

Immobilization of flame-retardant onto silica nanoparticle surface and properties of epoxy resin filled with the flame-retardant-immobilized silica (2)

Takashi Kawahara^a, Akira Yuuki^a, Kumi Hashimoto^b, Kazuhiro Fujiki^c, Takeshi Yamauchi^{a,d}, Norio Tsubokawa^{a,d,*}

^a Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan

^b Department of Material Science and Technology, Faculty of Engineering, Niigata University, 8050, Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan

^c Department of Environmental Science, Niigata Institute of Technology, 1719, Fujihashi, Kashiwazaki, Niigata 945-1195, Japan

^d Center for Transdisciplinary Research, Niigata University, 8050, Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan

ARTICLE INFO

Article history:

Received 4 September 2012

Received in revised form 2 January 2013

Accepted 4 January 2013

Available online 11 January 2013

Keywords:

Flame-retardant
Nanoparticles
Silicas
Surface grafting
Epoxy resin

ABSTRACT

To prepare silica nanoparticle having flame-retardant activity, immobilization of flame-retardant onto the surface was investigated. The immobilization of phosphorous flame-retardant was achieved by two-step reactions: (1) introduction of cyclotriphosphazene (PH) groups onto silica nanoparticle by the reaction of terminal amino groups of the surface with hexachlorocyclotriphosphazene and (2) immobilization of bis(4-aminophenoxy)phenyl phosphine oxide (BAPPO) onto silica having PH groups by the reaction of PH groups on the surface with BAPPO. The immobilization of BAPPO was confirmed by FT-IR and thermal decomposition GC-MS. The composite of epoxy resin filled with BAPPO-immobilized silica (Silica-PH-BAPPO) was successfully prepared by heating in the presence of curing agents. Thermal decomposition temperature and glass transition temperature of the epoxy resin filled with Silica-PH-BAPPO was higher than that of epoxy resin filled with untreated silica, free HCTP and BAPPO. Moreover, flame-retardant property of epoxy resin filled with Silica-PH-BAPPO was estimated by limiting oxygen index (LOI). The LOI value of epoxy resin filled with Silica-PH-BAPPO was higher than that of epoxy resin filled with untreated silica, free HCTP and BAPPO. This may be due the fact that char yield of the epoxy resin filled with Silica-PH-BAPPO was higher than that filled with free flame-retardant.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

We have reported that surface grafting of various polymers onto a silica nanoparticle by using previously introduced initiating groups on the nanoparticle surface, such as peroxyester, azo, acylum perchlorate, and potassium carboxylate groups [1–3]. In addition, we have succeeded in the grafting of functional polymers, such as biocompatible [4] and antibacterial polymers [5,6], onto silica surface; composite surfaces prepared from the antibacterial polymer-grafted silica and conventional polymers show strong antibacterial activity [5,6]. We have also reported immobilization of capsaicin onto hyperbranched poly(amidoamine)-grafted silica (Silica-PAMAM) surface and their properties [7].

On the other hand, most of organic polymers are combustible, because they contain hydrogen and carbon atoms. For their various applications in the building, electrical, transportation, mining and other industries, they have to fulfill flame-retardant requirements. Thus main objectives in development of flame-retarding polymers are to improve an ignition resistance and a reduction of flame

spread when flame-retardants were incorporated into flammable polymers [8]. Several types of flame-retardant additives are used to improve flame retardant properties of polymer materials. These flame-retardants can be divided into halogen, inorganic, phosphorous, nitrogen and nitrogen-phosphorous flame-retardant [9–12].

In the preceding paper, we have reported immobilization of halogen flame-retardant onto Silica-PAMAM and flame-retardant properties of epoxy resin filled with the flame-retardant-immobilized silica [13].

In the present paper, immobilization of phosphorous flame-retardant, bis(4-aminophenoxy) phenyl phosphine oxide (BAPPO), was investigated as shown in Schemes 1 and 2. In addition, thermal property, glass-transition temperature and flame-retardant activity of epoxy resin filled with the BAPPO-immobilized silica will be discussed.

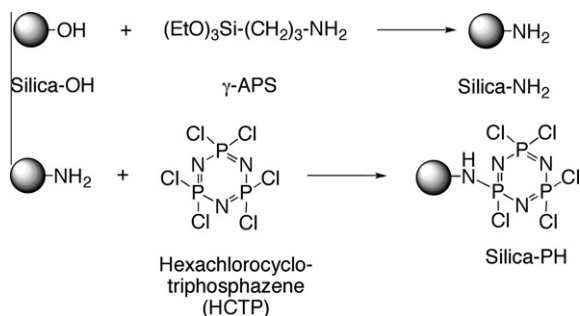
2. Experimental

2.1. Materials and reagents

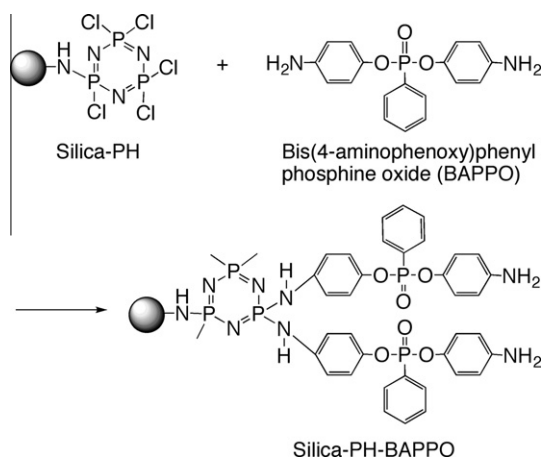
Silica nanoparticle used was Aerosil 200 and it was obtained from Nippon Aerosil Co., Ltd., Japan. The particle size, specific surface area, and silanol group content were 12 nm, 200 m²/g, and

* Corresponding author at: Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan.

E-mail address: ntsuboka@eng.niigata-u.ac.jp (N. Tsubokawa).



Scheme 1. Immobilization of chlorocyclophosphazene (PH) moieties onto Silica-NH₂ by the reaction with HCTP.



Scheme 2. Immobilization of flame-retardant onto Silica-PH by the reaction with BAPPO.

1.37 mmol/g, respectively. The content of silanol groups was determined by measuring volumetrically the amount of ethane evolved by the reaction with triethylaluminum [14,15]. The silica nanoparticle was dried *in vacuo* at room temperature before use.

Hexachlorocyclophosphazene (HCTP) obtained from Otsuka Chemical Co., Ltd., was used without further purification. *p*-Nitrophenol, phenyl phosphonic dichloride, γ -aminopropyltriethoxysilane (γ -APS), hexamethylenediamine (HMDA), and 4,4'-diaminodiphenylmethane (DDM) were also used without further purification. Triethylamine obtained from Kanto Chemical Co., Inc., was dried over sodium hydroxide and distilled.

Bisphenol-A type epoxy resin (Araldite AER 260) was obtained from Asahi-Chiba Ltd., Japan. Epoxy equivalent and viscosity of the epoxy resin were 180–200 g/eq and $1.2\text{--}1.6 \times 10^4$ mPa s, respectively. The epoxy resin was dried *in vacuo* at room temperature before use.

2.2. Bis(4-aminophenoxy)phenyl phosphine oxide (BAPPO)

Bis(4-aminophenoxy)phenyl phosphine oxide (BAPPO) was prepared by the reaction of *p*-nitrophenol with phenyl phosphonic dichloride according to the method of literature [16].

2.3. Immobilization of HCTP onto Silica-NH₂

The preparation of silica having surface amino groups (Silica-NH₂) was achieved by the treatment of silica with γ -APS in a solvent-free dry-system [17]. Then, immobilization of HCTP onto Silica-NH₂ was achieved by the reaction of Silica-NH₂ with HCTP

as shown in Scheme 1. A typical procedure was as follows. Into a flask was placed 2.0 g of Silica-NH₂, 0.5 g of HCTP, 60 mL of diethyl ether, and 0.2 mL of triethylamine as hydrogen chloride scavenger were added, and the mixture was stirred with a magnetic stirrer at 0 °C under nitrogen. After 18 h, the products were stirred with a large excess of heptane at 0 °C for 6 h. After the reaction, the resulting silica was centrifuged at 1.5×10^4 rpm and the supernatant solution containing unreacted HCTP was removed. The precipitated silica was dispersed in THF and centrifuged again, and the procedure was repeated until no more HCTP could be detected in the supernatant solution by use of UV-Vis spectra. The resulting silica was stored *in vacuo* at room temperature. The silica was abbreviated as Silica-PH.

2.4. Immobilization of BAPPO onto Silica-PH

Immobilization of BAPPO onto Silica-PH was achieved by the reaction of terminal P-Cl groups on the Silica-PH with BAPPO as shown in Scheme 2. A typical procedure was as follows. Into a flask was placed 2.0 g Silica-PH, 0.6 g BAPPO, 150 mL of toluene, and 1.0 mL of triethylamine as hydrogen chloride scavenger were added, and the mixture was stirred with a magnetic stirrer at 60 °C for 24 h under nitrogen. After the reaction, the resulting silica was centrifuged at 1.5×10^4 rpm and the supernatant solution containing unreacted BAPPO was removed. The precipitated silica was dispersed in THF and centrifuged again, and the procedure was repeated until no more BAPPO could be detected in the supernatant solution by use of UV-Vis spectra. The resulting silica was stored *in vacuo* at room temperature. The silica was abbreviated as Silica-PH-BAPPO.

2.5. Characterization of Silica-PH and Silica-PH-BAPPO

Characterizations of Silica-PH and Silica-PH-BAPPO were carried out by FT-IR spectra. Difference FT-IR spectra of silica between after and before treatment was recorded on a FT-IR Spectrophotometer (Shimadzu Co., FTIR-8200A) using KBr pellet. Thermal decomposition gas chromatograms and mass spectra (GC-MS) were recorded on a gas chromatograph mass spectrometer, Shimadzu Co., GCMS-QP2010 equipped with a double shot pyrolyzer, Frontier Laboratories Ltd., PY-2020D. The column was programmed from 70 °C to 320 °C at a heating rate of 20 °C/min and then held at 320 °C for 5 min.

2.6. Determination of PH group content on Silica-PH and BAPPO content on Silica-PH-BAPPO

Immobilized PH group content on Silica-PH and BAPPO content on Silica-PH-BAPPO were determined by the following equations:

$$\text{Immobilized PH (\%)} = (A/B) \times 100$$

$$\text{Immobilized BAPPO (\%)} = [(C - A)/B] \times 100$$

where A, B, and C are weight of HCTP, silica, HCTP and BAPPO immobilized onto the silica, respectively. The A and C were determined by measuring the weight loss when Silica-PH and Silica-PH-BAPPO, respectively, were heated at 800 °C using a thermogravimetric analyzer (TGA) (Shimadzu Co., TGA-50) in nitrogen.

2.7. Preparation of epoxy resin filled with Silica-PH-BAPPO

Silica-PH-BAPPO was dispersed in a mixture of epoxy resin and HMDA (DDM) by use of a rotation and revolution super-mixer (Thinky Co., AR-100). The mixture was poured into a Teflon mold, which was coated with a fluorine-releasing agent. The curing

Download English Version:

<https://daneshyari.com/en/article/5210054>

Download Persian Version:

<https://daneshyari.com/article/5210054>

[Daneshyari.com](https://daneshyari.com)