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Flame retardant polyoxymethylene with aluminium hydroxide/melamine/novolac resin synergistic system

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ABSTRACT

Polyoxymethylene (POM), having the lowest limiting oxygen index (LOI) (only ~ 15%), is well known as the most difficult to be flame retarded plastic among all the polymers. In this paper, a novel synergistic flame retardant system composed of aluminium hydroxide (ATH), melamine (ME) and novolac resin was designed and successfully applied to flame retard POM. ATH took effects through heat absorption and water release. Both ME and novolac could react with the decomposition product of POM, formaldehyde, thus improving the flame retardancy. Particularly, novolac resin and ME played the roles of macromolecular charring agent and gas source, enhancing the flame retarding actions in the condensed and gaseous phases, respectively. This ternary synergistic system exhibited fine flame retardancy for POM (UL94 V-1 rating for 1.6 mm bar), and the obtained flame retardant POM also showed good processability and mechanical properties due to the lubrication, compatibilization and aid-dispersion effects of novolac resin.

1. Introduction

Polyoxymethylene (POM) is a kind of polyacetal resins, which possesses good mechanical properties, lubricating performance, fatigue resistance, corrosion resistance, and processability [1]. Moreover, it is one of the few polymers synthesized through non-petroleum route at low cost. Therefore, POM has been widely used in industry, such as automobiles, electrical and electronic products, medical devices, and precision machines, etc.

However, the thermal stability of POM resin is poor due to its rapid thermal depolymerization mechanism (unzipping reaction [2]). It has the lowest limiting oxygen index (LOI) (~15%) compared to all the other polymers, and is therefore extremely flammable [3]. POM resin burns violently in blooming blue flame, producing a large number of flaming molten drops which makes the fire easily spread. This has restricted POM's applications in more fields.

Adding flame retardants, a convenient and efficient way to flame retard polymer materials, however, is relatively difficult for POM. Firstly, as POM chains are very sensitive to acidic or basic substances, many flame retardants easily aggravate the decomposition of POM during thermoplastic processing, resulting in the molding of flame retardant POM difficult and its mechanical properties seriously deteriorated. Secondly, the compatibility between POM resin and most additive fillers is relatively poor, and it is hard to realize a good dispersion of flame retardants in the resin. Thirdly, to achieve satisfactory flame retardancy, high loading level of flame retardant is generally needed due to the high inherent flammability of POM, which obviously will sabotage the original performances of POM resin.

Therefore, it is a big challenge worldwide to prepare flame retardant POM with high flame retardancy while maintaining other good comprehensive properties. Up to now, there have been very few literatures related to flame retardant POM [2,4–8]. In the 1960s, several USA patents referred to flame retardant POM containing halogen flame retardants [4,5], however, halogen flame retardants easily catalyzed the decomposition of POM due to the presence of the halide groups [2]. Moreover, the environment and safety problems arose from the pyrolysis of halogen flame retardants also restricted their applications. Recently, an alternative type of flame retardants, phosphorus-nitrogen synergistic flame retardants, has been used in flame retardant POM [2,6–8]. Du Pont Co. (US) [2] employed an ammonium salt of amidopolyphosphate named as "Victamide" to flame retard POM. Hatsuhiko Harashina, etc. [6] melt-blended red phosphorus, ME, and novolac with POM resin by a twin screw co-extruder under the protection of nitrogen gas, and the resulting flame retardant POM achieved UL94 V-1 rating. Asahi Kasei Co. (JP) [7] adopted a flame retardant system including red phosphorus, phenol resin, polycarbonate resin, and a metal salt of fatty acid to flame retard POM, and the obtained materials possessed relatively satisfactory properties. Polyplastics

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Co., Ltd. (JP) [8] also reported a compound flame retardant for POM, which is composed of a nitrogen-containing compound, an aromatic compound and a phosphorus-containing compound. However, the flame retardant POM compositions with phosphorus-nitrogen systems were still difficult to possess high flame retardancy, good mechanical properties and fine processability simultaneously.

Compared with phosphorus-nitrogen flame retardant systems, inorganic flame retardants, such as magnesium hydroxide (MTH) and aluminum hydroxide (ATH) have the advantages of low cost, good smoke suppression effects, and environment-friendliness. As a result, they have been increasingly applied in flame retarding polymer materials [9–15]. However, at present there have been very few reports about the application of this kind of flame retardants in POM due to too high loading level. Therefore, developing some effective synergists for MTH or ATH to reduce the loading level of the flame retardants is significant for preparing flame retardant POM with better comprehensive performance.

In this paper, a novel synergistic flame retardant system consisting of ATH, ME and novolac resin was applied to POM resin. The prepared flame retardant POM composites showed satisfactory flame retardancy and good mechanical properties. The synergistic effects of each component and the flame retardant mechanism were investigated.

2. Experimental

2.1. Materials

POM pellet (M90, acetal copolymer) was purchased from Yunnan Yuntianhua Limited Corporation, China. ATH, with an average particle size of 1250 mesh, was obtained from Yingkou Universal Powder Engineering Limited Corporation, China. ME was supplied by Sichuan Chemical Limited Corporation, China. Linear novolac resin, with a weight-average molecular weight of 650 and a melt temperature of 100 °C, was provided by Henan Bangde Chemical Engineering Company, China. Antioxidant (Ciba® IRGANOX® 245) was a kind of hindered phenol supplied by Ciba, Switzerland.

2.2. Equipment

Co-rotating twin screw extruder (TSSJ-25/33) with the screw diameter (ϕ) of 25 mm and the aspect ratio (L/D) of 33 was manufactured by KQCEC of Chenguang Research Institute of Chemical Industry, China. Injection-molding machine (K-TEC 40) used in this work was manufactured by Terromatik Milacron Corporation, Germany.

2.3. Preparation of flame retardant POM

Weighted amounts of POM pellets, ATH powder, synergistic agents and antioxidant were pre-mixed, and then melt-blended by a twin screw extruder at 170–185 °C with a screw rotation speed of 150–180 rpm. The extruded pellets were molded into standard bars for combustibility and mechanical performance tests through an injection-molding machine with a plasticizing temperature of 170–195 °C.

2.4. Measurements and characterization

2.4.1. Burning experiments

The vertical burning tests were conducted on a CZF-3 horizontal and vertical burning tester with specimen dimensions of $127 \times 12.7 \times 3.2$ mm^3 and $127 \times 12.7 \times 1.6$ mm^3 according to UL94-2006 standard.

The LOI values were measured by an LFY-605 limiting oxygen index instrument with specimen dimensions of $120 \times 6.5 \times 3$ mm^3 according to ASTM D2863-2009 standard.

2.4.2. SEM analysis

The injection-molding bars were frozen in liquid nitrogen for 20 min, and then were broken off. The ruptured surfaces and the residual chars of the burnt bars were gilt under vacuum before observed by a HITACHI S3400 scanning electron microscope (SEM) instrument, with an accelerate voltage of 10 kV.

2.4.3. FTIR analysis

The Fourier Transform Infrared (FTIR) spectra of ATH, ME, novolac and the char residue of the flame retardant POM after vertical burning test were recorded by a Nicolet 20SXB FTIR spectrometer through KBr disk method.

2.4.4. Cone calorimetry

An FTT cone calorimeter was used to evaluate the flammability of samples under an external heat flux of 35 kW/m^2, with specimen dimensions of $100 \times 100 \times 3$ mm^3 according to ISO 5660 standard. Time to ignition (TTI), total heat release (THR), heat release rate (HRR), mass loss rate (MLR) and other quantifiable parameters were recorded simultaneously.

2.4.5. Thermal analysis

The thermogravimetry (TG) analyses were carried out on a TA Q-500 TGA thermal analyzer, with a heating rate of 10 °C/min from 30 to 700 °C and an air or nitrogen flow rate of 100 ml/min.

2.4.6. Mechanical properties

The tensile strengths were measured by a REGEER material tester according to ISO527/1-1993 standard. The test specimens were dumb-bell-shaped of type 1A with width of 10 mm (narrow portion) and thickness of 4 mm, and the test speed was 50 mm/min.

The bending strengths were also examined by a REGEER material tester with sheet dimensions of $80 \times 10 \times 4$ mm^3 according to ISO178-2001 standard. The test speed was 2 mm/min.

The charpy notched impact strengths were measured using a ZBC-4B impact testing machine with specimen dimensions of $80 \times 10 \times 4$ mm^3 according to ISO179/1-2000 standard.

3. Results and discussion

3.1. Decomposition of POM

The flammability of POM resin can be explained by its decomposition and combustion behaviors [2,16]: the macromolecular chain of POM, mainly composed of $-CH_2-O-$ units, is extremely easy to depolymerize into formaldehyde in the presence of heat and oxygen. The resulting formaldehyde can be further oxidized to formic acid, which catalyzes the decomposition of POM. As combustible gases, the rapidly produced formaldehyde and formic acid provide fuel to the intense combustion of POM resin.

Fig. 1 showed the thermogravimetry curves of POM resin in different atmospheres. The onset decomposition temperature of POM was 365 °C in N_2 atmosphere. While in air, the existence of O_2 obviously accelerated the decomposition of POM, reducing the decomposition temperature to 312 °C and raising the maximum velocity of weight-loss to a greater extent. However, in both atmospheres, the residue weight ratio was close to zero, meaning that POM completely turned into small molecular products and