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Preparation, characterization of microencapsulated ammonium polyphosphate and its flame retardancy in polyurethane composites

Ming-Yuan Shen [a], Wei-Jen Chen [a], Chen-Feng Kuan [b], Hsu-Chiang Kuan [b], Jia-Ming Yang [c], Chin-Lung Chiang [c, *]

[a] *Department of Aviation Mechanical Engineering, China University of Science and Technology, Hsinchu County, 303, Taiwan*
[b] *Department of Computer Application Engineering, Far East University, Tainan, 744, Taiwan*
[c] *Green Flame Retardant Material Research Laboratory, Department of Safety, Health and Environmental Engineering, Hung-Kuang University, Taichung, 433, Taiwan*

HIGHLIGHTS

- A novel microencapsulated flame retardant was synthesized using in situ polymerization technology.
- The microencapsulation of ammonium polyphosphate with the polymer resin resulted in improved hydrophobicity.
- Polyurethane composites have excellent thermal stability and flame retardance.

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ABSTRACT

In this study, a novel microencapsulated flame retardant containing ammonium polyphosphate (APP) and an 4,4′-oxydianiline-formaldehyde (OF) resin as the core and shell material was synthesized using in situ polymerization technology. The structure and performance of OF microencapsulated APP (OFAPP) were characterized using Fourier transform infrared spectroscopy and scanning electron microscopy. The thermal properties of OFAPP were systematically analyzed through thermogravimetric analysis. Flame retardancy tests, such as limiting oxygen index (LOI) and UL-94, were conducted to evaluate the effect of varying the composition of APP and OFAPP in silanol-terminated polyurethane (Si-PU) composites. The results indicated that the microencapsulation of APP with the OF resin resulted in improved hydrophobicity. The results also revealed that the flame retardancy of the Si-PU/OFAPP composite (LOI = 37%) was higher than that of the Si-PU/APP composite (LOI = 23%) at the same additive loading.

1. Introduction

Polyurethane (PU) has received considerable attention in recent years because of its unique polymeric characteristics and favorable physicochemical properties [1–4]. Furthermore, PU can be specifically designed to satisfy the diverse requirements of conventional polymers used in coating, adhesive, foam, and thermoplastic elastomer applications [1,5,6]. However, the thermal instability and flammability of PU are major limitations of the material [7]. Therefore, numerous researchers have studied this specific problem to improve the thermal stability and flame retardancy of PU [8,9].

Flame retardants composed of ammonium polyphosphate (APP) have been developed for many years and have shown favorable performance in retarding the production of flames. Ammonium polyphosphate can play the role of flame retardant due to a strong dehydrating agent generated by polyphosphoric acid is, which can promote to form carbon residue on the surface of polymer matrix. The carbon residue containing phosphorus covered on the surface, which can block oxygen to prevent the spread of flammable gases and carbon gasification [10,11]. However, a flame retardant comprising solely APP alone cannot effectively yield favorable outcomes; therefore, researchers have adopted synergistic effects by combining APP with other flame retardants to effectively improve the flame retardancy of APP [12,13]. Hygroscopicity is a flaw associated with APP-containing flame retardants because it can reduce the effects of flame retardancy when APP is added to

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* Corresponding author.
E-mail address: dragon@sunrise.hk.edu.tw (C.-L. Chiang).

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polymeric composites [14,15]. Therefore, microencapsulation technology has been applied to modify APP to enhance the flame retardancy of APP surfaces. In addition, this approach facilitates converting the hydrophilicity of APP to hydrophobicity, which increases the compatibility of composite materials and decreases the hygroscopicity of APP [14,15].

Wu et al. [16] used polyvinyl alcohol (PVA) to modify melamine-formaldehyde resin to coat ammonium polyphosphate (VMFAPP), and to flame retardant polypropylene. The results showed that the microcapsules can greatly reduce the heat release rate of materials, and PVA content of melamine-formaldehyde prepolymer materials played an important role on water-resistant and flame retardant of the microcapsules. The silicon microcapsule has been widely used to encapsulate material by solegel process. Ni et al. used silica gel to microencapsulate APP and it used to flame retardant thermoplastic polyurethane [17]. Through microencapsulation, the water solubility, hydrophilicity, thermal properties of APP are greatly improved.

In the current study, PU was first modified to incorporate silicon to form siloxane linkage in the PU structure. Polysiloxanes offer high thermal stability up to 300 °C. That resistance results from the presence of Si—O bonds, for which the dissociation energy is higher (ca. 460.5 kJ/mol) in relation to C—O (358 kJ/mol), C—C (304 kJ/mol) and C—NH (98 kJ/mol) bonds [18,19]. A sol–gel reaction was subsequently applied to form a PU network structure that facilitates increasing the thermal stability of PU. An APP-containing flame retardant was then microencapsulated to produce carbonization agents on the surface, which convert APPs that are initially unexpandable to APPs exhibiting expandability. Moreover, microencapsulation converts the property of APPs from being hydrophilic to being hydrophobic, which enhances the compatibility of substrates to flame retardants.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, purity 98%), ethylenediamine (purity 99%), 3-aminopropyltriethoxysilane (APTS, purity 99%), 4,4'-oxydianiline (ODA, purity 98%), and formaldehyde (37 wt% sol., stab. 10%–15% methanol) were purchased from Acros Chemical Co, New Jersey, United States. Anhydrous stabilized tetrahydrofuran (THF) was supplied by Lancaster Co., Morecambe, Lancashire, United Kingdom. Arcol polyol 1007 (polyether polyols 700) were purchased from Bayer Material Science Ltd, Kaohsiung, Taiwan. Ammonium polyphosphate (APP, phase II, n > 1000) was purchased from San Jin Chemicals Corporation, Kaohsiung, Taiwan.

2.2. Preparation of Si-PU

IPDI (12.6 g) and arcol polyol 1007 (20 g) were placed in a four-neck flask inserted in an 80 °C oil bath and mechanically stirred in N_2 atmosphere. Subsequently, 1 g of the metal catalyst dibutyltin dilaurate was added into the four-neck flask. After 1.5 h of reaction, the temperature was reduced to 50 °C when viscosity of the prepolymer increased to a level similar to that of maltose. Next, THF (50 mL) and APTS (12.6 g) were added into the four-neck flask and stirred for 0.5 h, after which 0.5 mL of H_2O was added. The temperature was then raised to 70 °C, to reduce the volatility of the solvent and increase the solution viscosity. When the viscosity increased, the product (Si-PU) was placed in a container at room temperature for 6 h before vacuum drying at 80 °C for 12 h in a vacuum oven. The product was removed after 12 h and cooled at room temperature. The reaction is specified in Scheme 1.

2.3. Preparation of 4,4′-oxydianiline-formaldehyde microencapsulated APP

To prepare 4,4′-oxydianiline-formaldehyde microencapsulated APP (OFAPP), ODA (10 g) and formaldehyde (5.99 g) were added to a reaction tank, to which 40 mL of THF was added. Subsequently, ammonia solution was used to adjust the pH of the solution in the reaction tank to 8–9. The solution was then heated at 60 °C for 10 min, yielding a transparent solution following reaction completion. APP (40 g) and ethanol (500 mL) were placed in another reaction tank, preheated, and stirred at 80 °C for 0.5 h. Next, the transparent prepolymer was transferred into the APP-containing reaction tank, to which HCl was added to adjust the pH to 3–4. The reaction was allowed to proceed at 80 °C for 3 h, yielding powdered products. Following filtration, the powders were extracted and rinsed several times in ethanol and then placed in a convection oven at 80 °C for 12 h. The reaction is shown in Scheme 2.

2.4. Preparation of Si-PU/OFAPP composites

To synthesize the Si-PU/OFAPP composites, the OFAPP flame retardant was added to the Si prepolymer prepared according to Scheme 1. Next, 0.5 mL of H_2O was added and the temperature was adjusted to 70 °C, and the solution was observed for any reduction in solvent volatility or increase in viscosity. When the viscosity increased, the Si-PU/OFAPP product was placed in a mold at room temperature for 6 h before drying at 80 °C in a vacuum oven for 12 h. The final product (Si-PU/OFAPP composites) was then removed from the oven and cooled at room temperature.

2.5. Measurements

The FTIR spectra of the materials were obtained between 4000 and 400 cm^{-1} using a Nicolet Avatar 320 FT-IR spectrometer from the U.S.A. Thin films were prepared by solution-casting. A minimum of 32 scans were signal-averaged with a resolution of 2 cm^{-1}. The mean particle size and distribution of samples were measured by optical particle sizing instrument (Zeta-Sizer3000HS, Malvern Corporation, English). Before the measurement, the samples were dispersed in ethanol, and sonicated for 15 min. The morphology of the fractured surface of the composites was examined using a scanning electron microscope (SEM) (JEOL JSM 840A, Japan). The thermal degradation of the composites was examined using a thermogravimetric analyzer (TGA) (Perkin Elmer TGA 7) from room temperature to 800 °C at a heating rate of 10 °C/min in an atmosphere of nitrogen. The measurements were made on 6–10 mg samples. The LOI test was carried out following the ASTM D 2836 Oxygen Index Method, using a test specimen bar that was 7–15 cm long, 6.5 ± 0.5 mm wide, and 3.0 ± 0.5 mm thick. The sample bars were suspended vertically and ignited using a Bunsen burner. The flame was removed and the timer was started. The concentration of oxygen was increased when the flame on the specimen was extinguished before it had burned for 3 min or burning 5 cm away from the bar. The oxygen content was adjusted until the limiting concentration was determined. The vertical burning test was done inside a fume hood. Samples were held vertically with tongs at one end and burned from the free end. Samples were exposed to ignition source for 10 s then they were allowed to burn above a cotton wool until both sample and cotton wool extinguished. Observable parameters were recorded to assess fire retardancy. The UL 94 test classifies the materials as V-0, V-1 and V-2 according to the time period needed before self-extinction and the occurrence of flaming dripping after removing the ignition source. V-0 is the most ambitious and desired classification.