

Reactive flame retardant with core-shell structure and its flame retardancy in rigid polyurethane foam

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ABSTRACT: With a shell of poly (methyl methacrylate-co-hydroxyl ethyl acrylate) (PMMA-HA), microencapsulated ammonium polyphosphate (MHAPP) is prepared by in situ polymerization. The core-shell structure of the reactive flame retardant (FR) is characterized by Fourier transform infrared (FTIR) and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). The results of water leaching rate and water contact angle measurements show that ammonium polyphosphate (APP) is well coated by a hydrophobic shell. Due to the presence of active groups (–OH) and hydrophobic groups (–CH₃) in shell, MHAPP exhibits better compatibility, flame retardancy, and water resistance compared with neat ammonium polyphosphate (APP) in rigid polyurethane foam (PU). Compression strength of PU/MHAPP with suitable loading is higher than that of PU/APP and PU, the reason is that the active groups in shell can improve the compatibility of MHAPP in PU composite. From thermal stability and residue analysis, it can be seen that the presence of reactive flame retardant shows positive effect on thermal stability of PU composite at high temperature, results also indicate that MHAPP can promote the carbonization formation efficiency of PU composite during combustion process compared with APP. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42800.

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INTRODUCTION

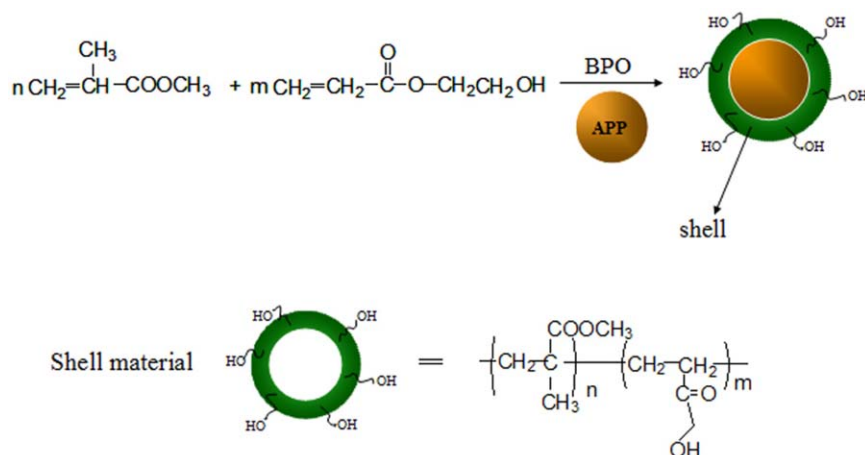
Rigid polyurethane foams (PU) are widely used as insulating, construction panels, and domestic appliances materials because of their superior mechanical properties and low density. However, their open cell physical structure and chemistry component make them susceptible to fire and thus limit their application.^{1–4} Therefore, it is critical to improve the flame retardancy of PU.

Conventional flame retardant (FR) treatment for PU foams includes the incorporation of flame retardant additives based on phosphorus, halogen, and nitrogen compounds. In recent years, considering the safety and environment protection requirements, there is an increased impetus to develop environmental friendly FR for PU foams.⁵ Due to the advantages of halogen-free, low-smoke, and low-toxicity, ammonium polyphosphate (APP) is one of the most widely used fire retardant additives for PU.⁶ However, APP is moisture sensitive, which means that APP is easily attacked by water and exudes from matrix during the service life, resulting in a decrement in the flame-retardant properties of the polymer

composites. Meanwhile, due to its poor compatibility in polymer matrix, APP may reduce the mechanical properties of PU.⁷ To overcome the disadvantage and improve the flame retardancy of APP, lots of work has been done. One method is microencapsulation. APP microencapsulated with melamine derivatives were reported and used in polypropylene and epoxy.^{8–11}

In this work, APP is microencapsulated with poly (methyl methacrylate-co-hydroxyl ethyl acrylate) (PMMA-HA) by in situ polymerization. PMMA-HA possesses abundant hydrophobic groups (–CH₃) and active groups (–OH). In one aspect, due to the presence of shell, MHAPP is endowed with better water resistance. In another aspect, the active groups can react with –NCO groups of the isocyanate, which can improve the compatibility of APP in PU. Moreover, PMMA–HA shell benefit for the formation of charred layer,¹² which can improve the flame retardancy of MHAPP.

The structure of the flame retardant is characterized by Fourier transform infrared (FTIR), scanning electron microscopy



Scheme 1. Scheme of the fabricated process of MHAPP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(SEM), and energy dispersive spectroscopy (EDS). The influence of microencapsulation on water resistance of APP is evaluated by water leaching rate and water contact angle measurements. Flame retardant and thermal behaviors are evaluated by limiting oxygen index (LOI), UL-94, and thermogravimetric analysis (TG). Mechanical strength and thermal degradation behavior of PU composites containing reactive MHAPP are studied.

EXPERIMENTAL

Materials

APP (phase II, the degree of polymerization >1000) was supported by Polyrocks chemical Co., China. 4,4'-diphenylmethane diisocyanate (MDI), benzoyl peroxide (BPO), and hydroxyl ethyl acrylate (HA, 96%) were purchased from Aladdin Industrial Corporation (China). Methyl methacrylate (MMA) was obtained from Chengdu Kelong Chemical Reagent Factory (Sichuan, China). Butanone and methylbenzene were supplied by Hengyang Kaixin Chemical Reagent Co., China. Polyether polyols (4110, Hydroxyl value = 410–450 mg KOH/g) was provided by Guangzhou Ruiyin Trading Co., China. N-Pentane was supplied by TianjingFuchen Chemical Reagent Factory (Tianjin, China). Dibutyltin dilaurate was purchased from Shanghai Lingfeng Chemical Reagent Co., China.

Preparation of Microencapsulated Ammonium Polyphosphate (MHAPP)

About 60 g portion of APP and 180 mL methylbenzene were put into a 500 mL three-neck flask with mechanical stirring equipment and stirred at 50°C. After stirring for 10 min, 6.3 mL MMA and 3.5 mL HA mixed compounds were added. When the mixture was heated to 60°C, 0.12 g portion of BPO was dissolved in 20 mL butanone and added to the mixture. After that, the resulting mixture kept at 80°C for 6 h at N₂ atmosphere. Finally, the obtained slurry was cooled to room temperature, filtered, washed with methylbenzene, and dried at 80°C. Then, the MHAPP powder was finally obtained. The preparing process is shown in Scheme 1.

Preparation of Flame Retarded PU

The Polyether polyols (10.00 g) was mixed with the other ingredients: foaming agent (N-pentane) (1.30 g), catalyst (dibutyltin

dilaurate) (0.11 g), flame retardant (APP or MHAPP), which was stirred well to homogenize, and then MDI (10.10) was added into the mixture with continuous stirring. Once the foam began to arise after mixing, it was poured into the mold. The foaming process was operated at room temperature. The container was then placed on a flat surface for 5 h at 70°C. The content of flame retardant based on the mass of final PU foam is at a mass of 7.4%, 10.7%, 13.7%, and 16.7%, respectively. Samples were cut into specific shapes as per the test requirement, and the foam properties were then measured.

Measurements

Fourier Transform Infrared Analysis (FTIR). FTIR spectra were recorded between 3800 and 400 cm⁻¹ using a RFX-65A (Analect) FTIR with KBr pellets for solid samples.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The SEM and EDS results of samples were recorded by Hitachi S3400N (Japan) scanning electron microscope (SEM) and X-ray energy dispersive spectroscopy (EDS, Bruker, Germany), respectively.

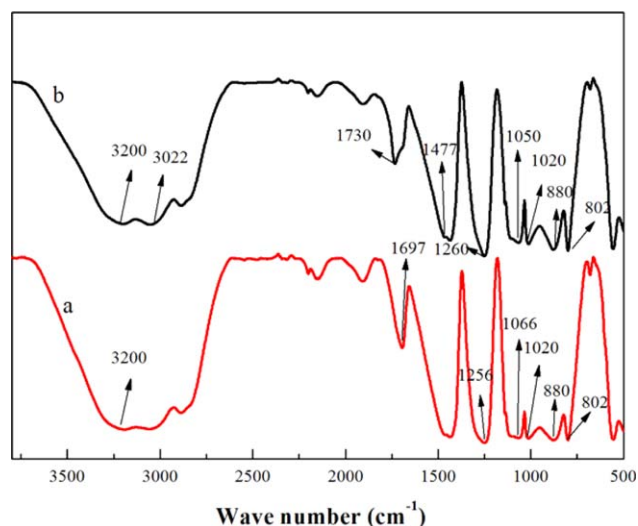


Figure 1. FTIR spectra of (a) APP and (b) MHAPP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

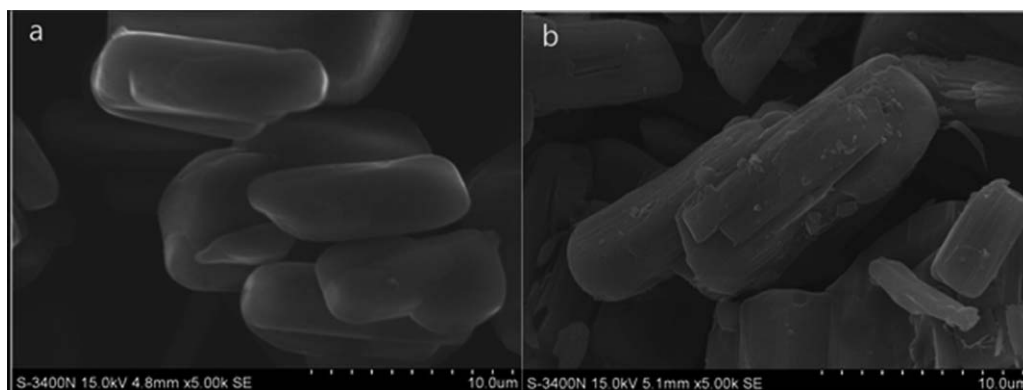


Figure 2. SEM photographs of (a) APP and (b) MHAPP.

Water Leaching Rate. About 8 g flame retardants (marked W_a) were packaged with the same filter papers (marked W_c). The specimens were put in about 2 L distilled water and the temperature was kept at different temperature for 36 h. Then removed and dried to constant mass at 80°C (marked W_t). The water leaching rate of the specimens can be expressed as $(W_t - W_c) / (W_a - W_c) \times 100\%$.

Water Contact Angle (WCA) Measurements. Samples were put on a platform. Water contact angle (WCA) of the samples was measured with a drop-shape analysis system (JC2000D1).

UL-94 Vertical Burning Test. The vertical test was carried out on a CFZ-3-type instrument (Jiangning Analysis Instrument Company, China) according to the UL-94 test standard (GB2408). The specimens used were of dimensions $120 \times 15 \times 8 \text{ mm}^3$.

Limiting Oxygen Index (LOI). LOI was measured according to ISO4589. The apparatus used was an oxygen index meter (JF-3, Jiangning Analysis Instrument Company, China). The samples used for the test were of dimensions $100 \times 10 \times 10 \text{ mm}^3$.

Compression Strength. The compressive strength of the rigid foams prepared was evaluated using M3030 (China) microcomputer control electronic universal testing machine based on GB/T 8813—88 standard. The test samples were prepared with a

diameter of 6 cm. The test was done at a cross head speed of 2 mm min^{-1} with 2 mm thickness compressed. Three specimens were tested for each sample.

Thermogravimetric Analysis (TG). Each sample was examined under air flow (30 mL min^{-1}) on a DTG-60H apparatus (Shimadzu Company, Japan) at a heating rate of $10^\circ\text{C min}^{-1}$. The mass of all samples was kept within 3–5 mg in an open Al pan.

RESULTS AND DISCUSSION

Characterization of APP and MHAPP by FTIR

The FTIR spectra of APP and MHAPP are shown in Figure 1. The typical absorption peaks of APP include 3200 (N-H) , $1697 \text{ (deformation vibration of N-H)}$, 1256 (P=O) , $1066 \text{ (P-O symmetric stretching vibration)}$, $880 \text{ (P-O asymmetric stretching vibration)}$, and $1020 \text{ (symmetric vibration of PO}_2 \text{ and PO}_3\text{) cm}^{-1}$. After microencapsulation, the spectrum of MHAPP shows an absorption band at 1730 cm^{-1} for the C=O stretching vibration of acrylate. In addition, new absorption peaks of MHAPP appear at $3022 \text{ (CH}_3 \text{ stretching vibration)}$, $1477 \text{ (CH}_2 \text{ bending vibration)}$, and $1050 \text{ (C-O stretching vibration) cm}^{-1}$, which demonstrate the presence of the PMMA-HA on the surface of APP.^{13,14}

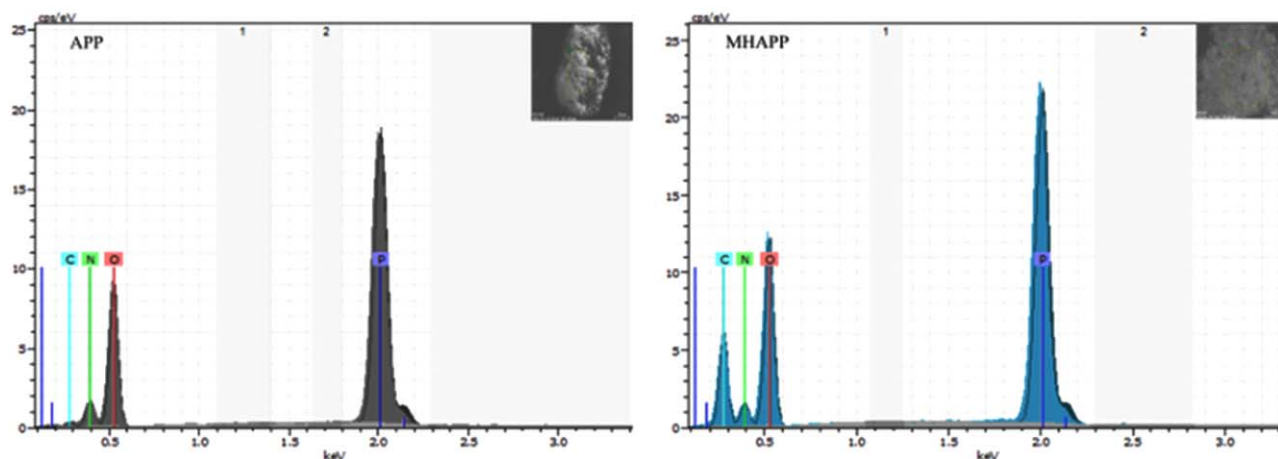


Figure 3. EDS spectra of APP and MHAPP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Surface Elemental Compositions of APP and MHAPP

Sample	C (mass %)	O (mass %)	N (mass %)	P (mass %)
APP	7.06	53.36	20.25	19.34
MHAPP	39.59	38.16	12.33	9.92

Surface Morphologies and Elements Analysis

The surface morphologies of APP and MHAPP particles are shown in Figure 2. It can be seen that APP particles is like a rod and exhibits smooth surface. After microencapsulation, MHAPP presents a comparably rough surface, which suggests that a coating exists on the surface of APP. The surface elemental compositions of APP and MHAPP are analyzed by EDS, and imagine of EDS are presented in Figure 3. The data is exhibited in Table I. As it shows, the O, N, and P atoms content of MHAPP are 38.16%, 12.33%, and 9.92%, respectively, which are lower than those of APP (53.36%, 20.25%, and 19.34%). Moreover, C atom content of MHAPP is 39.59%, which is much higher than that of APP (7.06%). These changes can be attributed to the coverage of the surface of APP particles with PMMA-HA, which indicates that APP was microencapsulated well.

Flame Retardancy

LOI values and UL94 rating tests are widely used to evaluate the flammability of flame retarded materials. The results are presented in Figure 4. Pure PU is highly combustible and its LOI value is only 16.7%. With the increasing of APP content in PU, LOI value of the PU increases. Obviously, PU containing MHAPP demonstrates higher LOI values compared with PU added with the same loading APP. The LOI value of the PU/APP (13.7 mass % APP) is 21.5%, and it can't pass UL94 V-0 rating. Whereas LOI value of the PU/MHAPP (13.7 mass % MHAPP) is 22.0%, what's more, PU/MHAPP (13.7 mass % MHAPP) obtains a UL-94 rating of V-0. This phenomenon might be ascribed to the flame retardant synergism of shell (PMMA-HA) and core (APP).¹⁵ It can be concluded that MHAPP obtains better flame retardancy than APP in PU.

Water Resistance

Table II shows the defined water leaching rate of APP and MHAPP at different temperature for 24 h. Water leaching rate of APP is 99.5% at 30°C, and at higher temperature, which increases to 100.0%. It makes clear that APP can be easily attacked by moisture or water. Due to the hydrophobic property of the shell after microencapsulation, water leaching rate of MHAPP are much lower than that of APP. Water leaching rate of MHAPP is only 13.7% at 30°C.

The surface hydrophobic properties of APP and MHAPP can be evaluated by water contact angle measurements. From Figure 5, it can be seen that the water is absorbed when it is dripped on the surface of APP. Water contact angle (WCA) of pure APP is only 35°, and then it decreases to 13° after 90 s, which indicates that the surface property of APP is hydrophilic. However, after microencapsulation, MHAPP shows a WCA of 144°, and it keeps above 135° as time increases. The above results suggest a hydrophobic coating exists on the surface of MHAPP.

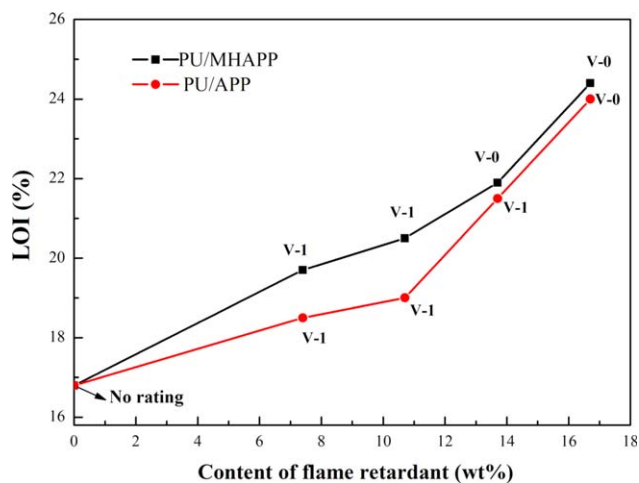


Figure 4. LOI value and UL94 rating of flame retarded PU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Furthermore, flame retardancy performance of flame retarded PU (16.7 mass % additive) after water treatment for 24 h at 60°C is evaluated by LOI value and UL 94 rating. From Table III, it can be seen that LOI value of PU/APP is decreased by 3.0% after water treatment. By comparison, that of PU/MHAPP is decreased by only 0.8%. PU/MHAPP can still maintain V-0 rating during UL94 testing, while, that of PU/APP falls to V-1 rating. Above result can be ascribed to hydrophobicity of MHAPP, which would prevent the flame retardant being exuded from PU matrix when soaked in water.

Compression Strength

Compression strength of PU is presented in Figure 6. As it shows, compression strength of PU decreases versus APP content, which is decreased from 216 to 195 kPa, and it is lower than that of pure PU. This indicates that APP has a negative effect on mechanical property in PU because of the poor compatibility of APP in PU matrix. However, compression strength of PU/MHAPP is higher than that of PU/APP. It might be attributed to the presence of active groups (-OH) outside APP, which can improve the compatibility of MHAPP in PU. In addition, due to the presence of active groups (-OH) in shell, the interaction and alignment of the PU polymer chains occur at the surface of additives. Thus, the evenly dispersed particles could partially absorb external stress, which results in higher compression strength of PU/MHAPP with suitable loading compared that of PU/APP and neat PU. While large amounts of additive might have deleterious effect on the dispersion of MHAPP in matrix. As a result, when MHAPP loading increases to 16.7%, compression strength of PU/MHAPP decreases.

Table II. Water Leaching Rate of APP and MHAPP

Temperature	MHAPP (mass %)	APP (mass %)
30°C	13.7	99.5
40°C	22.1	100.0
50°C	29.8	100.0
60°C	44.6	100.0

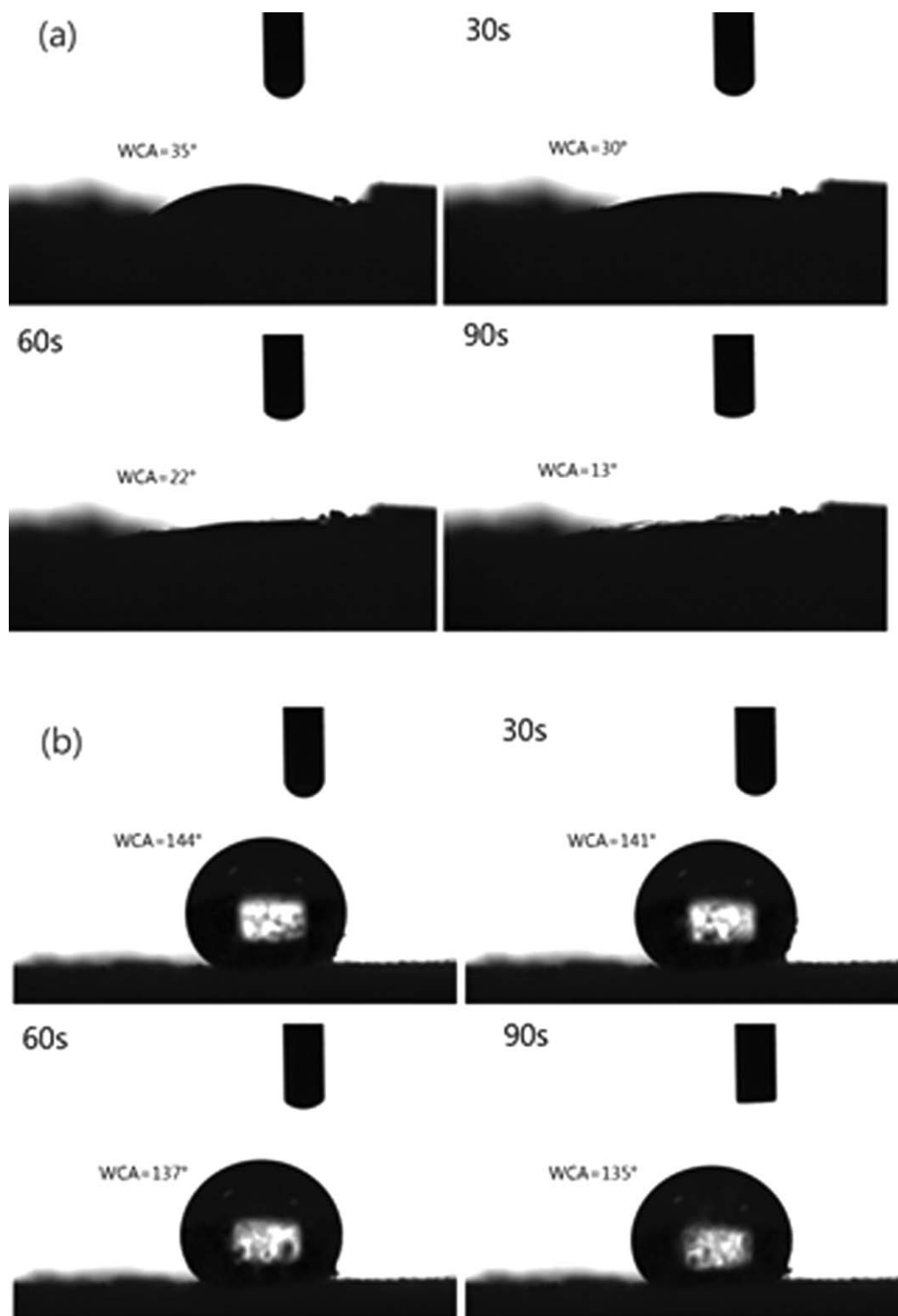


Figure 5. Water contact angle of (a) APP and (b) MHAPP.

Above results indicate that microencapsulation has a positive effect on mechanical property of PU.

Thermal Stability

The TG and DTG curves of APP and MHAPP are shown in Figure 7. APP has two main decomposition processes. The first decomposition stage begins at about 270°C, the rate reaching a

maximum at 310°C. In this step, polyphosphoric acid (PPA) is formed, and pyrolysis products are mainly ammonia and water, the mass loss is approximately 20%. At temperatures in excess of 485°C, there is a sharp increase in the rate of weight loss. The temperature of maximum mass loss rate (T_{max}) is 571°C, and within about 120°C, the weight loss increases from 20 to 70%. Residual mass of APP is 23.6% at 650°C.

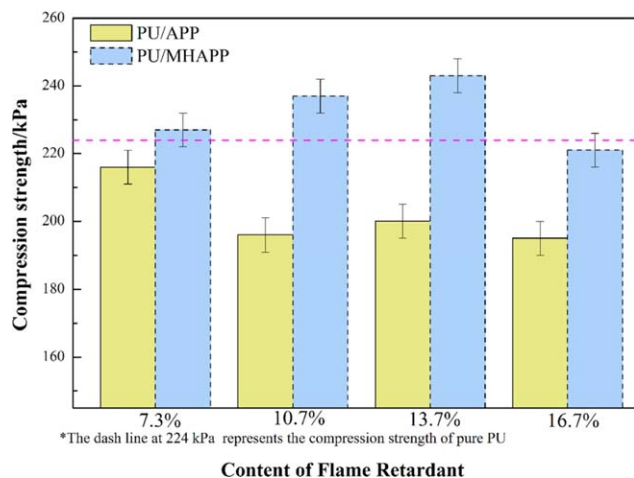
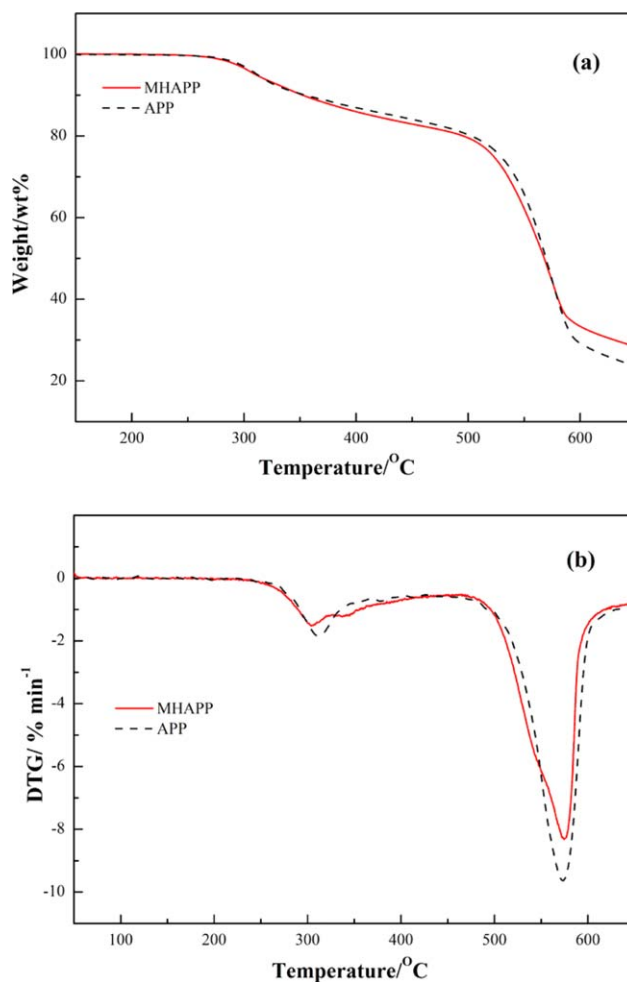
Table III. LOI Values and UL-94 Results of Flame Retarded PU Before and After Water Treatment (60°C, 24 h)

Sample code	PU/APP	PU/MHAPP
LOI/% (before treatment)	24.0	24.4
LOI/% (after treatment)	21.0	23.6
UL94 (before treatment)	V-0	V-0
UL94 (after treatment)	V-1	V-0

The thermal degradation behavior of MHAPP also shows two stages. When the temperature is between 370–550°C, MHAPP decomposes faster than APP. At a temperature above 550°C, the decomposition rate of MHAPP is lower than that of APP. The residual mass of APP is 28.3%, which is higher than that of APP. This phenomenon might be attributed to the presence of PMMA-HA shell outside APP. PPA released from APP can induce elimination of ester groups, which causes MHAPP decomposes faster than APP at low temperature. Meanwhile, as temperature increasing, PPA can catalyze PMMA-HA cyclization to forming anhydride. The cyclic anhydride structures block the chain depolymerization process, which results in the formation of chain fragments at high temperature.¹⁶ The large chain fragment decomposes to give charred layer with P–O–C bond, which contributes to a higher residual left of MHAPP than that of APP.

Figure 8 shows the decomposition behaviors of PU with 16.7 mass % flame retardant (PU/MHAPP, PU/APP) and pure PU under air atmosphere. It is clearly seen that pure PU begins to decompose at about 178°C and has almost completely decomposed at 650°C. The T_{max} for the decomposition for two stages is 321°C and 564°C, respectively.

PU/APP decomposes initially at about 218°C, which is higher than that of pure APP. Its thermal decomposition includes two steps. The first step of mass loss is the main decomposition of the composite, and T_{max} for this step is 281°C. Due to the acceleration effect of PPA on the decomposition of PU/APP, PU/

**Figure 6.** Effects of flame retardant on compression strength of composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 7.** TG (a) and DTG (b) of APP and MHAPP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

APP decomposes faster than pure PU between 253°C to 322°C at first stage. T_{max} value for the second process is 537°C. PU/APP leaves about 25.9% residue at 650°C.

For PU/MHAPP, its decomposition behavior at first stage is similar to that of PU/APP. When temperature is above 500°C, PU/MHAPP is more stable than PU/APP. The residual mass is 27.4% at 650°C, which is higher than that of PU/APP. The increase in the mass of the residue at higher temperature might be due to the formation of a more thermally stable carbonaceous char. From the above result, it can be concluded that MHAPP is better than APP in improving the thermal stability of PU at high temperature.

Residue Analysis

Figure 9(a–c) present the FTIR spectra obtained from pure PU, PU/APP (16.7 mass % additive), and PU/MHAPP (16.7 mass % additive) heated at different temperature in muffle. Pure PU shows peaks at 1720 (C=O vibration), 1307 (C–N stretching vibration), 1404 (CH₂ bending vibration), and 1093 (CH₂–CH₂ stretching vibration) cm⁻¹, and the typical absorptions of benzene ring skeleton are detected at 1600, 1527, 825, and 781 cm⁻¹, which are consistent with the absorptions of PU

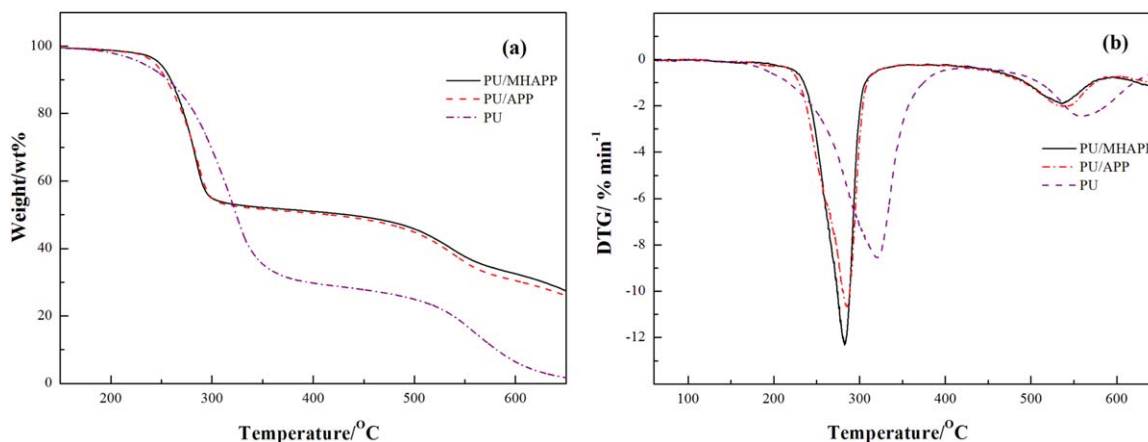


Figure 8. TG (a) and DTG (b) of pure PU, PU/APP (16.7 mass % additive), and PU/MHAPP (16.7 mass % additive). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported.^{17–20} It could be seen that the peaks of typical absorptions of benzene ring skeleton and C=O vibration absorptions decrease as temperature increasing. The obvious change happen

300–500°C, which is corresponding to the thermal degradation of PU presented by TG curve. The charred carbonaceous collected after heated at 500, 550 and 600°C shows the similar

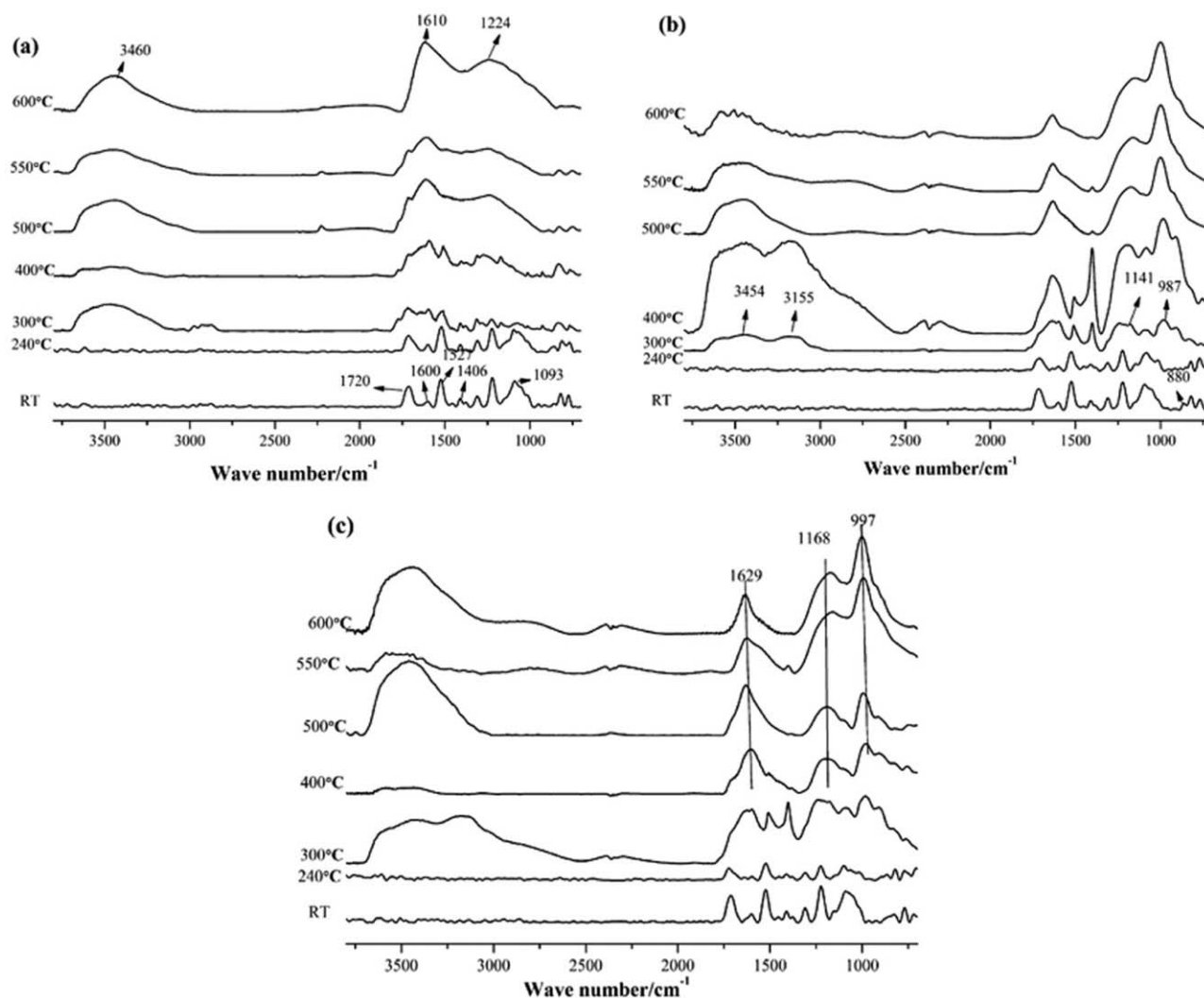


Figure 9. FTIR spectra of residue after heated at different temperature in muffle of (a) PU, (b) PU/APP (16.7 mass % additive), and (c) PU/MHAPP (16.7 mass % additive).

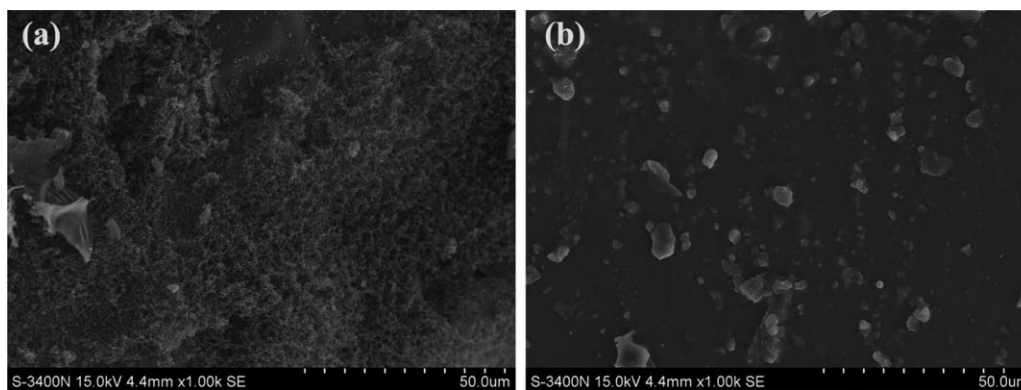


Figure 10. SEM micrographs of the char residues (a) PU/APP (16.7 mass % additive) and (b) PU/MHAPP (16.7 mass % additive).

FTIR spectra with absorption peaks at 3460 (O–H), 1610 (unsaturated C=O), 1224 (C–O) cm^{-1} . Above result indicates that charred carbonaceous structure contains –OH, unsaturated C=O and C–O, which is agreement with the literatures.^{21,22}

The FTIR spectra of PU/APP at room temperature (about 25°C) shows a new absorption peak at 880 cm^{-1} compared pure PU, which is assigned to the P–O asymmetric stretching vibration. Due to the presence of APP, residue after 300°C heated is different from pure PU after the same treatment, it presents vibration absorption peaks of –NH₂ (3454, 3155 cm^{-1}), P–O–C (1141 cm^{-1}), and C–O–C (987 cm^{-1}), and it become more obvious at higher temperature. C–O–C and P–O–C structures are the predominant component of the charred layer after 600°C.

PU/MHAPP presents the similar FTIR absorption with that of PU/APP at room temperature, and the charred layer also contains C–O–C and P–O–C structures after 600°C. However, it could be seen that the FTIR spectrum of residues for PU/MHAPP at 300 and 400°C are different from those of PU/APP. Moreover, FTIR spectra of charred carbonaceous collected after heated at 400, 500, 550, and 600°C are rarely changed.] It illustrates that the stable charred carbonaceous of PU/MHAPP is formed at 400°C. By comparison, this phenomenon occurs at 500°C for PU/APP. Above result demonstrates that MHAPP is more efficient than APP in carbonization formation in PU during combustion process, which could slow down heat mass transfer between gas and condensed phase and protects the underlying material from flame.

Furthermore, the residual chars are obtained after LOI value test and then the morphologies are observed by SEM. Figure 10 presents the photographs of above residual chars. For PU/APP, it could be seen that the char is porous. In another aspect, the char of PU/MHAPP is coherent. Consequently, the char could provide better flame shield for the underlying material during combustion.

CONCLUSION

In this study, PMMA-HA is used as shell material for microencapsulated APP. The microcapsule is successfully prepared and shows excellent hydrophobicity and thermal stability. Due to presence of reactive shell, the compatibility of MHAPP in PU is

enhanced. According to LOI values, UL-94 tests, and TG tests, it can be concluded that PU/MHAPP composites demonstrate a better flame retardancy and thermal stability than PU/APP. PU composites containing MHAPP can still maintain good flame retardant properties after hot water treatment. Compression strengths of PU/APP composites decreases as the amount of flame retardant increases, by comparison, that of PU/MHAPP increases and reaches a peak value at 13.7 mass % loading. This result shows that MHAPP has a positive effect on the mechanical property. MHAPP are more efficient in carbonization formation in PU compared with APP during combustion process.

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