PREPARATION, FLAME RETARDANCY AND MECHANICAL PROPERTIES OF OMMT/PFR/ PA66 NANOCOMPOSITE

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Abstract: *The organically modified montmorrillonite（OMMT）/phosphorus containing polymer flame retardant(PFR)/polyamide-6,6(PA66) nanocomposites were prepared via melt intercalation on a twin-screw extruder. The structure formed in nanocomposite system was investigated by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Transmission Electron Microscopy (TEM). Properties such as flame retardancy , notched impact strength，tensile strength, elongation at break, and flexural modulus were studied by limited oxygen index (LOI) approach，UL94, and mechanical property test. The results of the studies indicated that flame retardancy and mechanical properties of PA66 nanocomposite were all reinforced due to addition of OMMT and PFR. Maximum improvement in flame retardancy and mechanical properties was observed at 5wt.% loading of OMMT. LOI of 5wt. % OMMT/10 wt. % PFR /PA66 was 29.6, 5wt.% OMMT/15wt.% PFR /PA66 achieved UL94-V0. By the addition of 5wt.% OMMT, the notched impact strength increased about 48%, the elongation at break enhanced about 25%, and the tensile strength decreased slightly (8%) in comparison with virgin PA66.*

1、Introduction

Polyamide-6,6(PA66),as a typical kind of engineering polymer material, has been widely used in every field, for its high mechanical strength, outstanding corrosion resistance and good machinability. In the past decade, nanocomposite with PA66 as matrix has received considerable attention in fundamental research and industry exploitation. At present, most studies are focused on OMMT / PA66 nanocomposite[1-10].

Montmorillonite(MMT) is a kind of clay, which consists of silicate layers. OMMT was synthesized by a cation-exchange reaction between MMT and several kinds of intercalation-agents. Intercalation agent plays a key role on nanocomposite. The selection of appropriate intercalation agent on the modified montmorillonite is one of the keys to preparing OMMT/PA66 nanocomposite with excellent properties.

Several groups have done many fundamental researches on OMMT/PA66.The OMMT/PFR/PA66 nanocomposites were prepared via melt intercalation on a twin-screw extruder in this study. OMMT was synthesized by a cation-exchange reaction between MMT and four different kinds of intercalation-agents, such as 1227,1631,1827,1831. The effects of different intercalation-agents on the property of OMMT/PA66 nanocomposite were also studied. The results showed that there is a kind of mechanical synergistic effect and flame retardancy synergistic effect between OMMT and conventional flame retardants, flame retardancy and mechanical properties of PA66 were all reinforced due to addition of OMMT and PFR.

2 Materials and testing methods

2.1 Materials

1227（Dodecyl dimethyl benzyl ammonium Chloride）,1631 (Hexadecyl trimethyl ammonium chloride),1827(Octadecyl dimethyl benzyl ammonium chloride),1831（Octadecyl trimethyl ammonium chloride）and HTAB(Hexadecyl trimethyl ammonium bromide) used in present work were produced by Shanghai Jingwei Chemical Co. Ltd. MMT was provided by Institute of Chemistry, Chinese Academy of Sciences, with a particle size of 40-80 μm. Organophilic montmorillonite OMT_{v6-1} was also provided by Institute of Chemistry. PA66 was produced by Liaoyang Chemical Engineering Corp. Phosphate flame retardant (PFR) (average molecular weight 8200-8600) was provided by laboratory of special materials, School of Material Science and Engineering, Beijing Institute of Technology.

2.2 Preparation of OMMT

The soils MMT contains impurities such as quartz, feldspar, needs to be purified before use. MMT and deionized water were added to reaction kettle, made the suspension with the concentration of 2.5%, after sedimentation, took the upper suspension.

OMMT was synthesized by a cation-exchange reaction between MMT and several kinds of intercalation-agents. Take the preparing process of $OMMT_{1827}$ for instance. A water solution of octadecyl trimethyl ammonium chloride (1831) was added to MMT suspension at 80°C. The mixture was stirred for 6 h at 80 °C and then filtered to obtain a white precipitate, standing overnight. The precipitate was washed repeatedly with distilled water until no Cl^- was detected by adding 0.5%$AgNO_3$ solution[11]. The product was then dried in a vacuum oven at 80 °C to a constant weight and ground into a powder with particle size <50μm, in this way we can get $OMMT_{1831}$.$OMMT_{1227}$, $OMMT_{1631}$and $OMMT_{1827}$ were prepared in the same way.

2.3 Preparation of OMMT/PFR/ PA66 nanocomposites

The OMMT/PFR/PA66 nanocomposites were prepared via melt intercalation on a twin-screw extruder. The mixture of dried PA66 slice (moisture content 0.05%) with different proportion of OMMT, flame retardant and a few white oil were uniformly mixed in high-speed mixer and then extruded by SHL-35 homonymous twin-screw extruder. For example, the synthetic procedure of $OMMT_{1631}$/PA66 was as follows: PA66 was air-dried at 110℃ for 3 h to avoid moisture –induced degradation reactions. PA66 and $OMMT_{1631}$ (3, 5, 7and 9%) were mechanically mixed and then extruded by the extruder with a screw speed of 122 rpm, and a feed rate of 11 rpm. The temperature of profiles of the barrel were195℃,205℃,215℃,235℃,245℃,250℃,265℃, 265℃, 260℃ from the hopper to the die. These extrudates were pelletized, dried, and injected into standard samples for testing[12]. The process was similar for PA66, OMMT and other additives (such as$OMMT_{1827}$/PA66, 5%$OMMT_{1631}$/15%PFR/PA66, 5%$OMMT_{V6-1}$/8%FR1808/PA66).

2.4 Testing methods

Chemical structure of the OMMT was characterized by FTIR(Nicolet Magna-IR560) spectrometer. X-ray diffraction (XRD) patterns were obtained using a XD-D1 diffractometer with Cu $K\alpha_1$ radiation (λ =0.154 nm; 40 kV; 30mA). Transmission electron microscopy (TEM) images were obtained by HITACHI-700 with the acceleration voltage of 100 kV.

The mechanical property such as notched Izod impact strength, tensile strength and elongation at break, and flexural strength/modulus were tested, respectively according to Chinese National Standard GB1843-80, GB/T1040-1992, GB/T9341-2000.

Heat distortion temperature (HDT) and rockwell hardness(HRR) were tested respectively according to Chinese National Standard GB1634-79 and GB9342-8.

The flame retardant performance test such as limited oxygen index (LOI), vertical combustion performance and cone calorimeter, respectively according to Chinese National Standard GB/T2406-1993, GB/ T2408-2008 and GB/16172-200.

3、Results and discussion

3.1 IR of OMMT

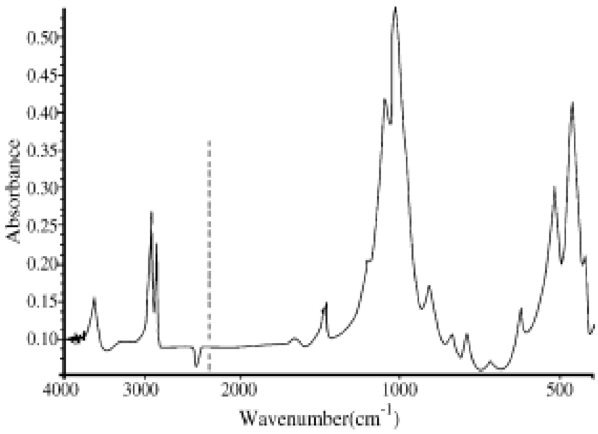


Figure 1. IR for $OMMT_{1631}$.

As shown in Figure 1, the peaks at 1050cm^{-1} are from stretching vibration of Si–O. The peaks at 400–700cm^{-1} are from flexural vibration of Si–O, Al–O. The peaks at 2850cm^{-1} are from stretching vibration of C–H. The peaks at 1470cm^{-1} are from flexural vibration of C–H. Thereby, organic cation have been inserted in the interlay spacing of MMT.

3.2 XRD of MMT, OMMT and $OMMT_{1631}$/ PA66

According to Bragg's law $2d\sin\theta = \lambda$ (d, the average distance between silicate layers; θ ,half the diffraction angle; λ ,the wavelength of incident X-ray), the layer distance of MMT ,$OMMT_{1631}$ and $OMMT_{1227}$ are 1.25 nm , 1.96 nm, 1.77 nm. It shows that there is ion exchange between organic cation and Na^+ in interlayers of MMT. With the organic cation entering into the interlayers of MMT, there was an increase in silicate layer distance. The bigger the spacing between the layers, the easier for the insertion of polymer in the preparation of OMMT/PFR/PA66 nanocomposites. OMMT is made to be dispersed well in the nanocomposites.

As shown in Figure 2, after OMMT was melt-mixed with PA66, the characteristic(001) diffraction of the OMMT disappeared. The absence of the (001) peak in (c) suggests that the ordered structure of OMMT is destroyed, and the OMMT layers are exfoliated in the polymer matrix. In other word, PA66 intercalates into the silicate layers, and disordered delaminated $OMMT_{1631}$/PA66 nanocomposite shows no peak in this region due to the loss of structural regularity of the layers. No more diffraction peaks are visible in the XRD pattern of exfoliated structures because the spacing between the layers is too large (>10 nm).The same results can be observed from the diffraction figures of MMT_{1827}/ PA66, MMT_{1227}/ PA66、MMT_{v6-1}/PA66.

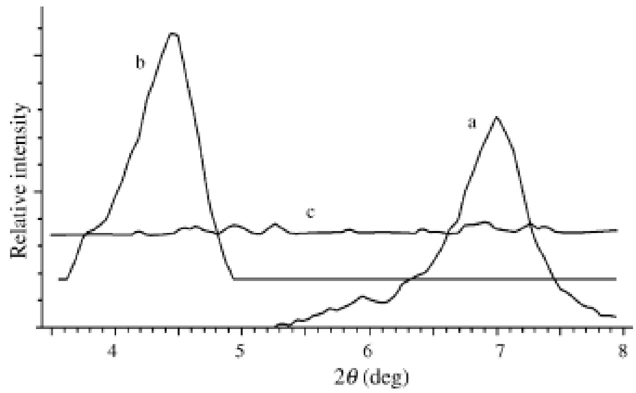
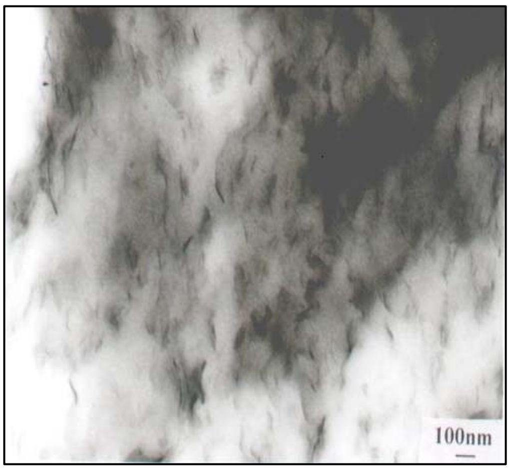


Figure2. XRD for (a) MMT, (b) $OMMT_{1631}$ and (c) $OMMT_{1631}$/PA66

3.3 TEM of OMMT/ PA66

OMMT layer is observed to be dispersed in PA66 matrix with TEM**.** Figure.3 and Figure.4 show that the white light area is PA66 matrix and the black area is silicate layers which homodisperse in PA66 matrix. The continuous phase is PA66, and OMMT is dispersed phase in PA66. Thickness of the silicate layers is about 20–50nm, while the interlayer spacing is far more than it. TEM micrograph suggests that the intercalation of the polymer chains increases the interlayer spacing of the OMMT. All those results demonstrate that almost all of the silicate layers are dispersed in nanoscale in matrix. The same results can be observed from the TEM micrograph of MMT_{1827}/PA66、MMT_{1227}/PA66、$MMT_{v6\text{-}1}$/PA66.



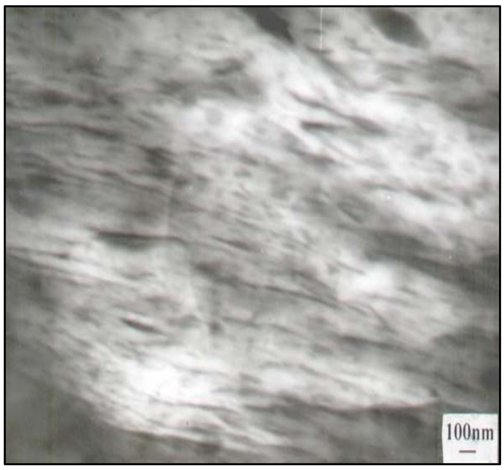


Figure3. TEM micrograph of $OMMT_{1631}$/PA66 Figure4. TEM micrograph of $OMMT_{v6\text{-}1}$/PA66

3.4 Mechanical properties of OMMT/PFR/PA66

For example, Table1 shows that a variety of mechanical properties of $OMMT_{1631}$/PA66 have been greatly improved, in comparison with virgin PA66.The mechanical properties of $OMMT_{1631}$/PA66 are superior to the other two samples, such as $OMMT_{1227}$/PA66,$OMMT_{1827}$/PA66. It is probably because the interaction strength between 1631 and matrix resin is greater than that of 1227 and 1827.

Sample	Notched Izod impact strength $/J\cdot m^{-1}$	Tensile strength /MPa	Elongation at break /%	Flexural strength /MPa	Flexural modulus /MPa
PA66	23.6.	65.8	48	106.7	2750
$OMMT_{1227}$/PA66	31.5	76.6	41	120.4.	2986
$OMMT_{1631}$/PA66	34.9	78.9	30	123.8	3534
$OMMT_{1827}$/PA66	26.2	71.4	38	117.3	3259

Tab.1 Mechanical properties of OMMT/PA66 nanocomposites

3.5 Heat distortion temperature (HDT) and rockwell hardness(HRR)of $OMMT_{v6-1}$/PA66

As shown in Figure5 and Figure6, the HDT and HRR of PA66 were improved with the addition of MMT_{V6-1}. The HDT was increased by 40.1% when the content of MMT_{V6-1} is 7%.

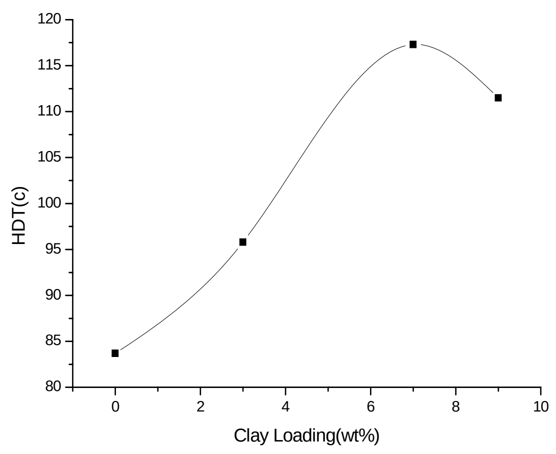


Figure5. HDT of $OMMT_{v6-1}$/PA66

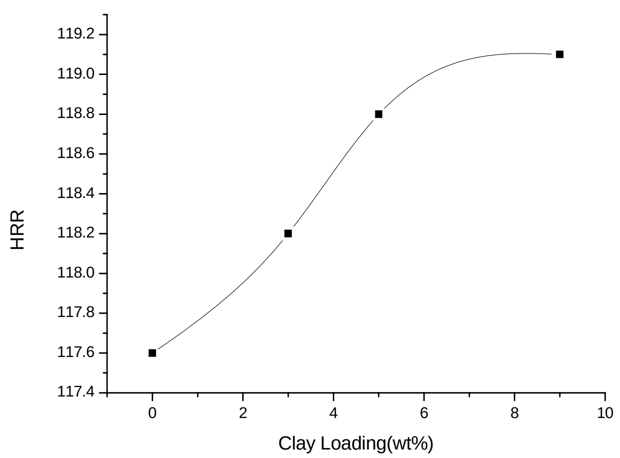


Figure6. HRR of $OMMT_{v6-1}$/PA66

3.6 Flame retardancy of PA66, OMMT/PA66 and OMMT/PFR/PA66

(1) OMMT/PA66 is not easy to ignite. It took a long time to ignite with butane gas and stopped

burning after the flame source is removed.

(2) It is found that there is almost not soot or smoke when OMMT/PA66and OMMT/PFR/PA66 burning, compared with virgin PA66. MMT has smoke suppression effect and doesn't break down at very high temperature.

(3) Burning PA66 drips heavily. There is still dripping-melt for PA66 with the addition of regular flame retardant. Dripping-melt of PA66 is hard to be solved. There is no dripping melt for OMMT /PA66 at all. For example, carbonaceous residue of 5% OMMT1827/PA66 keeps well after burning, which bend over but doesn't drop out. So OMMT is a kind of dripping-melt dripping-melt suppressor. Dripping-melt and carbonaceous residue of PA66 and OMMT1827/PA66 are shown in Figure 7 and Figure 8.

Figure7. Virgin PA66

Figure 8. 5% $OMMT_{1827}$/PA66

(4) LOI of 5wt.%OMMT/10wt.%PFR/PA66 was 29.6, 5wt. % OMMT/15wt.%PFR/PA66 achieved UL94-V0. LOI of OMMT/PFR/PA66 is higher than that of PFR/PA66 or OMMT/PA66.Perhaps there is a synergistic effect between OMMT and PFR at certain loading. PFR is a kind of effective flame retardant for OMMT /PA66.

4、Conclusion

(1) OMMT was synthesized by a cation-exchange reaction between MMT and several kinds of intercalation agents. In the process of preparing nanocomposites via melt intercalation, intercalation agent plays a key role. The selection of appropriate intercalation agent on the modified montmorillonite is one of the keys to preparing OMMT/PA66 nanocomposites with excellent properties. The use of different intercalated agent has great influence on the property of nanocomposite.

(2) The organically modified montmorillonite(such as $OMMT_{1631}$、$OMMT_{1831}$、$OMMT_{1227}$ and $OMMT_{1827}$)can improve the notched impact strength of PA66. By the addition of 5wt. % OMMT, the notched impact strength increased about 48%，the elongation at break enhanced about 25%, and the tensile strength decreased slightly (8%) in comparison with the virgin PA66. According to our research, the intercalation agent 1631 is better than others.

(3) There is a kind of mechanical synergistic effect and flame retardancy synergistic effect between OMMT and other flame retardants. The results of the studies indicated that flame retardancy and mechanical properties of PA66 were all reinforced due to addition of OMMT and PFR. Maximum improvement in flame retardancy and mechanical properties was observed at 5wt. % loading of OMMT.

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