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Full Length Article

# Melamine cyanurate tailored by base and its multi effects on flame retardancy of polyamide 6

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ABSTRACT

In this paper, nitrogenous bases adenine (A), guanine (G), cytosine (C), and uracil (U), were used to tailor the hydrogen-bonded network of melamine cyanurate (MCA) and were noted as A-MCA, G-MCA, C-MCA, U-MCA, respectively. The results showed that the size, morphology and thermal behavior of MCA are regulated by base due to the formation of hydrogen bonds between them. These modified MCAs were used to improve the flame retardancy of polyamide 6 (PA6) which was evaluated by using the limiting oxygen index (LOI) and the vertical burning (UL-94) test, etc. The results showed that the PA6 sample containing 9 wt% C-MCA achieves the UL-94 V-0 rating and has a LOI value of 30.7%, while the other samples with equal amounts of MCA only pass the UL-94 V-2 rating. The flame retardant mechanism was studied, and the results reveal that C-MCA with smaller size has greater contact area with PA6 which helps to catalyze the decomposition of PA6; Thus the PA6/C-MCA releases more $NH_3$, $CO_2$ etc., and produces more droplets than others, which dilutes combustible gas and takes away heat to make the samples extinguish.

## 1. Introduction

Polyamide 6 (PA6) was commonly used in electronic and electrical, instrument, traffic, architecture and etc., owing to its excellent performance of physical-mechanical property, oil resistance, attrition resistance and self-lubrication etc [1–5]. However, PA6 burns rapidly once ignited as most polymers. In addition, it produces a great quantity of combustible droplets which may cause the twice fire. So it is necessary to reduce the flammability of PA6. Adding flame retardants into PA6 is a popular method to modify the flammability of PA6. Among all, some halogen flame-retardants have gone out of use gradually with paying more attentions on friendly environment and putting forward stricter requirements worldwide. The ideal flame retardants are required effective anti-flammable performance combined with minimal environmental impact.

Melamine cyanurate (MCA), a nitrogen containing flame retardant, is suitable for PA6 [6]. The structure of MCA is a planar network bonded by nine hydrogen bonds between melamine and cyanurate [7–9]. The network is so large that it causes high viscosity of the system when it was synthesized. MCA works by melt-away mode, so the PA6/MCA is easy to achieve the UL-94 V-2 but is difficult to be classified the UL-94 V-0. There are numerous strategies used to modify the preparation and performance of MCA, for example, reducing the size of MCA [10–12], adding synergistic agents into MCA [13–17] or preparing modified MCA [18–20]. Wu et al. [12] prepared PA6/MCA nanocomposites by in-situ polymerization of ε-caprolactam in the presence of melamine derivatives. The MCA nanoparticles were dispersed uniformly in PA6 matrix, and the nanocomposites not only had good mechanical properties, but also reached the UL-94 V-0 rating with 6.8% MCA. Zhou et al. [17] studied the synergistic effects of $MoS_2$/Aluminium hypophosphite (AHP) and MCA in EVA composites. The results showed that the flame retardant properties and mechanical properties of EVA composites were enhanced meanwhile. Liu et al. [18] prepared polyamide resin-encapsulated MCA/melamine phosphate composites and it improved the flame retardancy of glass fiber-reinforced PA6 to the UL-94 V-0 rating at 25 wt% loading. Zhao et al. [19] prepared montmorillonite-MCA (MMT-MCA) and used it in PA6. The results indicated that 8 wt% MMT-MCA can make PA6 pass the UL-94 V-0 rating. These methods modify the performance of MCA and related composites. Among all, modifying the hydrogen bond structure of MCA is a good method to regulate the morphology and structure of MCA in molecular level.

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In theory, any matter which can form hydrogen bond may regulating the hydrogen-bonded networks of MCA. But to obtain good synergistic effects between the modifier and MCA, it is better that the modifier can not only form hydrogen bond with MCA, but also help improve the flame retardancy of PA6. Moreover, the flame retardants based on biomass are becoming an important alternatives with the increase in safety and environmental protection requirements. Bases for example, adenine (A), guanine (G), cytosine (C), and uracil (U) may form hydrogen bond with MCA because they contain amino group, carbonyl group etc. Once the hydrogen bonds between bases and MCA are formed, the nine hydrogen bonds structure between melamine and cyanurate will be destroyed. Thus the planar network of MCA will be tailored and the size and performance of MCA will be regulated. What is more important that bases containing nitrogen element can be used as nitrogenous flame retardants [20]. Therefore, these bases may both regulate the performance of MCA and modify the flame retardancy of MCA in PA6.

In this paper, the bases A, G, C, and U were used as modifiers to tailor the structure, morphology and performance of MCA. The modified MCAs are noted as A-MCA, G-MCA, C-MCA, U-MCA, respectively. These MCA were used to modify the flame retardancy of PA6. The modified MCA were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffractometer (XRD), Scanning electron microscope (SEM), and Thermogravimetric analysis (TGA). The flame retardant properties and mechanism of PA6/MCAs were investigated by using the limiting oxygen index (LOI), the vertical burning (UL-94) test, and the TG-IR, etc.

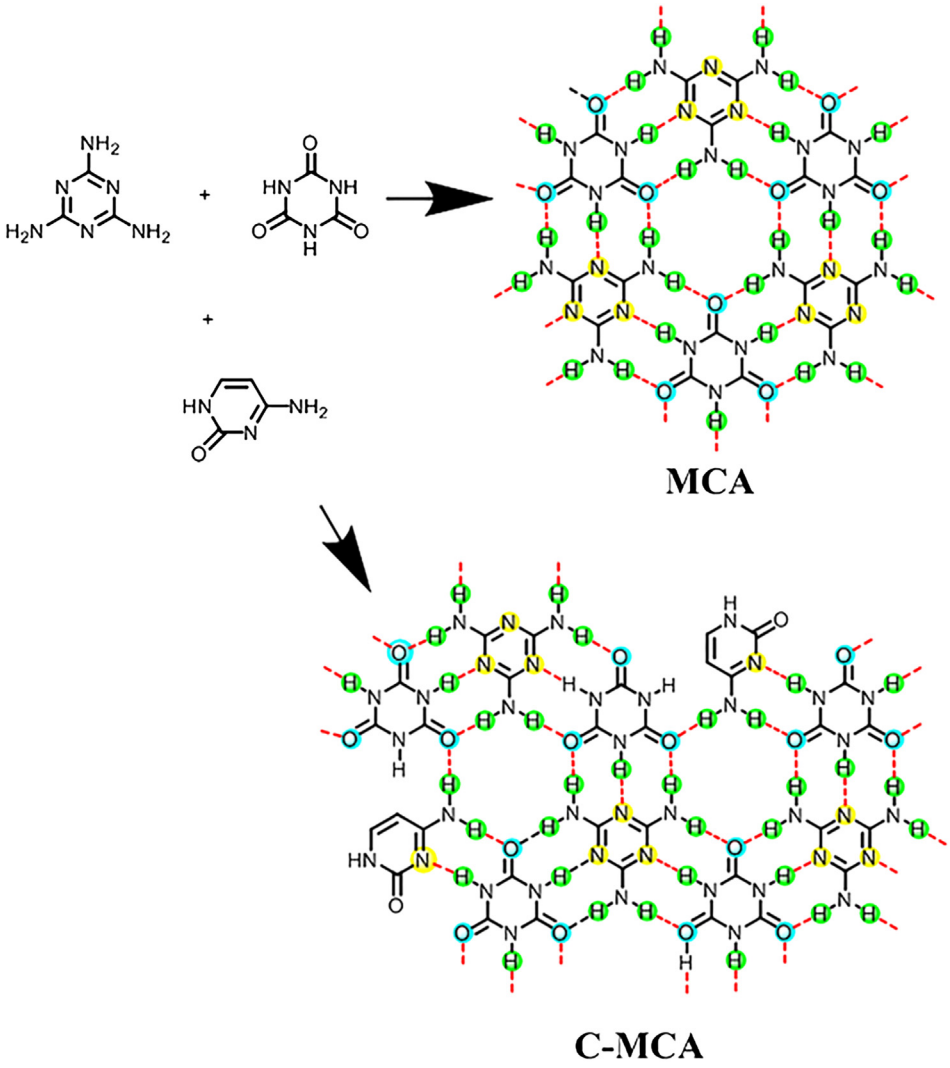
## 2. Experimental section

### 2.1. Materials

PA6 was supplied by Baling Petro-Chemical Co. Ltd. (Yueyang, China). Melamine (ME) was purchased from energy chemical Co., Ltd. Cyanuric acid (CA), A, G, C, U were bought from Aladdin Industrial Inc. (Shanghai, China). All reagents were used without further purification.

### 2.2. Synthesis of modified MCA

160 ml distilled water and 6.0 g C were added into 250 ml three necked flask with agitation, thermometer and reflux condenser. Keeping the temperature at 95 °C, 7.0 g ME and 7.0 g CA were mixed and added into the flask after the solution was dispersed homogeneously. Stirring for 3 h, then cooling down to room temperature. After being filtered, the white powder was collected and washed with deionized water for three times. Finally 19.2 g C-MCA was dried and the yield is 96.1%. Other bases-MCAs were prepared in the same way and the products are noted as A-MCA, G-MCA and U-MCA and their yields were 99.8%, 94.7%, 98.3%, respectively. MCA without bases was also prepared according similar method and the yield is 97.5%. The




**Scheme 1.** Preparation of C-MCA.