Properties of High-Fluidity Nylon 6/Modified MCA Flame-Retardant Composite Postprint

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Abstract

Graphene oxide (GO)-modified melamine cyanurate (mMCA) and unmodified melamine cyanurate (MCA) were melt-blended with high-fluidity nylon 6 (HFPA6) to prepare HFPA6/mMCA and HFPA6/MCA composites, respectively. The structure of MCA before and after modification, as well as the flame retardancy, thermal stability, and mechanical properties of the flame-retardant composites were investigated. The results indicated that the flame retardancy, tensile strength, flexural strength, and char formation effect of the HFPA6/mMCA composites were significantly enhanced compared to the HFPA6/MCA composites, while the impact strength was slightly reduced. When the flame retardant content was 14%, the flame retardancy of the composite achieved the UL 94 V-0 rating.

Full Text

Preamble

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Properties of High Flow-ability Nylon 6/Modified MCA Flame Retardant Composites

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Abstract

HFPA6/mMCA and HFPA6/MCA composites were prepared by melt blending high flow-ability polyamide 6 (HFPA6) with graphene oxide-modified melamine cyanurate (mMCA) and unmodified melamine cyanurate (MCA), respectively. The structure of MCA and mMCA, along with the flame retardant properties, thermal stability, and mechanical properties of the two HFPA6 composites were characterized. Results show that the flame retardancy, tensile strength, flexural strength, and char formation of the HFPA6/mMCA composite are superior to those of the HFPA6/MCA composite, while the impact strength is slightly lower. When the flame retardant content is 14%, the flame retardancy of the HFPA6/mMCA composite reaches the UL 94 V-0 rating.

Keywords: composites, high flow-ability nylon 6, melamine cyanurate, graphene oxide, flame retardancy

Introduction

High flow-ability nylon 6 (HFPA6) is a novel nylon resin developed in recent years. With its excellent fluidity, HFPA6 is expected to find widespread applications in ultra-thin products and precision instruments [1-3]. However, its limiting oxygen index (LOI) is relatively low (23-25), and its high flow-ability makes it prone to producing flaming molten drips during combustion, which can cause secondary ignition and makes it difficult to achieve the UL 94 V-0 rating. Currently, research on flame retardants for HFPA6 remains limited, making the development of flame-retarded HFPA6, particularly halogen-free formulations, an urgent priority.

Melamine cyanurate (MCA) is a nitrogen-based, halogen-free flame retardant with excellent comprehensive performance [4-6] that is widely used in nylon flame retardation [7-9]. However, MCA prepared by conventional methods exhibits unimproved surface properties, making it difficult to achieve good dispersion in PA6 matrices and strong interfacial bonding with PA6. Moreover, the molecular structure of HFPA6 differs significantly from conventional PA6, making it challenging to prepare MCA-flame-retarded HFPA6 composites with excellent flame retardant and mechanical properties. Building on our previous work [10], this study blends GO-modified MCA with HFPA6 to prepare flame-retarded HFPA6 composites and investigates their properties.

Experimental

Preparation of Materials

Graphene Oxide (GO): Prepared according to reference [11].

mMCA Preparation: In a three-neck flask, water was added and the pH was adjusted to 4 using dilute hydrochloric acid. The temperature was controlled at 95-98°C, then melamine (MA) and cyanuric acid (CA) were added. When the viscosity of the reaction system began to increase, the prepared GO sol was added. After continuing the reaction for some time, the product was washed, filtered, and vacuum-dried at 80°C to constant weight to obtain the mMCA flame retardant.

Composite Preparation: HFPA6/mMCA and HFPA6/MCA composites were prepared by first mixing mMCA (or unmodified MCA), industrial-grade HFPA6, and pentaerythritol (PER, analytical grade) in a high-speed mixer. The mixtures were then extruded and pelletized using a twin-screw extruder. The pellets were vacuum-dried at 85°C for 12 h and injection-molded into standard test specimens. Based on our previous work [10], different formulations and ratios were designed .

Characterization

The structure of GO, MCA, and mMCA was characterized using a Thermo Nicolet Corporation Nicolet 380 FTIR spectrometer and an Advanced-D8 X-ray diffractometer. Flame retardant properties were evaluated using an SH5304 horizontal-vertical burning tester according to UL94 standards, and LOI was measured using an SH5706A oxygen index instrument according to GB/T 2406-2009. Thermal degradation was analyzed using a Q-50 thermogravimetric analyzer at a heating rate of 10°C/min from 50-600°C. Tensile and flexural strengths were measured using a CMT4104 microcomputer-controlled electronic universal testing machine according to GB/T1040-92 and GB/T 9341-2000 standards, respectively. V-notched impact strength was characterized using an XJ11D-5.5 pendulum impact tester according to GB/T 1843-1996.

Results and Discussion

Structure of mMCA

The FTIR spectra of GO, MCA, and mMCA are shown in [Figure 1: see original paper]. For GO [Figure 1a: see original paper], characteristic absorption peaks appear at 3435, 1734, 1630, and 1090 cm^{-1}, corresponding to O-H, C=O, C=C, and C-O groups, respectively, consistent with the structural model of graphene oxide proposed by Ruess et al. [12,13]. For MCA and mMCA [FIGURE:1b and 1c], characteristic peaks appear at 3395, 3230, 1782, 1735, 1665, and 1385 cm^{-1}, corresponding to N-H, C-H, C=O, C=O, C=N, and C-N groups. The

GO absorption peaks are not clearly visible in [Figure 1c: see original paper], likely due to the low GO content, weak peak intensity, or masking by MCA absorption peaks.

The XRD patterns of GO, MCA, and mMCA are presented in [Figure 2: see original paper]. The peak at 2 = 11.95° in [Figure 2a: see original paper] is characteristic of GO [14], while peaks at 2 = 10.75°, 11.93°, 22.19°, 28.58°, and 33.75° in [FIGURE:2b and 2c] correspond to MCA characteristic peaks, consistent with literature reports [15]. The GO characteristic peak is not obvious in [Figure 2c: see original paper], possibly due to the low GO content or overlap with nearby MCA characteristic peaks.

Flame Retardant Properties

The flame retardant properties of HFPA6 composites are summarized in . Pure HFPA6 exhibits a long flame duration after the first ignition, accompanied by multiple molten drips. Most drips are flaming and can ignite cotton, with combustion lasting approximately 5-6 seconds. After the second ignition, the flame duration shortens but flaming drips still occur. The LOI of pure HFPA6 is 23.5, indicating poor flame retardancy. With MCA addition, flame retardant properties improve: LOI increases with flame retardant content, vertical burning flame duration decreases significantly, and the number of drips reduces without flaming drips. However, HFPA6/MCA composites only achieve UL94 V-2 rating, indicating limited improvement.

In contrast, HFPA6/mMCA composites show enhanced flame retardancy with increasing mMCA content without exhibiting the "candlewick effect." Although some drips occur, they are non-flaming and do not ignite cotton. Compared with unmodified MCA composites, LOI values are improved. When the modified MCA content reaches 12% (total flame retardant content of 14%), the HFPA6/mMCA composite achieves UL94 V-0 rating with an LOI of 32. MCA is an efficient intumescent flame retardant: gases produced during high-temperature decomposition dilute combustible gases in the burning zone and cause expansion, creating an insulating layer that prevents small flammable molecules from entering the combustion zone. Additionally, PER is an effective char-forming agent that promotes char layer formation. The GO component, with its inherent char structure, provides thermal insulation and prevents diffusion of combustible gases, further enhancing the flame retardant performance of mMCA compared to unmodified MCA.

Thermal Stability

The TG and DTG curves of HFPA6/MCA composites are shown in [Figure 3: see original paper] and [Figure 4: see original paper]. Pure HFPA6 exhibits a single weight loss step, beginning decomposition at approximately 340°C and completing decomposition around 415°C, with essentially zero char residue at 600°C, indicating poor char formation during thermal decomposition. With

MCA addition, two distinct weight loss steps appear. The first step at 300-370°C corresponds to flame retardant MCA decomposition, while the second step results from HFPA6 degradation. Overall, MCA addition reduces the initial decomposition temperature of HFPA6/MCA composites by approximately 50°C compared to pure HFPA6.

The TG and DTG curves of HFPA6/mMCA composites are presented in [Figure 5: see original paper] and [Figure 6: see original paper]. Similar to HFPA6/MCA composites, two distinct weight loss steps are observed, with initial decomposition temperatures lower than that of pure HFPA6. Notably, HFPA6/mMCA composites show even lower initial decomposition temperatures than HFPA6/MCA composites. A slight weight loss occurs around 140°C, attributed to decomposition of hydrophilic groups on the GO surface and small amounts of bound water. The weight loss at 300-370°C corresponds to MCA decomposition. At 600°C, HFPA6/mMCA composites retain a small amount of char residue, likely due to the char-forming effect of GO, which helps explain the improved flame retardant performance.

Mechanical Properties

The relationship between tensile strength and flame retardant content is shown in [Figure 7: see original paper]. For HFPA6/MCA composites, tensile strength decreases with increasing MCA content because MCA acts as rigid particles with poor interfacial bonding to HFPA6. For HFPA6/mMCA composites, tensile strength first increases then decreases with mMCA content. At 8% mMCA content, tensile strength increases by approximately 2% compared to pure HFPA6, achieving reinforcement. After GO modification, the abundant polar oxygen-containing functional groups on the GO surface enhance interfacial bonding between mMCA and HFPA6, improving tensile strength. However, as mMCA content increases, dispersion efficiency decreases and interfacial bonding deteriorates, reducing tensile strength. Nevertheless, HFPA6/mMCA composites still show improved tensile strength compared to HFPA6/MCA composites.

The V-notched impact strength versus flame retardant content is presented in [Figure 8: see original paper]. Both composites exhibit decreasing impact strength with increasing flame retardant content, likely because MCA and mMCA act as stress concentration points. Since mMCA has stronger interfacial bonding with HFPA6 than MCA, it is more prone to causing stress concentration under impact, resulting in lower impact strength for HFPA6/mMCA composites.

The relationship between flexural strength and flame retardant content is shown in [Figure 9: see original paper]. HFPA6/MCA composites show little change in flexural strength with MCA content, though some improvement is observed. In contrast, HFPA6/mMCA composites exhibit more significant changes: the polar oxygen-containing functional groups introduced by GO modification enhance interactions between mMCA and HFPA6 molecular chains, improving interfacial bonding and flexural strength. However, increasing mMCA content may aggravate agglomeration in HFPA6, leading to reduced flexural strength.

Conclusions

1. MCA addition improves the LOI of HFPA6, but HFPA6/MCA composites still produce molten drips during combustion and cannot achieve UL94 V-0 rating even at 18% flame retardant content (16% MCA + 2% PER). In contrast, mMCA addition also improves LOI, and when the total flame retardant content reaches 14% (12% mMCA + 2% PER), the composite achieves UL94 V-0 rating.
2. The introduction of both MCA and mMCA reduces the thermal stability of HFPA6 composites, resulting in two-stage weight loss curves. The incorporation of mMCA promotes char formation in HFPA6.
3. mMCA more significantly improves tensile and flexural strengths compared to MCA, though impact strength decreases slightly.

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Note: Figure translations are in progress. See original paper for figures.