) supplied by Xinhui Meida-DSM Nylon Chips Co., Ltd. The IFR system consists of APP and PER, and the weight ratio of APP to PER is 4:1. APP [(NH₄PO₃)₆, purity level > 90%] was supplied by Zhejiang Longyou Gede Chemical Factory (China). PER was supplied by Jinan Taixing Fine Chemicals Co., Ltd. LLDPE-g-MAH (TRD200L, MI = 2 g/10 min, d = 0.92 g/cm³) was supplied by Wujian Siruda Plastic Industry Co., Ltd. The amount of maleic anhydride in LLDPE-g-MAH was 1 wt %.

4.2. Preparation of Composites. All the materials were oven-dried for 12 h at 85 °C before extrusion and injection. The blends were extruded via a corotating twin-screw extruder with a barrel diameter of 20 mm and a barrel-length-to-diameter ratio of 25. Then the extruded blends were molded into sheets of suitable thickness at the injection pressure of 50 MPa via an injection molding machine. The formula of the blend is listed in Table 6.

Two processing methods were employed for preparing the blends.

Method 1: all the materials were melt-blended above the melt temperature of LLDPE and PA6 for preparing the blends. The temperatures from hopper to die were 140, 160, 190, 220, and 240 °C.

Method 2: two steps were employed to prepare the blends. In the first step, PA6 and LLDPE were melt-blended with IFR by Wujiang Siruda Plastic Industry Co., Ltd. The amount of maleic anhydride in LLDPE-g-MAH was 1 wt %.

Table 5. Mechanical Properties of the Blends Prepared by Different Methods

| sample code | tensile stress (MPa) | elongation at break (%) | impact strength (kJ/m²) |
|-------------|---------------------|------------------------|------------------------|
| C-0         | 7.1 ± 0.9           | 9.6 ± 3.5              | 3.0 ± 0.08             |
| C2-M1       | 8.3 ± 1.2           | 27.3 ± 8.3             | 2.0 ± 0.01             |
| C5-M1       | 9.0 ± 1.5           | 23.4 ± 9.3             | 3.3 ± 0.98             |
| C8-M1       | 9.0 ± 0.9           | 23.3 ± 10.2            | 3.5 ± 0.78             |
| C2-M2       | 11.9 ± 0.5          | 28.9 ± 4.9             | 3.7 ± 0.06             |
| C5-M2       | 11.7 ± 0.6          | 24.2 ± 8.2             | 4.3 ± 0.08             |
| C8-M2       | 11.9 ± 0.6          | 29.4 ± 7.1             | 4.4 ± 0.02             |
The tensile strength was measured by a tensile tester (LJ1000, Guangzhou Test Instrument Factory, China) according to ASTM D638.

The MFI of melting polymer blends was measured by a melt index instrument, and the measurement temperature was 225 °C; load was 2.16 kg.

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**Notes**
The authors declare no competing financial interest.

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**Table 6. Formulation of Blends**

| Sample code | LLDPE | PA6 | IFR | LLDPE-g-MAH | Processing method |
|-------------|-------|-----|-----|-------------|------------------|
| C-0         | 64    | 16  | 20  | 0           | Method 1         |
| C2-M1       | 62    | 16  | 20  | 2           | Method 1         |
| C5-M1       | 59    | 16  | 20  | 5           | Method 1         |
| C8-M1       | 56    | 16  | 20  | 8           | Method 1         |
| C2-M2       | 62    | 16  | 20  | 2           | Method 2         |
| C5-M2       | 59    | 16  | 20  | 5           | Method 2         |
| C8-M2       | 56    | 16  | 20  | 8           | Method 2         |

Table 6. Formulation of Blends

The bulk density of the blends was calculated as follows:

\[ \text{Bulk density} = \frac{W_0 - W}{W_0} \times 100 \]

where \( W_0 \) is the initial weight of the specimens before water immersion and \( W \) is the remaining weight of the specimens after water immersion and drying.
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