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Preparation and investigation of the combustion behavior of polypropylene/organomodified MgAl-LDH micro-nanocomposite

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ABSTRACT

Layered double hydroxides (LDHs) are considered as a new emerging class of clays and they have a promising future in the field of nanocomposites due to their highly tunable properties. In this research, polypropylene/organomodified magnesium–aluminum LDH (PP/O-MgAl-LDH) composites were prepared by direct melt compounding. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the samples. Both XRD and TEM images of the composites illustrate the formation of a mixed morphology of micro and nano scale dispersion of MgAl-LDH in the matrix. Its combustion behaviors were examined via microscale combustion calorimeter (MCC), and char residues investigated by SEM. The MCC results show that the addition of Mg-Al-LDH into PP can efficiently decrease the specific heat release rate (HRR), the heat release capacity (HRC), and total heat release (THR), indicating the flame retardancy of the composite are improved. Flame retardant properties of PP/O-MgAl-LDH micro-nanocomposite were further enhanced with the increasing amounts of MgAl-LDH concentration.

1. Introduction

Polypropylene (PP) is widely applied in engineering materials, electronic cases, interior decoration, etc. regarding its excellent insulation properties, low cost, ease of fabrication and processing. Many of these applications carry severe risk of flame related occasions and loss of valuable properties due to high flammability of polypropylene. Introducing flame retardant additives into matrix polymer, therefore, is an essential step and phosphorous or metal oxide containing flame retardants are mostly employed in this manner to maintain flame retardancy. Besides microscale conventional flame retardant technologies, nanocomposites seem to be a promising alternative and, most of the ongoing investigations focus on a sub-class of nanocomposites, polymer/layered silicate nanocomposites [1–3]. However, in the recent years, polymer/layered double hydroxide (LDH) nanocomposites have drawn an enormous attention among polymer-clay nanocomposites [4–6].

LDH is a host–guest material consisting of positively charged metal hydroxide sheets with intercalated anions and water molecules [7]. The surface characteristic of pristine LDH is hydrophilic and it is difficult to realize the intercalation of polymer into the interlayers because of the integrated hydrogen-bonding network between the hydroxide layers, intercalated anions and water molecules. Furthermore, the organo modification for LDH is often considered as an essential and vital step before further utilizing it as a nanofiller. In comparison to conventional modification methods, like regeneration or anionic exchange method, in latest study we have successfully prepared organomodified LDH via one step method without requirement of carbonate free environment [8,9].

In the present work, we reported the preparation of PP/O-MgAl-LDH micro-nanocomposites by melt compounding directly. O-MgAl-LDH was synthesized by one step method as previously reported and a third component, maleic anhydride grafted polypropylene (MAH-g-PP) was used to assist dispersion of the layered inorganic materials. The MgAl-LDH to MAH-g-PP weight ratio was kept constant (1:1) in all compositions. The structural characterizations of PP/O-MgAl-LDH mixed micro-nanocomposite and the residues after combustion test were investigated by wide angle X-ray scattering (WAXS) and transmission electron microscopy (TEM). Their combustion behaviors have been studied by microscale combustion calorimetry (MCC).

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2. Experimental

2.1. Materials

The metal nitrate salts ($Mg(NO_3)_2$, $Al(NO_3)_3$), and sodium dodecylbenzenesulfonate (Na-DBS, Purity: 91%) were obtained from Aldrich Chemical Company for the purpose of organomodified synthesis of Mg/Al-LDH and used without further purification. Deionized water was used to dilute the solutions and to wash the filtered precipitates. Polypropylene (PP, homopolymer, HD 120 MO) was purchased from Borealis, Porvoo, Finland. Maleic anhydride grafted polypropylene (MAH-g-PP, Exxelor PO1020) was supplied by the Exxon Mobil Chemical.

2.2. Preparation of organomodified MgAl-LDH samples via one step route [8]

The synthesis of organomodified MgAl-LDH was carried out by the slow addition of a mixed magnesium and aluminium metal salt solution (with Mg^{2+}:Al^{3+} ratio equal to 2:1 and a total metal ion concentration of 0.3 M) to a Na-DBS solution with a continuous stirring at 50 °C. During the synthesis the pH value was kept to be 10 ± 0.2 by adding required amount of 1 M NaOH solution. After the addition of the mixed metal salt solution, the resulting slurry was continuously stirred at the same temperature for 0.5 h and then thermal treatment was applied for the following 18 h at 75 °C. The final products were filtered and washed several times with distilled water to get rid of non-reacted surfactant molecules until the pH of the supernatant solution was about 7. Organomodified MgAl-LDH (O-MgAl-LDH) was then dried in oven at 80 °C till the constant weight. For the comparison, pristine MgAl-LDH was also synthesized using the same principle mentioned above.

2.3. Preparation of PP/O-MgAl-LDH samples

PP, MAH-g-PP and O-MgAl-LDH were melt-compounded by a corotating twin-screw microextruder (15 cm^3 microcompounder, DSM Xplore, Geleen, The Netherlands) based upon certain weight ratios. Melt-compounding conditions were defined as 190 °C, 200 rpm screw speed and 10 min mixing time. The concentrations of MgAl-LDH in the composites were determined based on an approximate metal hydroxide content of the filler in whole matrix-filler system. In this research, 1.2 wt%, 2.4 wt%, and 4.8 wt% concentrations of MgAl-LDH in the composites, were investigated.

2.4. Characterization

Wide angle X-ray scattering (WAXS) was performed using 2-circle diffractometer XRD 3003 θ/θ (GE Inspection Technologies/Seifert-FPM, Freiberg) with Cu-Kα radiation ($\lambda = 1.542$ Å) generated at 30 mA and 40 kV in the range of $2\theta = 0.5$–$25°$ using a scintillation detector (0.05° as the step length, 15 s as measuring time per step). The Fourier transform infrared spectra (FTIR) of the LDH materials were obtained using the BRUKER VERTEX 80V spectrometer over the wave number range of 4000–400 cm^{-1}. The powdered samples were mixed with KBr and pressed in the form of pellets for the measurement of FTIR analysis. The morphological analysis was carried out using transmission electron microscopy (TEM) with microscope LEO 912. The conditions used during analysis were room temperature, 120 kV acceleration voltage and bright field illumination. The ultra-thin sections of the samples were prepared by ultramicrotome at −120 °C with a thickness of 80 nm. Microscale Combustion calorimeter (MCC-1, FTT) was used to investigate the combustion behavior of PP and PP/O-MgAl-LDH micro-nanocomposites. In this system, about 5 mg samples were heated to 700 °C at a heating rate of 1 °C/s in a stream of nitrogen flowing 80 cm^3/min. Prior to entering a 900 °C combustion furnace the volatile, anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm^3/min stream consisting of 20% oxygen and 80% nitrogen. The scanning electron microscopy (SEM) (microscope model: Ultra Plus, Carl Zeiss SMT) was used to study morphological features of the residues of samples. The voltage = extra high tension (EHT) and aperture size was standing in the picture in the annotation bar. The samples are sputtered with 2 nm platinum.

3. Results and discussion

3.1. Structural characteristics of O-MgAl-LDH and PP/O-MgAl-LDH micro-nanocomposite

The FTIR spectra of the unmodified MgAl-LDH and organomodified MgAl-LDH were shown in Fig. 1. In comparison to unmodified MgAl-LDH, the FTIR spectrum of the organomodified MgAl-LDH reveals the presence of DBS anion in the filler. The characteristic vibration bands were detected for SO_3^- stretchings (symmetric stretching at 1038 cm^{-1} and asymmetric at 1183 cm^{-1}), the benzene group (C–C stretching at 1460 cm^{-1}, C–H in plane bending at 1004 and 1140 cm^{-1}) and alkyl group (asymmetric stretching of CH_3 and CH_2 at 2963 and 2925 cm^{-1}, respectively; symmetric stretching of CH_3 and CH_2 at 2872 and 2851 cm^{-1}, respectively). The bands recorded below 800 cm^{-1}, especially the sharp and strong characteristic band around 452 cm^{-1} appear due to the vibration of metal-oxygen bond in the brucite-like lattice. Besides, more direct evidences can be obtained from WAXS in Fig. 2, which is one of the powerful technologies to characterize the layered structure of nano-materials. The WAXS patterns of unmodified MgAl-LDH and organomodified MgAl-LDH reveal that modifier anion was efficiently intercalated within the MgAl-LDH layers with respect to its first basal reflection (0 0 3) at $2\theta = 2.90°$ corresponding to an interlayer distance of 3.05 nm, while the interlayer distance of unmodified MgAl-LDH is 0.89 nm. All these evidences show that the DBS anion was successfully intercalated into the interlayers of Mg/Al-LDH, which is consistent with the previous report [8].

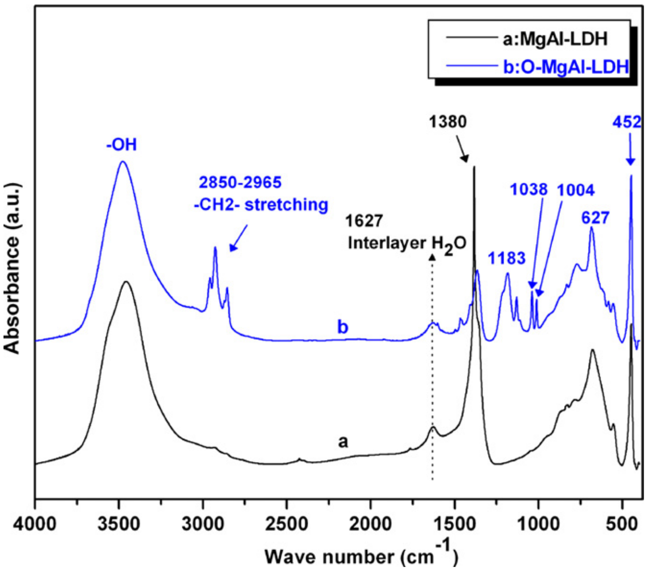

Fig. 1. FTIR spectra of (a) MgAl-LDH and (b) O-MgAl-LDH.

In comparison to (0 0 3) basal reflection of O-MgAl-LDH, PP/O-MgAl-LDH composites show almost no shift of the first basal reflection, while the second and the third basal reflections become weak and broad, or even non-existent for the composites with low LDH concentrations. This might be originated from a mixed morphology of micro- and nano-scale dispersion of MgAl-LDH in the matrix instead of complete nano-scale dispersion. The reason of inhomogeneous dispersion might be due to the difference in polar-

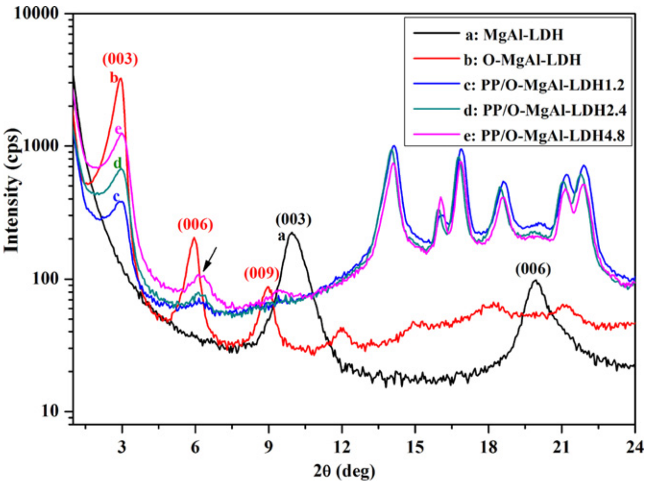

Fig. 2. WAXS patterns of MgAl-LDH, O-MgAl-LDH and PP/O-MgAl-LDH composites.

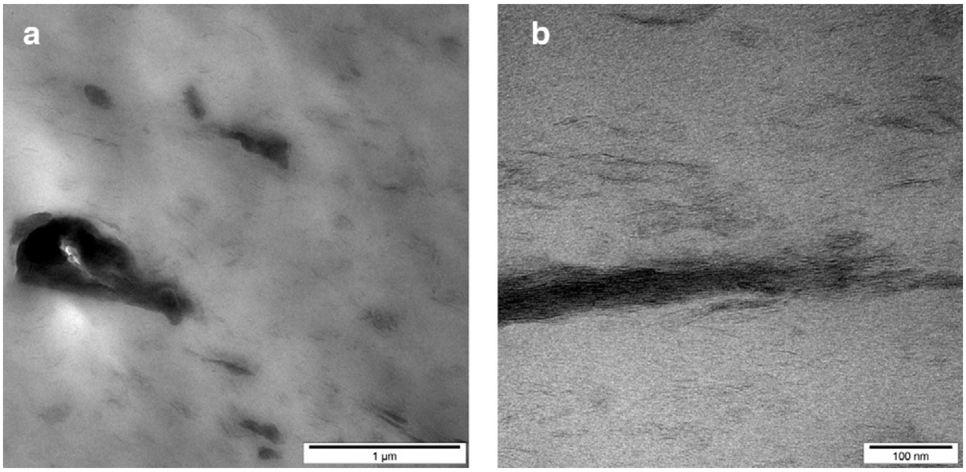

Fig. 3. TEM images of PP/O-MgAl-LDH showing nature of dispersion of LDH particles in matrix: (a) low magnification and (b) high magnification.

ity of LDH and PP. Non-polar character of PP causes compatibility problem with polar LDH and exfoliation of LDH in PP remains still as a big challenge [10].

The TEM analysis gives direct information about the state of dispersion of O-MgAl-LDH particles in the nanocomposite. The morphology of composite (represented by PP/O-MgAl-LDH2.4) is investigated by TEM and shown in Fig. 3. LDH aggregations in the size range of around 1 μm can be observed in the polymer matrix. Most parts of the visual field, however, shows good dispersion of MgAl-LDH layers in the PP matrix, providing a direct evidence of crystal layer exfoliation.

3.2. Combustion behaviors of PP/O-MgAl-LDH micro-nanocomposite investigated by MCC

Thermal decomposition behavior is important to study the combustion behavior of materials. Thermogravimetric analysis (TGA) is a common technique for evaluating thermal stability of various polymers. The thermal stability of organic MgAl-LDH has been reported in the previous publication [11]. In this work, the thermal decomposition behavior of materials is studied by TGA. Fig. 4 shows the TGA curves of PP and PP/O-MgAl-LDH composites. The results show that O-MgAl-LDH in the polymer composite causes earlier initial decomposition of the polymer matrix. At the same time, the maximum thermal decomposition temperature of PP/O-MgAl-LDH composites is also lower. It is also noted that the residues at the high temperature are improved with increased loading of LDH. The reason could be that LDH has a role for catalytic degradation of PP. This means LDH does not improve the thermal stability of the matrix; it rather changes the decomposition mechanism of PP [12].

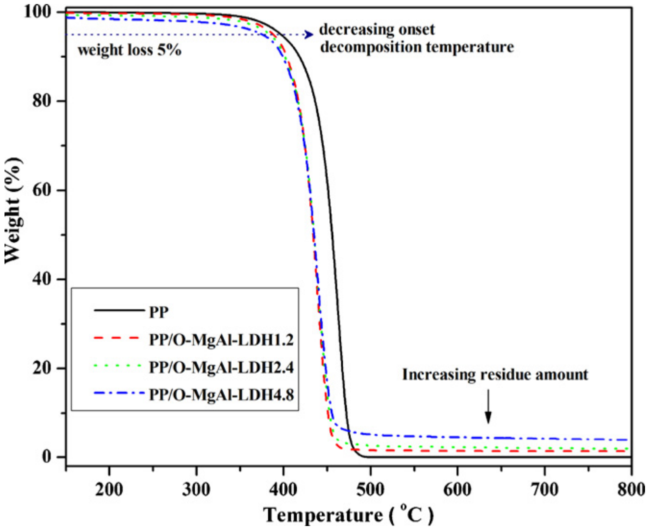

Fig. 4. Thermogram curves of PP and PP/O-MgAl-LDH nanocomposites.

Microscale combustion calorimeter (MCC) is a small-scale flammability testing technique to screen polymer flammability

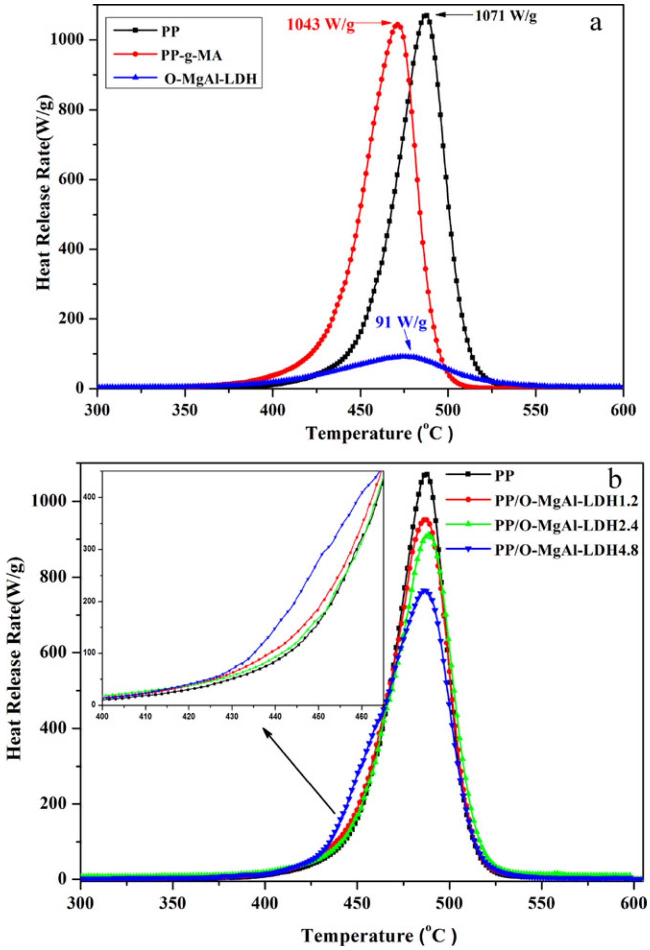

Fig. 5. The HRR curves of samples from MCC: (a) PP, PP-g-MA and O-MgAl-LDH and (b) PP and PP/O-MgAl-LDH micro-nanocomposite.

Table 1
Data recorded in MCC measurement.

Samples	pHRR-cal (W/g)	pHRR-mea (W/g)	THR (kJ/g)	HRC-cal (J/g K)	HRC-mea (J/g K)	Tem$_{max}$ (°C)
PP	–	1071	38.8	–	1055	487
PP-g-MA	–	1043	39.8	–	1030	471
O-MgAl-LDH	–	91	8.9	–	113	475
PP/O-MgAl-LDH1.2	1058	952	38.4	1043	941	489
PP/O-MgAl-LDH2.4	1046	911	37.0	1031	901	490
PP/O-MgAl-LDH4.8	1022	765	35.4	1018	849	487

pHRR: peak heat release rate; THR: total heat release; HRC: heat release capacity; Cal: calculation; Mea: measurement.

prior to scale-up of a large size. It is a convenient and relatively new technique developed in recent years and was regarded as one of the most effective bench scale methods for investigating the combustion properties of polymeric materials [13,14]. Similar to the cone calorimetry, MCC has a working principle based on oxygen consumption. During MCC measurements, several important parameters are recorded, such as specific heat release rate (HRR), heat release capacity (HRC), total heat release (THR). These outcomes are very important in manner of reflecting the combustion properties of materials and a reasonable estimate of flame hazard could be achieved using small quantities of samples.

HRR plots of PP, PP-g-MA, O-MgAl-LDH, PP/O-MgAl-LDH1.2, PP/O-MgAl-LDH2.4, PP/O-MgAl-LDH4.8 are shown in Fig. 5 and the corresponding combustion data are presented in Table 1. In Fig. 5(a), it can be found that HRR values of PP and PP-g-MA are similar and O-MgAl-LDH has a low HRR values (91 W/g). According to each individual components and their relative proportion, the calculated values of HRR and HRC for the PP/O-MgAl-LDH can be obtained if there is no interact influence on burning behavior of material. The peak HRR values of PP/O-MgAl-LDH micro-nanocomposites decrease with the increasing MgAl-LDH content. Peak HRR (pHRR) value of pristine PP is 1071 W/g, and pHRR of PP/O-MgAl-LDH1.2, PP/O-MgAl-LDH2.4, PP/O-MgAl-LDH4.8 composites are 952 W/g, 911 W/g and 765 W/g, respectively, indicating the improvement in flame retardancy of material. In comparison to the calculated values of HRR, it is clear to find the measured HRR values of PP/O-MgAl-LDH micro-nanocomposite are much lower. It means there is a significant effect on improving the flame retardancy of the material after introduction of small amounts of LDH. The possible catalytic effect of LDH on PP during the burning procedure could be one of the main flame retardant mechanisms. But the detailed flame retardant mechanism for this system should be investigated in the further study. A small peak rises between 410 °C and 450 °C for PP/O-MgAl-LDH micro-nanocomposites and its height (value) varies with increasing LDH content, in comparison to HRR curve of PP. This small peak might be corresponding to the combustion of surfactant (DBS) present in the interlayer of LDH. The heat release capacity (HRC) is an important parameter used to predict and evaluate the flame hazards and HRC values of neat PP and composites shown in Table 1. PP was found to have the highest HRC of 1055 J/g K, while the PP/O-MgAl-LDH micro-nanocomposite showed lower HRC values. The addition of MgAl-LDH led to the reduction in HRC. The HRC values of PP/O-MgAl-LDH1.2, PP/O-MgAl-LDH2.4, PP/O-MgAl-LDH4.8 are 941, 901 and 849 J/g K, respectively and show similar change trend as in case of pHRR. In comparison to the calculated HRC values in Table 1, the measured HRC values are also much lower. Therefore, the same conclusion as for above HRR values can be obtained, showing that the addition of a small amount of LDH leads to a significant improvement of flame retardancy of the composite.

Total heat release (THR) calculated from the total area under the HRR peaks is another important parameter for flame hazard evaluation. THR values of neat PP and PP/O-MgAl-LDH micro-nanocomposites with an increasing metal composition are 38.8, 38.4, 37.0 and 35.4 kJ/g, respectively. The trend is similar to the HRR and HRC. Additionally, the temperature at maximum pyrolysis rate (T_{max}) shows no significant difference between the micro-nanocomposites and the neat polymer.

The char obtained from the combustion of micro-nanocomposite (represented by PP/O-MgAl-LDH2.4) in microscale combustion calorimeter test was investigated via SEM and the representative result is shown in Fig. 6. In case of neat PP, the material was completely burnt out and no char was obtained. Formation of black colored char is probably an evidence of carbonaceous content in micro-nanocomposites. These residues are beneficial to reduce the heat transfer by forming the barrier [2,15]. To understand the structure of residues, the measurement of WAXS for the residues from both LDH and PP/O-MgAl-LDH has been investigated and the results are shown in Fig. 7. It can be found the residue structure from LDH is spinel phase ($MgAl_2O_4$) [16]. By comparison, it is obvious that the main structure of the composite residues is spinel phase as well.

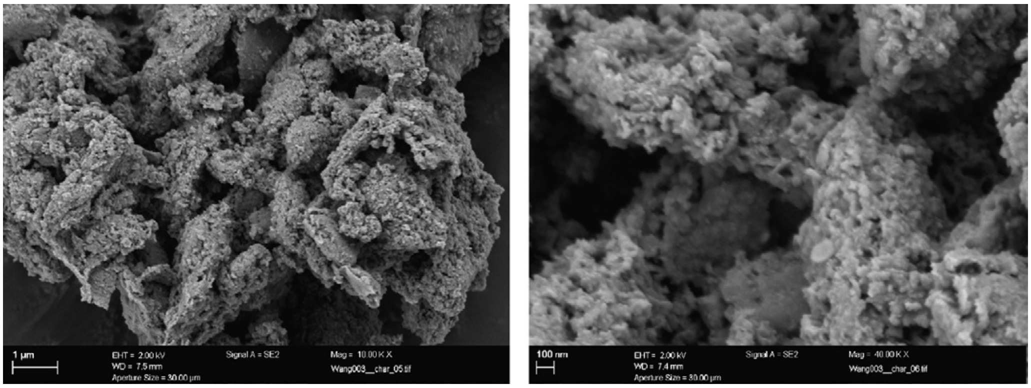

Fig. 6. Morphology of the char residue of PP/O-MgAl-LDH micro-nanocomposite after microscale combustion calorimeter test.

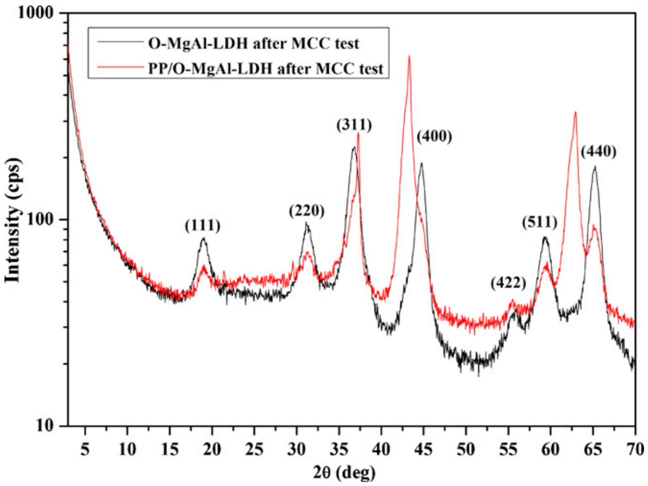

Fig. 7. WAXS patterns of the residue of O-MgAl-LDH and PP/O-MgAl-LDH micro-nanocomposite after microscale combustion calorimeter test.

4. Conclusion

A flame retardant PP/O-MgAl-LDH micro-nanocomposite has been prepared based on organomodified MgAl-LDH and PP by melt compounding directly in the presented work. Structural characterization by XRD and TEM illustrate the formation of a mixed morphology of micro and nano scale dispersion of MgAl-LDH in the matrix. The significant difference in combustion behaviors of PP and PP/O-MgAl-LDH micro-nanocomposite (LDH concentration contains 1.2 wt%, 2.4 wt%, 4.8 wt%, respectively) was observed from microscale combustion calorimeter results. As expected, the flame retardancy of PP/O-MgAl-LDH micro-nanocomposite is improved with the increasing MgAl-LDH content. PP/O-MgAl-LDH micro-nanocomposites show lower pHRR, HRC and THR values compared to neat PP. Char formation was not observed for neat PP. In case of PP/O-MgAl-LDH micro-nanocomposite, however, amount of black char residue was increased proportional to LDH content in composite, indicating the existence of carbonaceous materials in the residues. The reason could be relevant to the catalytic effect of LDH on PP during the burning procedure. These results are pointing out that incorporation of LDH and flame retardants to improve the flame retardancy of PP have a big potential for the future studies.

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