

Preparation and Properties of Environmental Friendly Nonhalogen Flame Retardant Melamine Cyanurate/Nylon 66 Composites

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ABSTRACT: Melamine cyanurate (MCA) was utilized as an environmental friendly additive to prepare the nonhalogen flame retardant MCA/Nylon 66 composites by melt blending technique. Because of the strong hydrogen bond interactions and fine interfacial compatibility between MCA and Nylon 66, the resultant even dispersion of MCA filler in polymer matrix leads to the better toughness and strength of MCA/Nylon 66 composites than those of neat Nylon 66. Both Nylon 66 and MCA/Nylon 66 composites exhibit similar α -crystalline structure, but the presence of MCA influences the distribution of $\alpha 1$ and $\alpha 2$ crystalline

phases in Nylon 66 by inducing its hydrogen-bonded sheet separation. Moreover, the blending of MCA and Nylon 66 increases the crystallization temperature and exothermicity but decreases the thermal stability of Nylon 66 and accelerates the degradation of MCA. The MCA/Nylon 66 composites show better flame retardancy at intermediate MCA contents of 10 and 15 wt %. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1688–1697, 2011

Key words: composites; flame retardance; nylon; MCA; nonhalogen

INTRODUCTION

Nylon is an important thermoplastic resin widely used in the fields of fiber, film, and engineering plastic because of its superior advantages in mechanical, thermal, and electrical properties, which makes its properties of thermal stability and fire resistance of great significance for application, especially electrotechnical applications.^{1–3} The low flammability of Nylon exhibiting intensive flammable dripping and fire hazard is usually improved by incorporating the flame-retardant additives such as halogens, phosphorus, or other halogen- or phosphorus-free compounds into the polymer matrix. Through the flame retardancy modification, the material propensity to burn, the burning/heat release rate, or the smoke and toxic combustion products of Nylon can be greatly reduced.⁴

Halogen- and phosphorus-containing fire retardants show very effective flame retardancy in Nylon materials, but the evolution of corrosive and toxic products generated during the combustion process has limited their application in polymer matrix.^{2,5,6}

Therefore, the usage of novel environmental friendly flame retardant has drawn more and more attentions of researchers and industrialists. As for Nylon 66 material, it was reported that the polymer-organic char former (PVA system) can reduce the peak rate of heat release and increase the char yield due to the “synergistic” carbonization effect, and the binary system of Si and SnCl₂ can also act as an effective inhibitor of gaseous phase flame reactions, which makes them possess optimistic application prospects as new type of ecologically safe flame-retardant in Nylon matrix.⁷ It is also found that when clay is added in Nylon 6 or Nylon 66, the obtained polymer-layered silicate nanocomposites (PLSNs) exhibit an obvious decrease in the peak heat release rate (PHRR) and the mass loss rate with a change in the char structure during combustion in a calorimeter, besides the enhancement of the mechanical, thermal, dimensional, and barrier property.^{1,4,8–11} In recent years, melamine cyanurate (MCA) has been proved to be very effective for increasing the oxygen index (OI) and lowering the volatilization temperature of polyamides even at a relatively low level of about 10 wt %.^{2,12} Besides the flammability improvement, low addition of MCA helps to maintain the intrinsic mechanical and electrical properties of the polymer matrix.

Melamine and its salts are regarded as an intumescent type fire retardant, which can lead to the formation of polymeric products on heating and protect polymer from the action of flames. It is deduced

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from TGA results that the cyanuric acid has a catalytic role in the formation of polymeric melamine and this formation efficiency is limited by the decomposition of cyanuric acid to volatile cyanic acid.⁵ When the decomposition gas of MCA in Nylon 66 matrix is detected by the pyrolysis technique, it is found that the variability of decomposition products depends on the heating rate, and fast heating rate promotes the formation of volatile melamine and cyanuric acid. Moreover, Nylon 66 matrix accelerates the decomposition of cyanuric acid to cyanic acid. The actual flame-retardance mechanism of MCA is commonly described as "drip promoter" with modified smaller and extinguished burning drips formed by polyamides during combustion in the presence of MCA, and this drip promoter action is usually explained by the decrease of the molecular weight and viscosity of the polymer matrix. In this study, the nonhalogen flame retardant MCA/Nylon 66 composites with different MCA contents were prepared, and the morphology, structure, thermal property, mechanical property, and flame retardancy of these Nylon 66 composites were also investigated in detail.

EXPERIMENTAL

Materials

Nylon 66 (21ZLV) is a product as pellets from Vydne Company (USA), with a density of 1.38 g/cm³ and a saturated moisture adsorption of 5.4 wt % at 23°C. The MCA (C₆H₉N₃O₃) with nitrogen content greater than 98 wt % and average particle size of 5 μm was purchased from Shouguang Weidong Chemical (Weifang, China).

Preparation of MCA/Nylon 66 composites

During the preparation of the flame retardant MCA/Nylon 66 composites, Nylon 66 was melt blended with MCA at 230°C by the use of twin-screw extruder after the components were physically premixed in an SHR-10A high-speed mixer for 15 min at room temperature, and the obtained Nylon 66 composites were designated as N66, 5MCA-N66, 10MCA-N66, 15MCA-N66, and 20MCA-N66, corresponding to the MCA contents of 0, 5, 10, 15, and 20 wt % contained in the composites, respectively. After melt blending in the twin-screw extruder, the extruded strands were cooled in a cold water bath, pulled, palletized to granules, and dried at 110°C for 3 h before injection molding. By utilizing a HD 95G screw injection-molding machine, the pellets of MCA/Nylon 66 composite were injection molded into ASTM standard specimens for mechanical measurements at 260°C with an injection pres-

sure of 70 MPa. All the specimens were conditioned at 23°C for 48 h before testing.

Morphology observation

The morphology of the MCA/Nylon 66 composites was observed with a JSM-7401 field emission scanning electron microscope (JEOL, Japan) operated at 5 KV. Before examination, the liquid nitrogen freeze-fractured samples from injection-molded strips were coated with a thin gold layer to increase the surface conductivity.

Structure analysis

A D/max-2200/PC X-ray diffractometer (Rigaku, Japan) equipped with a Ni-filtered CuK_α radiation was used for X-ray diffraction studies. The measurements were carried out at 40 kV and 100 mA from 1 to 50° with a scanning rate of 5°/min and an interval of 0.02°. Moreover, the detailed structural information was achieved by the use of Fourier transform infrared (FTIR)-Raman Spectrometer (Perkin-Elmer, USA), and the FTIR spectra were recorded from 450 to 4000 cm⁻¹. These above measurements were all operated at room temperature, and the test specimens were obtained from the injection molding of the composite pellets.

Thermal analysis

The differential scanning calorimeter (DSC) measurements were performed in a Q10 differential scanning calorimetry (TA Instrument, USA) calibrated with indium standard at the atmosphere of nitrogen. The samples, prepared from the palletized granules, were first heated from room temperature to 300°C at 10°C/min and held there for 5 min to remove the thermal history, and cooled to room temperature at 10°C/min to record the crystallization behavior, and then reheated to 300°C at 10°C/min to trace the melting behavior. Values of crystallization and melting entropy (ΔH_c and ΔH_m) were calculated from the exothermic and endothermic peak areas, and the exothermic and endothermic peak temperatures were taken as crystallization and melting temperatures (T_c and T_m). For the MCA/Nylon 66 composites, the crystallization and melting entropy were also normalized by the weight fraction of MCA (χ) to be $\Delta H_c/\chi$ and $\Delta H_m/\chi$ for accurate comparison. With the use of a TG209 F1 Iris Thermogravimetric Analyzer (NETZSCH, German), the weight change of the MCA/Nylon 66 composites was investigated from room temperature to 700°C at a heating rate of 20°C/min in a nitrogen atmosphere.

Mechanical property test

As for the MCA/Nylon 66 composites, the hardness was measured by an XHR-150 Plastic Rockwell Hardness Tester (Shanghai Material Testing Machine, China) according to the standard of ASTM D785, and the melt flow index (MFI) was determined by a RL-11B Melt Indexer (Shanghai S.R.D. Scientific Instrument, China) referring to the standard of ASTM D1238 with a load of 0.325 kg at 275°C. A CMT6104 Universal Tensile Tester (Sans Testing Machine, China) was employed to evaluate the tensile and flexural property according to the ASTM standards of D638 and D790 with the cross-head speeds of 5 and 2 mm/min, respectively. The Izod impact strength of the notched specimens was measured by using an XC-2.75 Pendulum Impact Tester (Chengde Jingmi Testing Machine, China) following the ASTM D256 standard with the hammer weight of 0.818 kg and the impact energy of 2.75 J. Five specimens for each sample were tested to obtain the average value for determination.

Flammability measurement

The flammability of the MCA/Nylon composites is studied by using the traditional vertical burning test (UL94) and OI test. UL94 test is conducted on a CZF UL94 horizontal/vertical flame chamber (Nanjing Shangyuan Analytical Instrument, China) for the sheets of 3.2-mm thickness, and OI is conducted on an HC-2 Oxygen Indexer (Nanjing Jiangning Analytical Instrument, China) from 10 to 35°C according to the standard of ASTM D2863.

RESULTS AND DISCUSSION

Morphology observation

Scanning electron microscope (SEM) is an effective media for morphology observation, providing the direct and detailed information of the dispersion of additives in polymer matrix, the compatibility between the filler and polymer matrix and brittle-toughness fractured breakage. Figure 1 shows the SEM photographs of the cryofractured surface of Nylon 66 and the flame retardant MCA/Nylon 66 composites. In Figure 1, MCA particles appear short-layered slices and even dispersion in the Nylon 66 matrix. With the increase of MCA content, more layered slices of MCA tending to aggregate are in visual field, and the fractured surface of the MCA/Nylon 66 composites turns rougher than that of pure Nylon 66, which implies that there may be some interfacial interaction between polar Nylon and polar MCA molecules with abundant hydroxyl and amino groups forming large amounts of hydrogen bonds.¹² It seems that due to the formation of hydro-

gen bonds in the interfacial region and the resultant fine compatibility between the filler and polymer matrix, the good dispersion of MCA filler in Nylon 66 matrix results in the better toughness and strength of the MCA/Nylon 66 composites than those of neat Nylon 66, which is also approved by the latter mechanical property analysis.

Structure analysis

Nylon 66 is a kind of polycrystalline polymer in which triclinic α -crystalline phase and pseudo-hexagonal γ -crystalline phase are the most important crystalline phases, and with temperature rising the room temperature triclinic α -phase structure will be transformed into the high temperature γ -phase structure in Nylon 66.¹¹ In general, the characteristic diffraction of Nylon 66 shows two distinct peaks of 20° ($\alpha 1$ phase) corresponding to the (200) plane and 24° ($\alpha 2$ phase) corresponding to the (002) and (202) planes at room temperature.

The X-ray diffraction patterns of MCA, Nylon 66, and the flame retardant MCA/Nylon 66 composites are given in Figure 2. Both Nylon 66 and MCA/Nylon 66 composites show the same characteristic diffraction peaks of the α -crystalline phase structure of Nylon 66 at 20.4° ($\alpha 1$ phase) and 23.3° ($\alpha 2$ phase). Different from the experimental results of clay/Nylon 66 nanocomposites,^{11,13} the MCA filler does not induce the generation of γ -crystalline phase of Nylon 66 in the MCA/Nylon 66 composites. However, a great difference of the relative peak intensity of $\alpha 1/\alpha 2$ occurs similarly for Nylon 66 after MCA addition. The $\alpha 1$ peak of Nylon 66 originates from the distance between hydrogen-bonded chains in sheets, and the $\alpha 2$ peak originates from the separation of the hydrogen-bonded sheets.¹⁴ As for the MCA/Nylon 66 composites, the remarkable decrease of the relative peak intensity of $\alpha 1/\alpha 2$ may indicate that the presence of MCA influences the arrangement of Nylon 66 molecules in the α -crystalline phase by inducing the separation of the hydrogen-bonded sheets of Nylon 66 through the strong hydrogen bond interactions between MCA and Nylon 66 molecules. It is the formation of hydrogen bonds between MCA and Nylon 66 molecules that changes the crystalline structure of Nylon 66, but the effect of MCA content on the crystalline phase distribution of Nylon 66 in the MCA/Nylon 66 composites is not very evident.

In fact, compared with the neat components, the MCA/Nylon 66 composites exhibit separate characteristic diffraction peaks of MCA and Nylon 66 with no change in position but obvious change in intensity, and the peak intensity change of MCA appears much greater than that of Nylon 66. The characteristic diffraction peaks of MCA at 11.0°, 12.0°, and

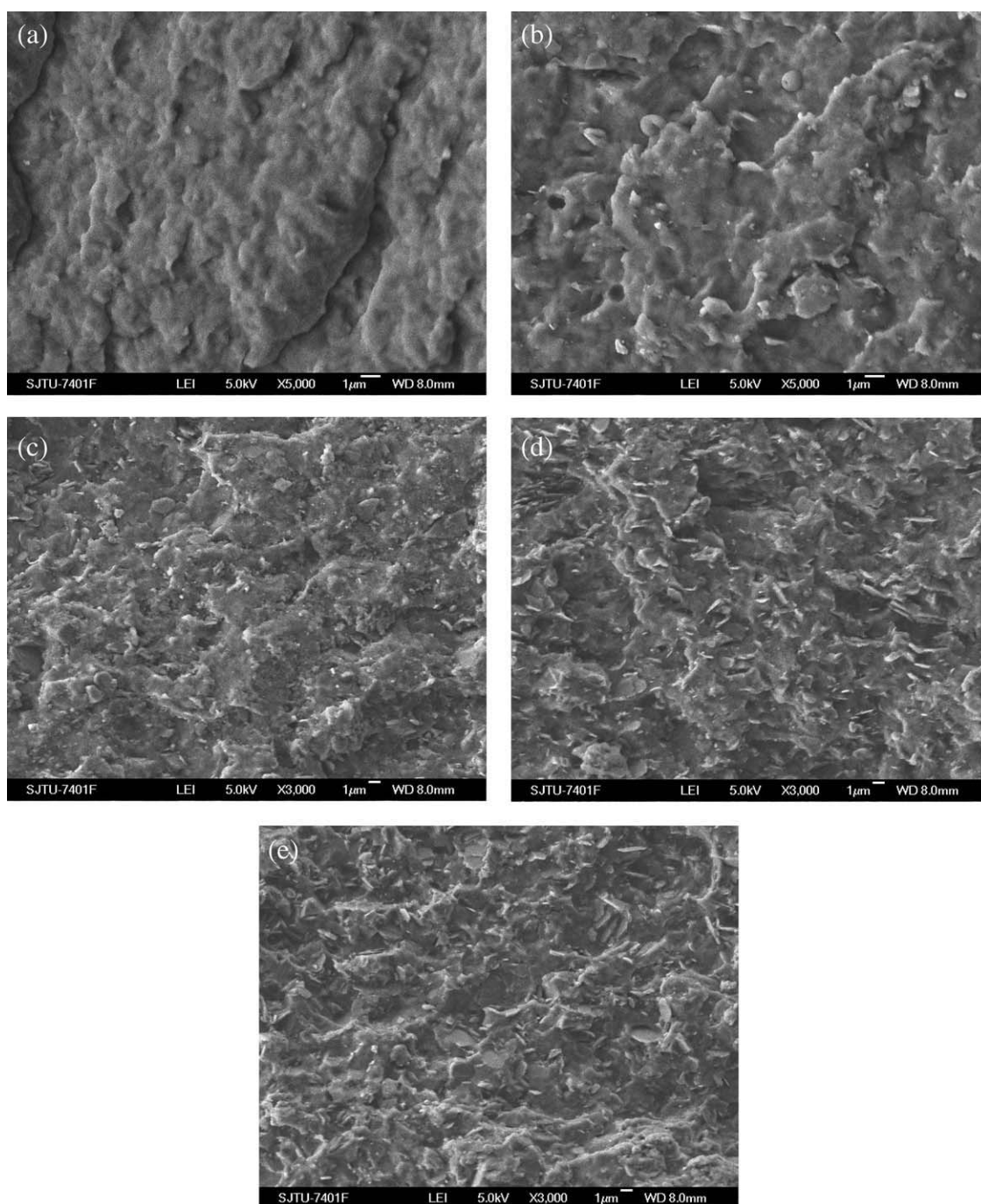


Figure 1 SEM photographs of the cryofractured surface of Nylon 66 and the flame retardant MCA/Nylon 66 composites: (a) N66, (b) 5MCA-N66, (c) 10MCA-N66, (d) 15MCA-N66, and (e) 20MCA-N66.

28.1° increase in intensity with the increase of MCA content in the Nylon 66 matrix, but other characteristic diffraction peaks of MCA are not visible in the diffraction patterns of the MCA/Nylon 66 composites. Because of the less incorporated amount of MCA, the intensity of the MCA diffraction peaks at 11.0° and 12.0° of the MCA/Nylon 66 composites are significantly weaker than that of pure MCA, while the intensity of the MCA diffraction peak at

28.1° of the MCA/Nylon 66 composites is much stronger than that of pure MCA, which also reveals that there are indeed strong molecular interactions between MCA and Nylon 66 because of the existence of their abundant hydroxyl and amino groups. This strong hydrogen bond interaction formed between MCA and Nylon 66 molecules not only changes the crystalline structure arrangements of Nylon 66 matrix but also induces the special

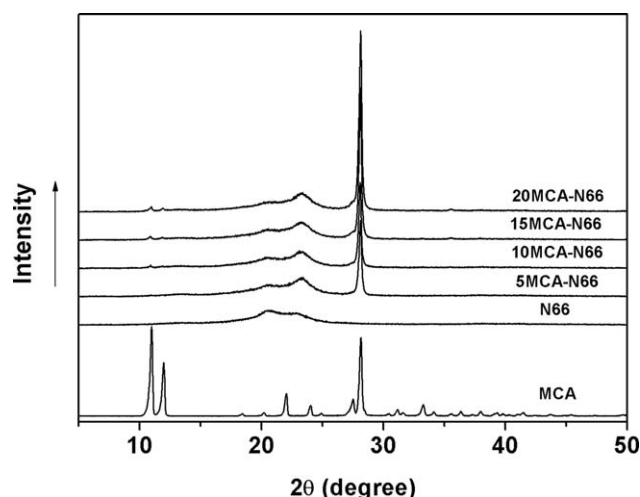


Figure 2 X-ray diffraction patterns of MCA, Nylon 66, and the flame retardant MCA/Nylon 66 composites.

diffraction strengthening of the certain crystalline plane of MCA in the MCA/Nylon 66 composites.

To obtain the detailed structural information and examine the bond interactions within the MCA/Nylon 66 composites, FTIR experiments were performed on the MCA/Nylon 66 composites and the pure components for comparison. Figure 3 illustrates the FTIR spectra of MCA, Nylon 66, and the flame retardant MCA/Nylon 66 composites. Just as seen in Figure 3, MCA exhibits three characteristic absorption peaks of 1782, 1533, and 1447 cm^{-1} from cyanurate, melamine, and an overlapping band of melamine and cyanurate, respectively,¹⁵ and Nylon 66 exhibits the characteristic absorption peaks of polyamide at 1627 cm^{-1} from amide I, 1534 cm^{-1} from amide II, 2931 and 2861 cm^{-1} from the stretch vibration of methylene group in the Nylon 66 oligomer.⁵ The absorption bands from stretching vibration of N—H bond appear at different positions with two peaks of 3396 and 3234 cm^{-1} for MCA and two peaks of 3295 and 3078 cm^{-1} for Nylon 66. Similar to the X-ray diffraction experimental results, the MCA/Nylon 66 composites still show separate characteristic absorption of MCA and Nylon 66, and these absorption peaks almost keep the same position but change in intensity in the FTIR spectra. The characteristic absorption peaks of MCA in the MCA/Nylon 66 composites become stronger with the increase of MCA content in the Nylon 66 matrix. Moreover, it can also be noted from Figure 3 that as for the MCA/Nylon 66 composites, the absorption bands 3396 and 3234 cm^{-1} of MCA appear as shoulder attached on those of Nylon 66, while the absorption band 1665 cm^{-1} of MCA disappears, which may also provide an advantageous support for the molecular interaction between MCA filler and Nylon 66 matrix.

Thermal property

The DSC cooling and heating scan results of Nylon 66 and the flame retardant MCA/Nylon 66 composites are shown in Figure 4, and the values of temperature and enthalpy during the crystallization and melting processes are shown in Table I. During DSC measurements, it was found that MCA had neither exothermic nor endothermic peaks in the temperature range from 50 to 300°C, thus indicating that the crystallization and melting behaviors of the MCA/Nylon 66 composites over the measured temperature region are directly related to those behaviors of Nylon 66 matrix. As for Nylon 66 and its composites, in the first heating scan merely one melting peak appears, and in the second heating scan after crystallization there is still one melting peak except for an extra shoulder peak for the 5MCA-N66, 10MCA-N66, and 15MCA-N66 composites, weakening with the increase of MCA content and disappearing until MCA content of 20 wt %. Different from the results reported by Li and Klein,^{12,16} in this study, we did not observe two melting peaks for our Nylon 66 and Nylon 66 composites due to the secondary crystallization of Nylon 66. In the first cooling scan, there is only one crystallization peak for Nylon 66 and its composites except for an extra shoulder peak for the 5MCA-N66 composite.

From Table I, it can be observed that the addition of MCA greatly influences the crystallization and melting processes of Nylon 66, with obvious rising of crystallization temperature, increase of normalized crystallization, and melting enthalpy except for a decrease for 5 wt % addition of MCA, and a little decrease of melting temperature. It is the nucleation agent effect of MCA that leads to the quick crystallization rate of Nylon 66, thus resulting in the decreasing of the crystallization supercooling degrees and the strengthening of the crystallization

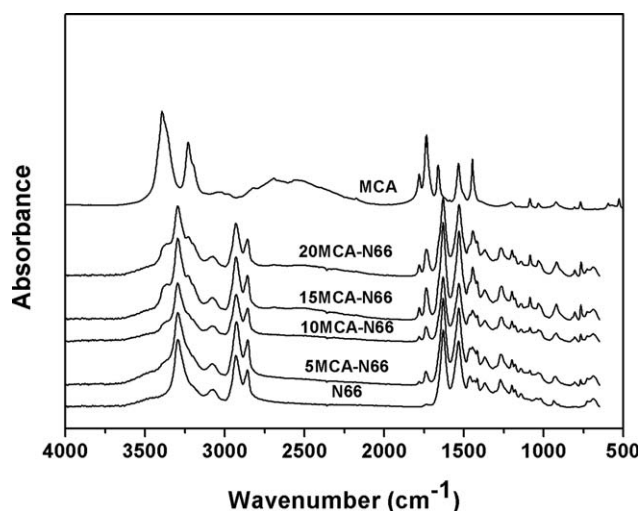


Figure 3 FTIR spectra of MCA, Nylon 66, and the flame retardant MCA/Nylon 66 composites.

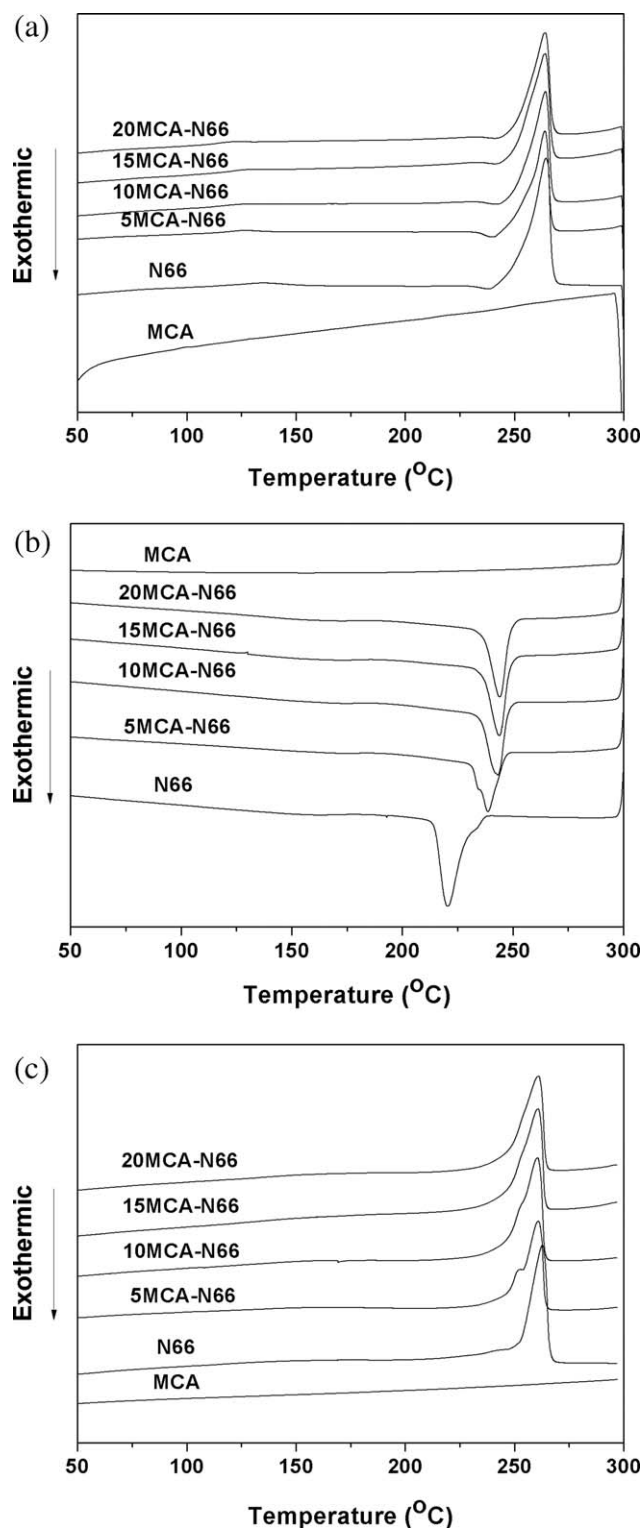


Figure 4 The DSC curves of MCA, Nylon 66, and the flame retardant MCA/Nylon 66 composites: (a) first heating scan, (b) first cooling scan, and (c) second heating scan.

exothermicity of the MCA/Nylon 66 composites during the crystallization process. For glass fiber-reinforced Nylon 66 composites and nanohydroxyapatite-filled Nylon 66 composites, the fillers of glass fiber and hydroxyapatite also show the same nuclea-

tion agent effect on Nylon 66 crystallization with similar increase of crystallization temperature.^{12,17} The appearance of the shoulder crystallization and melting peaks and little decrease of the crystallization and melting enthalpy of the MCA/Nylon 66 composites with low MCA content may be attributed to the reduction of the perfection degree of the Nylon 66 crystallites with more crystalline defects during cooling process because of the heterogeneous filling of MCA in the Nylon 66 matrix. The little decrease of melting temperature of the MCA/Nylon 66 composites is also related to the reduction of the crystallization perfection degree of Nylon 66. Moreover, lots of NH bonds in MCA filler can facilitate the strong molecular interactions between MCA and Nylon 66, and the resultant strengthening of the compatibility between the filler particles and polymer matrix can improve the nucleating activity of the filler.^{18,19} Therefore, the quick growth of microcrystallites of Nylon 66 during the cooling process due to the nucleation agent of MCA leads to the enhancement of the crystallization exothermicity and melting endothermicity of the MCA/Nylon 66 composites with high MCA content.

The TGA and DTG curves of Nylon 66, MCA, and the flame retardant MCA/Nylon 66 composites are given in Figure 5 to confirm the effect of MCA on the thermal stability of Nylon 66 matrix, and the thermal parameters of 10 wt % loss temperature (T_{10} wt %), peak decomposition temperature (T_p), peak decomposition rate (R_p), and residue during the thermal decomposition processes obtained from the TGA and DTG results of Nylon 66 and the flame retardant MCA/Nylon 66 composites are listed in Table II. Both Nylon 66 and MCA exhibit a single degradation process, while the MCA/Nylon 66 composites exhibit two degradation processes related to MCA at low-temperature region and Nylon 66 at high-temperature region, respectively. The weight loss of MCA appears in the temperature range from 276 to 425°C with a maximum degradation rate at 395.7°C [see Fig. 5(b)] and without any residue. The weight loss of Nylon 66 appears in the temperature range from 336 to 500°C with a maximum degradation rate at 453.5°C [see Fig. 5(b)] and a stable char residue of about 1%. The degradation of MCA is intimately related to the evaporation of the unaltered salt and its thermal dissociation to melamine and cyanuric acid.^{1,2} The degradation of Nylon 66 should be attributed to the main chain breakdown with the formation of the gases of NH_3 , H_2O , CO , CO_2 , and hydrocarbons.²⁰ After MCA is added in Nylon 66, the obtained composites show similar onset degradation temperature to that of MCA but much lower temperature for maximum degradation rate than that of MCA in the first degradation process at low-temperature region, and lower onset degradation

TABLE I
The Thermal Parameters of Crystallization Temperature (T_c), Melting Temperature (T_m), Normalized Crystallization Enthalpy ($\Delta H_c/\chi$), and Normalized Melting Enthalpy ($\Delta H_m/\chi$) During the Crystallization and Melting Processes Obtained from DSC Measurements of Nylon 66 and the Flame Retardant MCA/Nylon 66 Composites

Sample	N66	5MCA-N66	10MCA-N66	15MCA-N66	20MCA-N66
T_c (°C)	229.7	238.72	243.25	248.65	248.95
$\Delta H_c/\chi$ (J/g)	66.77	54.65	62.93	72.82	77.46
T_m (°C)	262.86	260.89	260.46	260.66	260.98
$\Delta H_m/\chi$ (J/g)	71.6	62.71	80.83	86.36	86.28

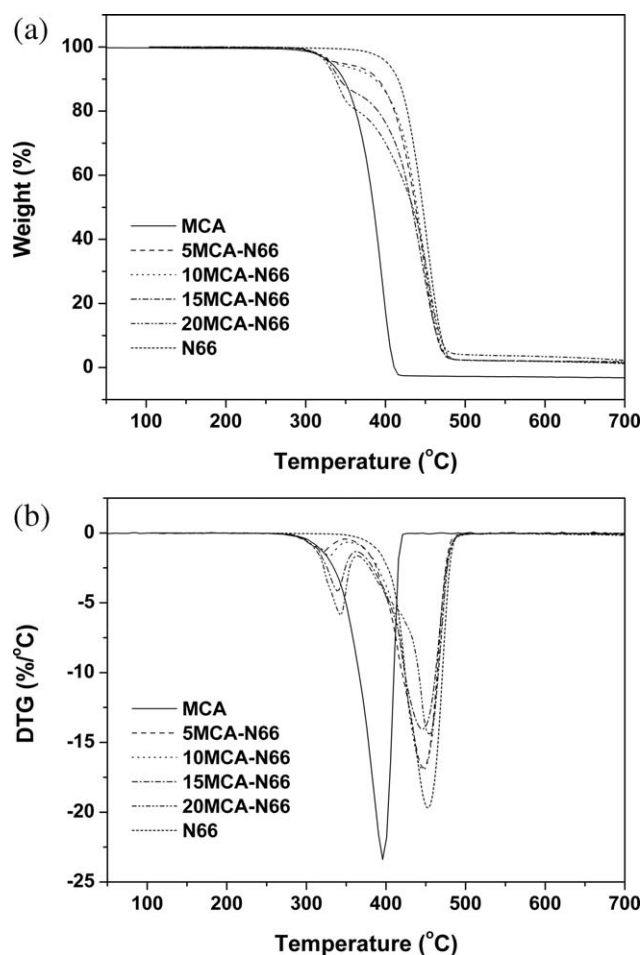


Figure 5 The TGA (a) and DTG curves (b) of MCA, Nylon 66, and the flame retardant MCA/Nylon 66 composites.

temperature than that of Nylon 66 in the second degradation process at high-temperature region. The blending of MCA and Nylon 66 has great influences on the temperature for maximum degradation rate of MCA and the onset degradation temperature of Nylon 66 with a temperature difference of 70 and 20°C, respectively, and this influence becomes greater with the increase of MCA concentration. However, the blending of MCA and Nylon 66 has no remarkable influences on the onset degradation temperature of MCA and the temperature for maximum degradation rate of Nylon 66. Thus, it can be seen, the great difference between the thermal stability of MCA/Nylon 66 composites and that of neat components indicates the stronger molecular interactions of MCA and Nylon 66 formed during heating, which is also verified by the TGA and DTA thermal behaviors of MCA-filled polyamide copolymer.² MCA facilitates the thermal decomposition of Nylon 66 with the decrease of the onset degradation temperature of Nylon 66, probably because MCA interferes with the hydrogen-bonding network of Nylon 66 and exhibits basic catalysis effect, due to the strong hydrogen bond interactions between MCA and Nylon 66 molecules.¹ Furthermore, the overlapping of the TGA curves of the 5MCA-N66 and 10MCA-N66 composites implies that in the first step of degradation, the weight loss is not simply proportional to the MCA content in the MCA/Nylon 66 composites and also not a simple volatilization of the flame-retardant MCA. Actually, Nylon 66 resin can accelerate the decomposition of cyanuric acid to cyanic acid,² which then accelerates the latter

TABLE II
The Thermal Parameters of 10 wt % Loss Temperature ($T_{10 \text{ wt } \%}$), Peak Decomposition Temperature (T_p), Peak Decomposition Rate (R_p), and Residue During the Thermal Decomposition Processes Obtained from the TGA and DTG Results of Nylon 66 and the Flame Retardant MCA/Nylon 66 Composites

Sample	N66	5MCA-N66	10MCA-N66	15MCA-N66	20MCA-N66	MCA
$T_{10 \text{ wt } \%}$ (°C)	415.7	389.3	385.7	343.4	338.1	346.9
T_p , MCA (°C)	–	321.0	328.5	338.4	343.3	395.7
T_p , N66 (°C)	453.5	446.1	446.0	446.1	453.6	–
R_p , MCA (%/°C)	–	–1.39	–1.68	–4.15	–5.89	–23.38
R_p , N66 (%/°C)	–19.7	–16.82	–16.99	–14.06	–14.39	–
Residue (%)	1.06	1.21	1.54	1.83	1.97	0

TABLE III
The Mechanical Property Parameters of Nylon 66 and the Flame Retardant MCA/Nylon 66 Composites

Sample	N66	5MCA-N66	10MCA-N66	15MCA-N66	20MCA-N66
Hardness	120	120	120	118	118
MFI (g/10 min)	18	12	10.8	9.6	7.8
Tensile strength (MPa)	78.5	77.2	76.6	72.0	67.1
Elongation at break (%)	4.1	7.39	7.74	4.99	2.77
Flexural strength (MPa)	96.4	97.4	99.8	98.5	100.2
Flexural modulus (MPa)	2585.3	2772.5	3034.0	3102.4	3447.5
Impact strength (J/m)	42.9	46.4	44.7	42.2	40.4

degradation of MCA and makes its maximum degradation rate appear and its degradation complete at lower temperature without changing its onset degradation temperature. It should also be noted that the MCA addition hardly changes the char residue of the Nylon 66 matrix after complete degradation, and the residue is still related to the final carbonaceous char products of Nylon 66 combustion.

Mechanical property

The mechanical property parameters of Nylon 66 and the flame retardant MCA/Nylon 66 composites are given in Table III. It can be found in Table III that after the addition of MCA filler, the hardness of the resultant Nylon 66 composites is nearly unchanged, while the MFI is decreased nearly half with the weakening of the thermoplastic processability. As for the tensile property, when MCA content is below 15 wt %, the tensile strength of the MCA/Nylon 66 composites is nearly unchanged with a decrement of <3%, while with the further increase of MCA content to 15 and 20 wt %, the tensile strength of the MCA/Nylon 66 composites is decreased to 92.7 and 85.5% of the original strength of Nylon 66 without filler, respectively. However, compared with pure Nylon 66, the elongation at break of the MCA/Nylon66 composite increases continuously until 10 wt % content of MCA with an increment of >80%, and then the increment decreases to 21.7% for the 15MCA-N66 composite, even decreases to -32.4% for the 20MCA-N66 composite below the original toughness of Nylon 66 matrix. Thus, it can be seen, less incorporation of MCA in Nylon 66 matrix no >10 wt % content can significantly improve the toughness of Nylon 66 material without sacrificing its rigidity, which can also be verified by the elevation of the impact strength of the 5MCA-N66 and 10MCA-N66 composites with an increment of 8.2 and 4.2%, respectively, when compared with that of pure Nylon 66. This phenomenon should be attributed to the layered structure of MCA and the strong hydrogen bonding interactions between MCA and Nylon 66 molecules. It is also this strong

molecular interaction between MCA and Nylon 66 that weakens the mobility of Nylon 66 molecular chains and then reduces the melt fluidity and MFI of the MCA/Nylon 66 composites. On the other hand, when MCA content is >15 wt % in Nylon 66 matrix, the strength and toughness of the MCA/Nylon 66 composites are greatly reduced, even lower than that of pure Nylon 66 matrix. Too much MCA particles cannot be wrapped by the Nylon 66 polymer matrix well and the redundant filler will aggregate together due to the hydrogen bond interactions, which will cause the negative effects on the tensile strength and fracture toughness of the MCA/Nylon 66 composites. As for the flexural property, compared with neat Nylon 66, the flexural strength of the MCA/Nylon 66 composites does not change remarkably with only an increment of <4%, but the flexural modulus increases continuously until 20 wt % MCA addition with a final increment of 33.3%. From the above analysis, it can be deduced that the MCA/Nylon 66 composite shows the best integrated mechanical property at MCA content of 10 wt %. Similar improvement of the mechanical property of the Nylon 66 composites with flame retardant filling has also been reported by other researchers. When the Zn²⁺-modified melamine polyphosphate (Zn-MpolyP) flame retardant was added in Nylon 66 matrix, the tensile strength of the Nylon 66 composites was slightly decreased, but the flexural strength was obviously improved and showed a maximum at filler content of 10 wt %.⁶

Flame retardancy

It is widely accepted that UL 94 and OI are very important measurements to check the flammability of the polymer materials.⁸ UL 94 is a vertical combustible test measuring the ease with which a polymer may be burned or extinguished,¹ and the flammability is usually classified from V-0 to V-2, among which V-0 rate is the best flame retardancy with a burning time <10 s and without any dripping-melt. OI, as another indication of the effectiveness of the fire-retardant additive in gas phase,

TABLE IV
Flame Retardancy Results of Nylon 66 and the Flame Retardant MCA/Nylon 66 Composites

Sample	N66	5MCA-N66	10MCA-N66	15MCA-N66	20MCA-N66
UL94 test	V-2	V-2	V-0	V-0	V-2
OI (%)	22	24.5	33	33.5	30.5

represents the minimum oxygen concentration required to support the candle-like downward flame combustion of the materials. The higher the OI is, the better the flame retardancy is, and the OI of >26 is regarded as qualification of self-extinguishing. The results of UL94 test and OI of Nylon 66 and the flame retardant MCA/Nylon 66 composites are listed in Table IV.

In UL94 test, Nylon 66, 5MCA-N66, and 20MCA-N66 composites get V-2 level with burning and failure in the test, while the 10MCA-N66 and 15MCA-N66 composites get V-0 level. As for Nylon 66, flammable volatile products formed in the thermo-oxidative degradation process during burning endow the polymer continuous flame. The incorporation of MCA into Nylon 66 matrix remarkably reduced the combustion time with flame extinguishment, but dripping and igniting cotton phenomenon still occurred for the 5MCA-N66 and 20MCA-N66 composites. Thus, it can be seen, 5 wt % MCA is not sufficient for realizing high flame retardancy, while 20 wt % MCA is too much and cannot be wrapped by the Nylon 66 matrix with good dispersion, thus inducing melt dripping in vertically burning. In practical application, less dripping and no dripping are favorable from safe point of view. In this case, MCA contents of 10 and 15 wt % are better choice for the usage of flame retardant in Nylon 66 to obtain good flame retardancy.

It can also be observed from Table IV that the OI of the MCA/Nylon 66 composites increases with the increasing of MCA content from 22% for N66 to 33.5% for the 15MCA-N66 composite, and then decreases to 30.5% for the 20MCA-N66 composite. Similar to the UL94 test result, the appropriate amount of MCA for getting better fire resistant property also lies in the intermediate MCA content, such as 10 and 15 wt %, and both too less and too much content of MCA will cause negative effect for the improvement of the flame retardancy of Nylon 66 material. Compared with the clay, MCA still shows superior flame retardancy for Nylon material with the OI of >30 when MCA content reaches 10 wt %, besides stronger interfacial compatibility between the filler and the polymer matrix and better toughness of the obtained Nylon 66 composites. For clay, when filler content is increased continuously and reaches 10 wt % in Nylon 6 matrix, the OI of the Nylon 6 composites still does not exceed 24.⁸

CONCLUSIONS

Through melt blending method, the nonhalogen flame retardant MCA/Nylon 66 composites were prepared, and effects of MCA content on the morphology, structure, thermal property, mechanical property, and fire resistant property of the MCA/Nylon 66 composites were also investigated in detail. The strong molecular interactions between polar MCA and Nylon 66 leads to the good interfacial compatibility between the filler and the polymer matrix, thus resulting in the good dispersion of MCA particles in the Nylon 66 matrix and better toughness of the MCA/Nylon 66 composites without sacrificing the strength than that of pure Nylon 66. Both Nylon 66 and MCA/Nylon 66 composites show the same α -crystalline phase structure, but the remarkable decrease of the relative peak intensity of α_1/α_2 implies that the presence of MCA has influenced the arrangement of Nylon 66 molecules in the α -crystalline phase. This phenomenon should be attributed to the formation of hydrogen bonds between MCA and Nylon 66 molecules, which is also verified by the analysis of X-ray diffraction and FTIR spectra of the MCA/Nylon 66 composites and neat components. Because of the nucleation agent effect of MCA, the crystallization temperature and normalized crystallization exothermicity of Nylon 66 in the MCA/Nylon 66 composites are obviously increased during the crystallization process. Furthermore, the blending of MCA and Nylon 66 accelerates the degradation of MCA and decrease the thermal stability of Nylon 66 but has no significant effects on the final amount of the stable char residue of Nylon 66. The MCA/Nylon 66 composites show better flame retardancy at intermediate MCA contents of 10 and 15 wt %.

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