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Application of cyclophosphazene derivatives as flame retardants for ABS

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ABSTRACT

Cyclotriphosphazene derivatives were synthesized for use as a non-halogen flame retardant for ABS. Hexachlorocyclotriphosphazene was reacted with phenol, catechol, or 2,3-dihydroxynaphthalene, respectively, and the fire retardant ability of each product in ABS resin was characterized by UL 94 and LOI tests. The mechanical properties of ABS compounds containing one of these flame retardants were also examined. The derivative (HNCP) synthesized from 2,3-dihydroxynaphthalene showed the best flame retardance among these derivatives studied. Synergistic effects with novolac were observed in the cases using the derivative (PNCP) obtained from phenol, but little synergistic effects were observed in cases using HNCP.

1. Introduction

With the increasing consumption of plastics, there has been growing interest in the development of flame-retarded plastics, particularly the importance of the flame retardant. Whenever there is a large fire in a city area, it is essential to seriously consider the problem of burning plastics. There are many methods for producing flame-retarded plastics. Among them, the most economic and convenient method is the addition of a flame retardant. Most flame retardants currently used are halogen derivatives. However, many environmentalist have highlighted problems with using these halogen derivatives because toxic gases are produced from these flame retardants during a fire. Therefore, it is important to develop new flame retardants as substitutes for halogen-based flame retardants [1–5].

ABS resin is a copolymer formed with acrylonitrile, butadiene, and styrene. This copolymer has the combined properties of insulation, easy processing, shining surface (from polystyrene), thermal stability, good mechanical strength, resistance to oil, resistance to weather (from polyacrylonitrile), and improved impact strength (from polybutadiene). ABS resin is used in automobile parts, toys, office supplies, and electric appliances, such as refrigerators, washing machines, electric fans, televisions, etc. Highly flame-retarded ABS is very difficult to produce.

Cyclophosphazene has a cycle structure comprised of nitrogen and phosphorus atoms. Many studies of flame retardants have focused attention on these atoms. The flame retardants reported in many papers have these hetero-atoms [6–8]. Hence, the phosphazene structure may have good flame retardant properties, and cyclophosphazene compounds might be used as flame retardants [9–19].

In this study hexachlorocyclotriphosphazene was reacted with phenol, catechol or 2,3-dihydroxynaphthalene to synthesize three cyclophosphazene derivatives, respectively, and their flame retardant properties in ABS resin were examined.

2. Experimental

2.1. Materials and instruments

Hexachlorocyclotriphosphazene (HCCP), phenol, catechol, 2,3-dihydroxynaphthalene, antimony(V) oxide, formaldehyde, and oxalic acid dehydrate were purchased from Aldrich Chemical. Pure ABS with a density and tensile strength of 1.04 g/cm^3 and 392 kg/cm^2, respectively, was obtained from Cheil Co. This ABS was manufactured by blending ABS with SAN (copolymer of styrene and acrylonitrile, the weight percent of SAN is 70). Thermogravimetric analysis (TGA) was performed using a PerkinElmer TRY 910. The physical properties of the samples were measured using a universal test machine SFM 10 (United Calibration). A limiting oxygen index (LOI) experiment was carried out using MKM JD-14.

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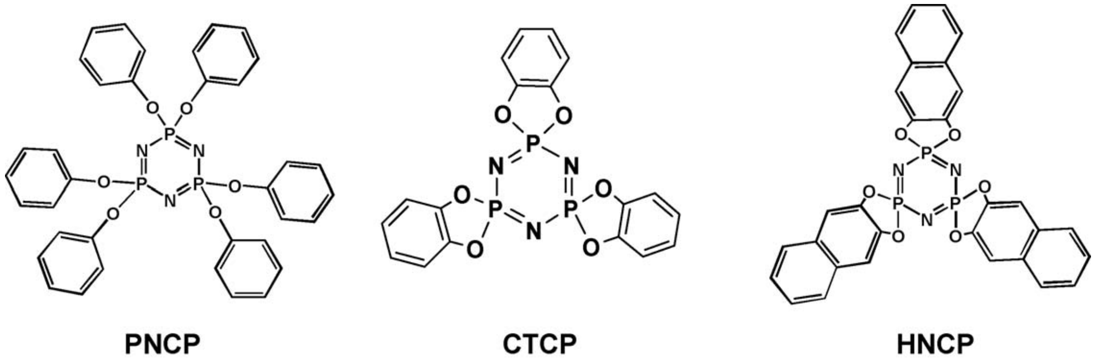

Scheme 1. Molecular structure of the flame retardants.

2.2. Synthesis of cyclotriphosphazene derivatives and novolac

PNCP (phenol derivative of cyclotriphosphazene) [20], CTCP (catechol derivative of cyclotriphosphazene) [21], and HNCP (2,3-dihydroxynaphthalene derivative of cyclotriphosphazene) [22] were synthesized by reacting HCCP with phenol, catechol and 2,3-dihydroxynaphthalene, respectively, using already reported methods. Novolac was synthesized from phenol, 37% formaldehyde, oxalic acid dehydrate using reported methods [23].

2.3. Sample manufacture

The experimental samples were manufactured using Haake Rheo-corder 90 for compounding and Fuse Mp-50 press for compression molding. 50 g of ABS resin was placed into a Rheo-corder 90, which was preheated at 180 °C. The synthesized flame retardants were then mixed with this resin for 10 min. The mixed resins were removed from the Rheo-corder, placed into a compression molding press that was preheated at 190 °C, and then pressed to make plate-shaped samples. The mean thickness of these samples was 3.0 ± 0.5 mm, and these samples were cut for use in the UL 94 test and LOI experiment.

2.4. UL 94 test

Plate-shaped samples were cut to the following size for the UL 94 vertical test: 120 ± 1 mm in length, 13.0 ± 0.5 mm in width, and 3.0 ± 0.5 mm in thickness. In the UL 94 vertical test, the sample was placed into a Bunsen burner flame for 10 s. The firing sample was then removed from the fire, and the first afterflame time until the fire went out was recorded. After the fire went out completely, the sample was placed into the fire again for 10 s and then removed. The second afterflame time until the fire went out was recorded again. A total of 10 results were obtained using 5 specimens in each experiment, which were graded into the following 3 classes: V-0, V-1, and V-2. The V-0 class indicates that the afterflame time does not exceed 10 s and a summation of all the afterflame time for five specimens does not exceed 50 s. Additionally, a piece of cotton placed under the tested sample must not be ignited during the burning test. The V-1 class indicates that the afterflame time does not exceed 30 s and a summation of all the afterflame time for five specimens does not exceed 250 s. Additionally, a piece of cotton placed under the tested sample must not be ignited during the burning test. The V-2 class indicates that the afterflame time does not exceed 30 s and a summation of all the afterflame time for five specimens does not exceed 250 s. Additionally, a piece of cotton placed under the tested sample could be ignited during the burning test.

2.5. LOI experiment

Plate-shaped samples were cut to the following size for LOI experiment: 120 ± 1 mm in length, 6.5 ± 0.5 mm in width, and 3.0 ± 0.5 mm in thickness. A line was drawn at 50 mm from the top of the sample. The sample was placed perpendicularly into the LOI test equipment. The concentrations of oxygen and nitrogen were controlled to burn for 3 min if the sample did not burn up to 50 mm from the top for 3 min after ingnting the sample at the rop. The oxygen concentration was increased if the time was more than 3 min, and conversely the oxygen concentration was lowered if the time was less than 3 min. Therefore, the oxygen concentration was measured when at 3 min until the sample was burned up to 50 mm. Ten samples were used in each experiment, and the average results were obtained from repeated experiments.

$$\frac{\mathrm{LOI}}{100} = \frac{[\mathrm{O_2}]}{[\mathrm{O_2}] + [\mathrm{N_2}]}$$

3. Results and discussion

3.1. Thermal stability of cyclotriphosphazene derivatives

Scheme 1 shows the molecular structure of the cyclotriphosphazene derivatives synthesized in this study. The thermal stability of the cyclotriphosphazene derivatives were tested under nitrogen gas using a thermogravimetry analyzer. The results are shown in Fig. 1.

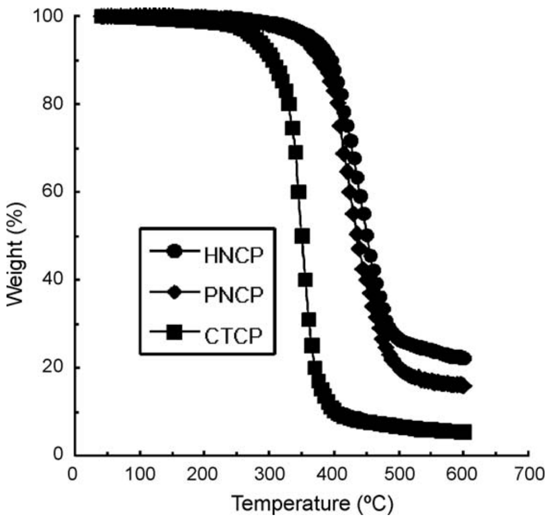

Fig. 1. TGA of PNCP, CTCP and HNCP.