Research on new nylon-6 nanocomposites with flame retardancy

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Introduction

In recent years, more and more environmental legislations have limited or prohibited the application of halogen-containing flame retardants in polymer materials. Considerable research has been focused on inorganic fillers and organosilicones as halogen-free flame retardants.[1-5] However, inorganic flame retardants are usually less effective and the addition level of up to 60 wt% is normally required in order to achieve acceptable resistance to combustion.[3] Such high level addition will in turn lead to deteriorated toughness and processability.[3,6] Some elastomers could be used to improve the toughness of flame retardant plastics,[6,7] but makes the processability even worse. Recently, a new flame retardant approach via polymer/clay nanocomposites has attracted a great deal of interest, because the addition of small amount clay brings out a large enhancement of flame retardance.[8-15] However, the polymer/clay nanocomposites are usually more brittle than pure polymer and organic modification of clay makes the manufacturing process of polymer/clay nanocomposites costly.[16-22] The organosilicone can only be used in aromatic thermoplastics, such as polycarbonate, polystyrene and acrylonitrile-butadiene-styrene copolymer (ABS), and also decrease the toughness and stiffness of thermoplastics.[4,5] Therefore, a composite with good flame retardance, balanced mechanical properties and good processability is much desired, but extremely hard to achieve.

In this study, some new halogen free, elastomeric flame retardants, such as silicone elastomeric nanoparticle (S-ENP) with T_g of -120℃, clay/S-ENP compound and nano-size $Mg(OH)_2$/CNBR-ENP compound etc have been used in nylon-6 modification.

Results and discussion

S-ENP/Nylon-6 and Clay/S-ENP/Nylon-6 nanocomposites. The nanocomposites were prepared by the patented method[23]. The raw material for producing S-ENP was common silicone latex. After premixed with cross-linking agent, the silicone latex was irradiated with γ ray and changed into highly cross-linked rubber particle with much higher crosslinking degree on the particle surface.[25,26] S-ENP was finally produced by spray drying the highly cross-linked rubber latex. The preparation of clay/S-ENP compound is similar to that of S-ENP. Firstly, clay powder was dispersed into water by using an emulsifier for 30 min to form a clay slurry containing 2 wt% of clay. The highly crosslinked silicone rubber latex was added into the clay slurry at a dry weight ratio of 4/1 and stirred for 60 min to form a uniform mixture, in which the clay platelets and the crosslinked silicone rubber particles were interpenetrated. clay/S-ENP compound can be obtained after spray drying the mixture. After spray drying, the special microstructure that S-ENP particles and exfoliated clay platelets partitioned each other was retained. The nylon-6/S-ENP and nylon-6/S-ENP/Clay nanocomposites were prepared by using a conventional co-rotating twin-screw extruder. During melt blending, the exfoliated clay platelets are hardly aggregated due to the partitioning effect of S-ENP. It can be found that the cost of preparing processes for S-ENP, S-ENPC and nanocomposites is quite low.

The flammability properties of the composites were characterized by means of cone calorimetry. The heat release rate (HRR) plots for pure nylon-6 and the composites at 35 kW/m² heat flux are shown in figure 1 and some cone calorimetry data are listed in table 1. It can be seen that the nylon-6/S-ENP composite shows a 60% lower peak heat release rate (PHRR) compared to pure nylon-6, which indicates that the addition of S-ENP can significantly decrease the flammability of nylon-6. Furthermore, the PHRR of nylon-6/S-ENP/clay is 68% lower than that of nylon-6, even lower than that of nylon-6/S-ENP composite. The similar trends are seen for mean HRR. It is obvious

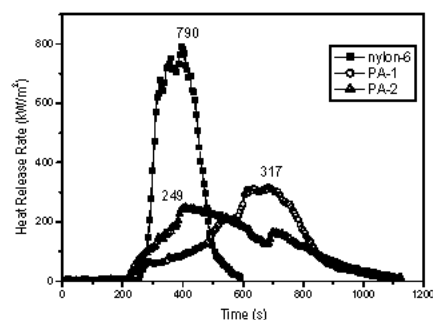that S-ENPs and exfoliated clay platelets exhibit a synergistic flame retardant effect on nylon-6.

Figure 1. Heat release rate (HRR) plots for pure nylon-6, nylon-6/S-ENP (PA-1) and nylon-6/S-ENP/Clay (PA-2) at a heat flux of 35 kW/m².

Table 1. Cone calorimeter data at a heat flux of 35 kW/m².

samples	peak HRR (kW/m²) (Δ%)	mean HRR (kW/m²) (Δ%)
Nylon-6	790	370
PA-1	317 (60)	129 (65)
PA-2	249 (68)	110 (70)

Nylon-6/CNBR/nano-Mg(OH)₂ composites. The preparation process is similar to that of nylon-6/S-ENP/clay. In order to make comparison, we also prepared the same composite by using "conventional process", which is simply blending the three components together. Time to ignition (TTI) data of the above samples from cone calorimetry test is shown in Figure 2. The none-filled samples A0 needed 108s to ignite and both filled sample markedly postponed the ignition time. The result was in accordance with others regarding the MH function of prolonging the materials' ignition time. However, the two nano-MH filled samples were different, A1 (prepared by our new process) requires much longer ignition time than A2(conventional process).
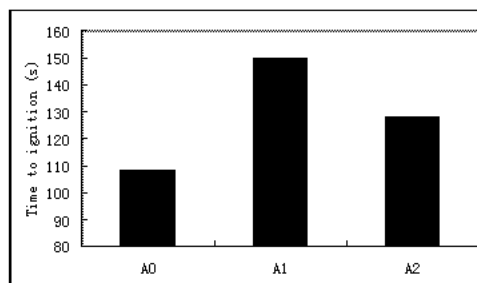

Figure 2 TTI(s) of nilon-6 and its composites under heat flux of 35kW/m² (nylon-6/CNBR-ENP/nano-Mg(OH)₂, 90/40/60, wt)

Mean HRRs (within 5 minutes after ignition) of the three samples were given in Figure 3. It is obvious that mean HRRs of A1 and A2 after ignition were far lower than those of A0 in the beginning 300 seconds. Furthermore, the mean HRR of A1 was 28kW/m² lower than that of A2 for the starting 60 seconds, and 19kW/m² lower for the starting 120 seconds after ignition. Although the mean HRRs for longer periods after ignition were similar for the two ternary composites, it is a common understanding that the decreasing of average HRRs at the beginning several minutes are much more important than those afterwards. Therefore, A1 exhibits better flame retardancy than A2 in terms of mean HRRs. It is important for us to know why the two ternary composites with the same formulation perform differently on flame retardancy. In order to find out the reason that A1 and A2 performed differently on flame retardancy, especially on the ignition time and mean HRR within 3 minutes after ignition, TEM was used to observe the dispersion of nano-sized MH particles in the above two ternary composites.
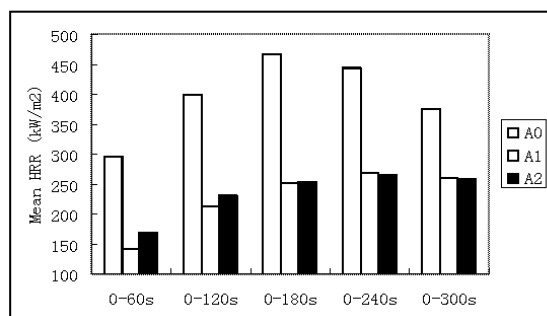
Figure 3   Mean HRRs in different periods after ignition

Figure 4 showed the TEM images of ternary composites A1 and A2. The rubber domains in A2 have a wide distribution in size, with diameters of 0.5 to 10μm, while the ENP particles were dispersed at a much smaller size and narrower distribution in A1. Besides, well-dispersed nano-MH fillers can be observed both in and outside the rubber domains of A1. On the contrary, serious agglomerations were found for both nano-MH particles and ENPs in A2, and no nano-MH particles were observed inside the rubber domains of A2. It is obvious that nano-MH and CNBR particles were dispersed more evenly in A1 than in A2.
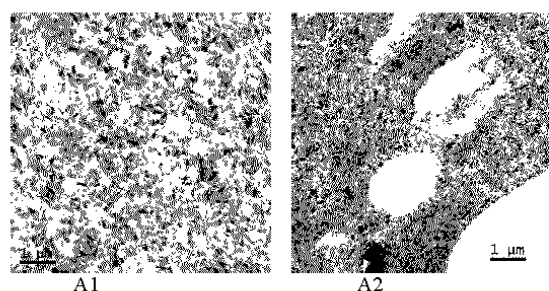

Figure 4   TEM image of the ternary composites A1 and A2

It is believed that better dispersion of nano-MH in A1 is the main reason that A1 exhibit better flame retardancy than A2. The combustion of polymers arises from their thermal degradation at a certain temperature and the release of highly flammable decomposition products. The function of MH as a flame retardant filler is that its endothermic decomposition cools the condensed phase and the released water also cools and dilutes the flammable products in the vapour phase. The residue of Magnesium oxide crust after combustion can also protect the underlying polymer from the outside heat. The nano-MH particles in the ternary composites of A1 dispersed very well; therefore, the decomposition of nano-MH undergo evenly on the surface of the sample and the sample was also cooled evenly without locally overheated by the external heat flux. As to the image of sample A2, there exist some rubber domains in which no nano-MH platelets dispersed. The temperatures should be higher near such domains than other zones. As a result, earlier ignition of A2 than A1 occurred at the same conditions. Besides, better dispersion of nano-MH platelets in the ternary composites ensured a more compact heat insulate layer on the sample's surface, which also prevented the released combustible gases or low molecular organic compounds from passing through. Even after the decomposition of MH, the inorganic residue of magnesium oxide (MgO) remained on the surface still maintained the compact structure which might also has the function of a thermal insulating barrier between the underlying polymer substrate and the external heat source.

Conclusions

Some of novel halogen-free, elastomeric flame retardants for nylon-6 have been developed. It is found that the S-ENP and clay have a synergistic flame retardant effect on nylon-6 resulted from the formation of two barriers on the nanocomposite residue surface at the end of combustion. A novel flame retardant ternary nanocomposite of nylon-6/ENP/nano-Magnesium hydroxide was also fabricated. The new ternary composite has better flame retardancy and thermal stability than the conventional one because nano-MH can disperse

much more homogeneous in the new ternary composite than in the conventional one.

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