PREPARATION AND FLAME RETARDANCY OF POLYURETHANE COMPOSITES USING MICROENCAPSULATION TECHNOLOGY

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Abstract

In this study, a novel microcapsulated 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 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]. Furthermore, PU can be specifically designed to satisfy the diverse requirements of conventional polymers used in coating, adhesive, foam, and thermoplastic elastomer applications [1-3]. However, the thermal instability and flammability of PU are major limitations of the material [4]. Therefore, numerous researchers have studied this specific problem to improve the thermal stability and flame retardancy of PU [5-6].

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Flame retardants composed of ammonium polyphosphate (APP) have been developed for many years and have shown favorable performance in retarding the production of flames. 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 [7-8]. Hygroscopicity is a flaw associated with APP-containing flame retardants because it can reduce the effects of flame retardancy when APP is added to polymeric composites [9-10]. 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 [9-10].

In the current study, PU was first modified to incorporate silicon in the PU structure. A sol-gel reaction was subsequently applied to form a PU network structure that faciliates 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 N2 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 H2O 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 powedered 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 H2O was added and the temperature

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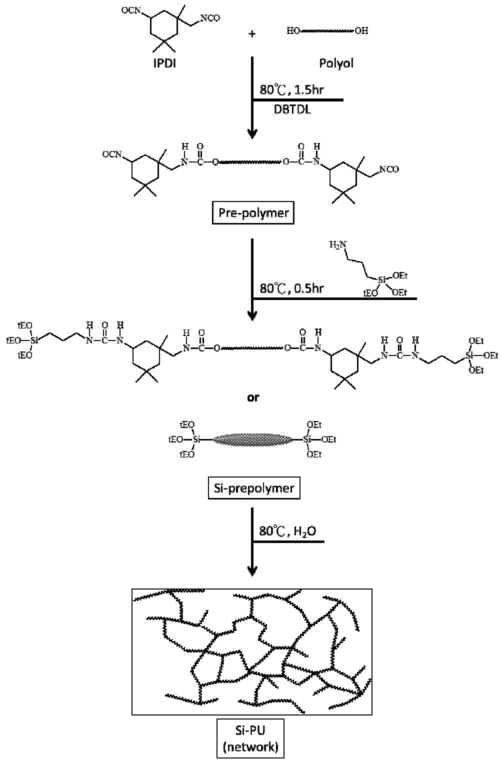
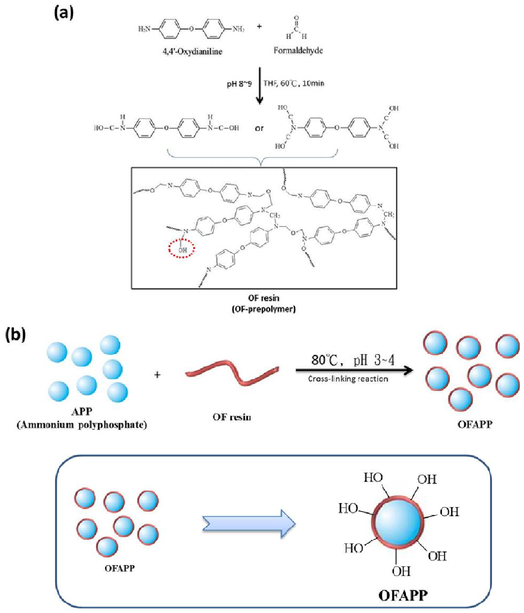
was adjusted to 70 °C, and the solution was observed for any reduction in solvent volatility or increase in viscosity. When the viscosity increased, the Si-PU/OFAPP product was placed in a mold at room temperature for 6 h before drying at 80 °C in a vacuum oven for 12 h. The final product (Si-PU/OFAPP composites) was then removed from the oven and cooled at room temperature.



Scheme 1. Reaction of Si-PU composites.



Scheme 2. Reaction of OFAPP.

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3. Results and Discussion

3.1 Structure characterization of OFAPP

Fig. 3 depicts the FTIR spectra of APP before and after the microencapsulation. The spectra were analyzed to preliminarily determine the structures of APP and peak variations. These spectra show typical APP peaks at 3200 (N-H), 1253 (P=O), 1070 (P-O symmetric stretching), 1017 (symmetric vibration of PO2 and PO3), 882 (P-O asymmetric stretching) and 800 cm-1(P-O-P) [15]. Several new peaks were also observed, suggesting the formation of microencapsulated OFAPP, such as at 3375 (-OH), 2823 (C-H), 1625 (C=C), 1495 (benzene), 1308 (C-N), 1120 (C-O-C), and 823 cm-1 (para-position of benzene) [16–18].

In the OFAPP spectra, the peaks representing the OF shell and typical APP peaks were identified. This result suggests that APP was successfully microencapsulated, forming the microencapsulated APP flame retardant.

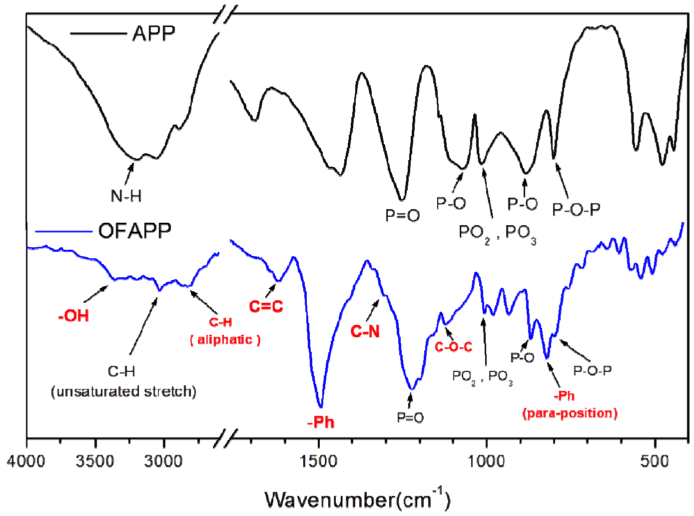

Figure 3. FTIR spectra of APP and OFAPP.

3.3 Surface morphology and hydrophobicity of OFAPP

Figure 5 shows the changes in the surface morphology of APP before and after the microencapsulation. As showin in Fig. 5 (a), the APP particles, predominantly presented in the form of long rods, exhibit smooth surface morphologies, with partial cracks on the surface. Fig. 5 (b) shows the OFAPP particles, the surface morphology of which differed from that of APP in that a coarse-surfaced shell was observed on the surface of the OFAPP particle. In addition, no cracks as those observed on the surface of APP particles were identified. In summary, an additional outer shell on the APP particles was observed after the microencapsulation, revealing a surface morphology considerably different to that of OFAPP.

The insets show a water contact angle of 22.49○ for APP; this is primarily attributed to the hydrophilicity of NH4+ in APP, thus resulting in low water contact angles [20]. OFAPP exhibited a water contact angle of 74.92○, indicating increased hydrophobicity, which is attributable to the benzene structures on the microencapsulated shell. APP featured superior water compatibility and hence a lower water contact angle than OFAPP did; this indicates that APP is hydrophilic and OFAPP is hydrophic. Therefore, the microencapsulation of shell materials can reduce the attack of water vapor and increase the compatibility of APP with polymers due to its hydrophobicity when mixed with it, thus improving the dispersion of additives in the polymer matrix.

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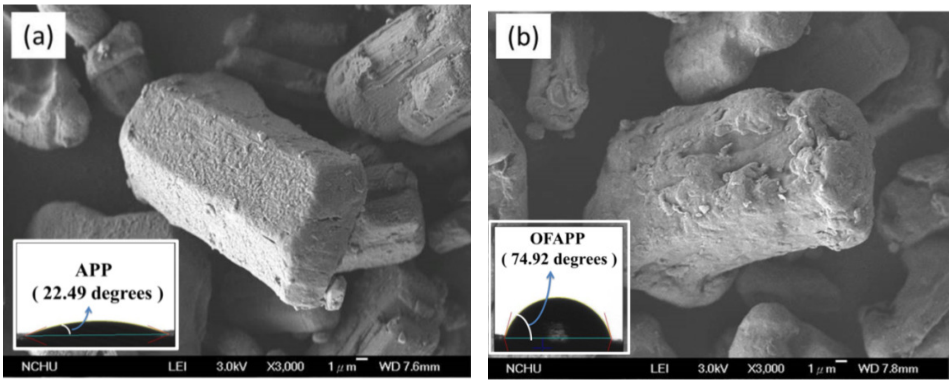

Figure 5. SEM photographs of (a) APP and (b) OFAPP particles. The insets are pictures of the water contact angle.

3.4 Thermal properties of Si-PU/OFAPP composites

According to the data shown in Figure 6 (a) and Table 1, pristine PU has a Td5 of 306 °C, which increased to 328 °C after PU was modified into Si-PU. This result can be attributed to the Si element migrating on the surface of PU, subsequently forming the Si-O-Si char layers, which improved thermal resistance and enhanced antioxidative effects. Consequently, thermal decomposition was delayed to a point that it commences at a higher temperature [19-20]. In the APP and OFAPP composites, APP released NH3 and H2O at 220–400 °C, reacting with the outer shell; therefore, the Td5 temperature ranged between those of pure PU and Si-PU. Furthermore, the weight of Si-PU (Fig. 6 (a)) continued decreasing after 500 °C because of the composite material's inability to withstand high thermal energy. Nevertheless, the weight of Si-PU stabilized at 600 °C. In the OFAPP composite, complex reactions constantly occurred at 220–500 °C; therefore, OFAPP composites decomposed earlier than Si-PU did, suggesting that the temperature at which OFAPP decomposed was lower than that for Si-PU. However, the thermal stability of OFAPP composites after 500 °C was superior to that of the Si-PU composite. This is because the series of precedent reactions resulted in dense barrier layers that prevented the thermal destruction of polymers in the inner layers, thus explaining the high amount of char residue at the high temperature stage.

Fig. 6 (b) depicts the variations of the thermal decomposition rates. The decomposition rates of pure PU and Si-PU are -30.4 and -16.1 wt%/min, respectively. The rates for both the APP- and OFAPP-added composites were lower than that of Si-PU (-16.1 wt%/min), and only the sample Si-PU/OFAPP 40% exhibited a rate (-17.8 wt%/min) closest to that of Si-PU. This can be explained by the excellent thermal stability of the char layer produced by Si-PU at 500 °C. When temperatures exceeded 500 °C, the Si-char layer could no longer resist high temperatures and the structure gradually disintegrated. Furthermore, in the OFAPP-added composites, a series of reactions occurred at 220–500 °C including the volatilization of inflammable gases and the formation of char layers. Therefore, the thermal decomposition rate of this composite was lower than that of Si-PU because the APP- and OFAPP-added composites both exhibited thermal stability at high temperature (> 500 °C). In addition, compared with pure PU, the thermal decomposition rates of Si-PU/OFAPP 10%–40% were -24.8, -22.7, -19.7, and -17.8 wt%/min, respectively, showing a decreasing trend. When the composition of OFAPP was increased by 40% (i.e., Si-PU/OFAPP 40%), the thermal decomposition rate slowed by -12.6 wt%/min (approximately 58%), suggesting improved thermal stability.

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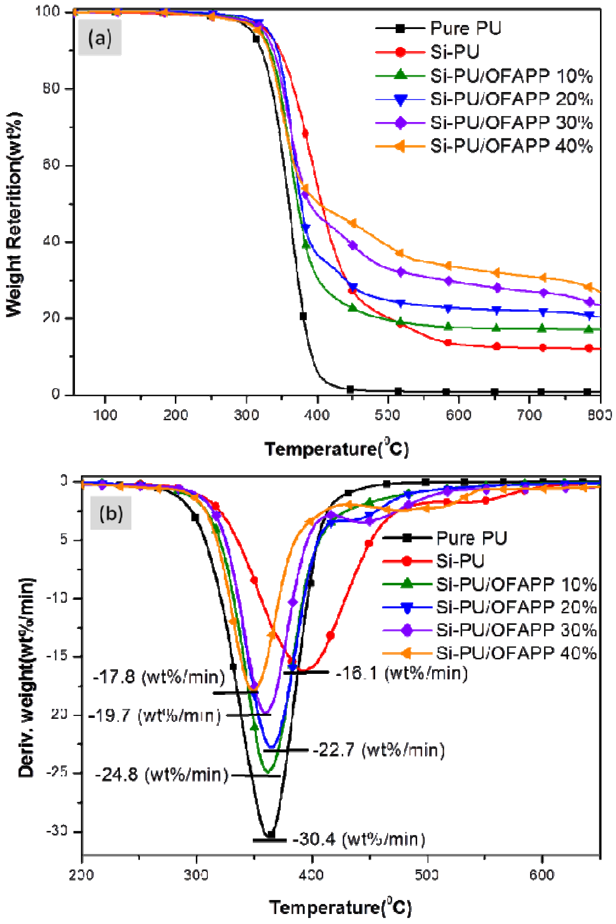

Figure 6. (a) TG and (b) DTG curves of pure PU, Si-PU, and Si-PU/OFAPP 10–40% composites.

3.6. Flame retardancy of Si-PU/OFAPP composites

Figure 8 prsent the limiting oxygen index (LOI) of the composite materials and the values obtained from Underwriters Laboratories' Standard for Safety and Flammability of Plastic Materials for Parts in Devices and Appliances testing (UL-94). Pristine PU exhibited an LOI of 17%, failed the UL-94 test, and demonstrated dripping effects, meaning that pristine PU is flammable. After PU was modified, Si-PU exhibited only a slight improved LOI (18%), but demonstrated antidripping effects from UL-94 results. Next, the LOI values of the 10%, 20%, 30%, and 40 wt% OFAPP-added composites were 20%, 24%, 37%, and 41%, respectively. Among these samples, the Si-PU/OFAPP 20% and Si-PU/OFAPP 30% measured LOI values that differed by 13%. These samples demonstrated a marked advancement from V-1 to V-0 (the top level) in the UL-94 ratings, suggesting that excellent flame retardancy can be obtained when a sufficient concentration of OFAPP is added.

In the Si-PU/APP 30% and Si-PU/OFAPP 30% samples, the LOI values were 23% and 37% and their UL-94 rankings were Fail and V-0, respectively. A comparison indicated that Si-PU/OFAPP 30% exhibited satisfactory flame retardancy because of the excellent synergistic effect between the outer shell of OFAPP and internal core of APP. In addition, the subsequent reaction with the substrate Si char layer formed dense and expandable char layers, which provided excellent flame retardancy.

The flame retardancy data of the composite materials after hydrothermal treatments (75 °C for 24 h) showed that the LOI value of the Si-PU/APP 30% composite dropped from 23% to 21%, whereas that for the Si-PU/OFAPP 40% composite decreased from 41% to 40%. Si-PU/APP 30% was not ranked in the UL-94 test before the hydrothermal treatment; therefore, variations cannot be observed through the

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treatment process. The UL-94 results for Si-PU/OFAPP 30% before and after hot water treatment showed a drop in ranking from V-0 to V-1. Regarding the flame retardancy before and after the treatment, the LOI values of the APP-added composites varied considerably, whereas the LOI values of the OFAPP-added composites remained unchanged.

In summary, the LOI and UL-94 results showed that dripping effects were no longer present in the modified Si-PU composite. The OFAPP- and APP-added composites demonstrated considerable differences in their flame retardancy. Moreover, the OFAPP-added composite exhibited no apparent variations in flame retardancy after the hydrothermal treatments, suggesting that microencapsulation effectively enhanced the flame retardancy of the OFAPP flame retardant.

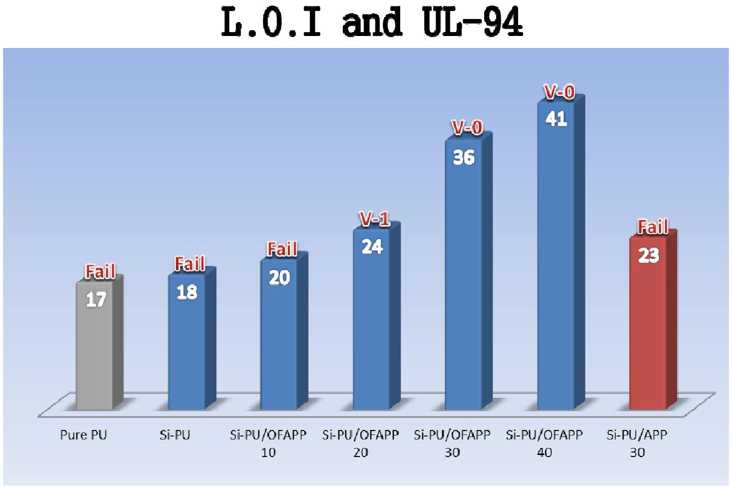

Figure 8. LOI values of the pristine PU, Si-PU, Si-PU/APP 30%, and Si-PU/OFAPP 10–40% composites.

4. Conclusion

A novel microencapsulated flame retardant was developed through microencapsulation, in which the surface of APP was encapsulated with an OF resin, thereby forming an OFAPP-containing flame retardant. The TGA results showed that adding 40% flame retardant in the polymer matrix resulted in approximately 26.9 wt% of char and high flame retardancy (LOI = 41%). The TGA curves verified the presence of the protective mechanism of OFAPP at various temperatures; this mechanism increased the thermal stability of OFAPP and promoted char formation. According to the comparison of the APP before and after microencapsulation, the microencapsulated OFAPP demonstrated excellent flame retardancy in terms of thermal stability. Overall, the findings of this study revealed that the novel microencapsulated flame retardant can enhance the flammability, flame retardance, and the applicability of PU.

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