

Microencapsulation of ammonium polyphosphate with hydroxyl silicone oil and its flame retardance in thermoplastic polyurethane

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Abstract Microencapsulated ammonium polyphosphate (MAPP) is prepared using hydroxyl silicone oil by in situ polymerization and characterized by XPS. Microencapsulation gives MAPP better water resistance and flame retardance compared with APP in thermoplastic polyurethane (TPU). Thermal stability and fire resistance behavior have been analyzed and compared. The LOI value of the TPU/MAPP composite is higher than that of the TPU/APP composite. The UL 94 rating of the TPU/MAPP composite is V-0 at the 20 wt% additive level, whereas TPU/APP gives V-2 rating at the same loading level. The water resistant properties of the TPU composites are studied. Results of the cone calorimeter and microscale combustion calorimeter experiment show that MAPP is an effective flame retardant in TPU compared with APP.

Keywords Microencapsulation · Flame retardant · Thermoplastic polyurethane

Introduction

Intumescent flame retardants (IFRs) have attracted considerable attention in recent years because they are more environmentally friendly than the traditional halogen-containing flame retardants. The typical and widely studied IFRs system is the combination of ammonium polyphosphate, pentaerythritol, and melamine (APP/PER/MEL). There are many publications on the studies of the APP/PER/MEL

compositions in polyolefin [1–10]. Bourbigot and co-workers have carried out extensive studies on the APP IFR system in polyolefins [2, 4, 5] and have reviewed recent developments of IFR systems in great detail [11]. However, these systems are not durable due to the weak water resistance and low compatibility with organic materials of APP. When they are exposed to water or a moisture environment, migration and exudation of them may occur, which lead to a decrease in the properties of the polymer composites, not only flame retardancy (FR), but also some other properties [11]. To deal with the above problems, microencapsulation with water insoluble polymers can be employed.

Microencapsulating APP with melamine–formaldehyde (MF) and urea–melamine–formaldehyde (UMF) resin has been reported [12, 13]. Compared with APP, the microencapsulated APP (MCAPP) coated with MF or UMF resin can be dispersed well in the PP matrix and has lower water solubility. Ni and co-authors have reported microencapsulated ammonium polyphosphate (APP) with polyurethane (MCAPP) [14, 15]. The results showed that the PU/MCAPP had better thermal stability and flame retardance, due to the stable char forming by APP and PU shell. Moreover, the water resistance of flame retardant PU composite was greatly improved. It has been reported that silicone additive can highly improve the flame retardant performance of APP in PP composites [16–19]. Furthermore, Our group have recently reported that hydroxyl silicone oil can be used synergism with intumescent flame retardant [20, 21]. Hydroxyl silicone oil can decrease heat release rate (HRR), mass loss, mass loss rate (MLR), carbon dioxide, etc. It also can enhance the high temperature stability and morphological structure of char residue of the intumescent flame retardant systems. Furthermore, it is well known that silicone compounds have excellent hydrophobic properties. Our aim is to synthesize microencapsulated ammonium

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Table 1 The formulations of the flame retardant TPU composites

Sample code	PP/%	APP/%	MAPP/%	LOI		UL 94	
				Not treated	Treated	Not treated	Treated
TPU-0	100.0	–	–	23.0	23.0	No rating	No rating
TPU-1	90.0	10.0	–	25.1	23.8	V-2	No rating
TPU-2	90.0	–	10.0	25.5	24.9	V-1	V-1
TPU-3	80.0	20.0	–	28.0	25.8	V-2	No rating
TPU-4	80.0	–	20.0	29.3	28.2	V-0	V-0

polyphosphate which may have better flame retardance and higher water resistance in the polymer, compared with APP.

In this article, microencapsulated APP (MAPP) with hydroxyl silicone oil was prepared by in situ polymerization and characterized by X-ray photoelectron spectroscopy (XPS). The use of MAPP as a flame retardant in TPU is evaluated by limiting oxygen index (LOI), UL 94, thermogravimetric analysis (TG), cone calorimetry, and microscale combustion calorimeter (MCC), and the results from MAPP and APP are compared. Moreover, the water resistant properties of the TPU composites containing MAPP (or APP) are studied by LOI test and UL 94.

Experimental

Materials

Thermoplastic PU (TPU 4190, melt index: 190 °C, 8700 g) was purchased from Zhejiang Yongkang Tiantian plastic Co., Ltd China. TPU was dried in vacuum oven at 105 °C for 3 h before used. The commercial products APP (phase II, the degree of polymerization > 1000, the mesh size is 1000) was a product of Shandong Dezhou Shian Chemical Engineering Co., Ltd, China. Hydroxy silicone oil, colorless transparent liquid, (QLS-203, viscosity (25 °C), mm² s⁻¹: ≤30; content of hydroxyl: ≥8.5%) was supplied by Wuxi Quanli Reagent Chemical Factory, Wuxi, China.

Preparation of microcapsules

Preparation of microencapsulated ammonium polyphosphate: APP (60 g) was first dispersed in 150 mL dioxane. Then 3 g hydroxyl silicone oil solution was added into the mixture. The resulting mixture was heated at 80 °C for 2 h. After that, the mixture was cooled to room temperature, filtered, washed with distilled water, and dried at 105 °C. The MAPP was finally obtained.

Preparation of flame retardant TPU composites

All flame retardant TPU composites were mixed in a Brabender-like apparatus at a temperature about 160 °C for

15 min. After the mixing, the samples were hot-pressed at about 160 °C under 10 MPa for 10 min into sheets of suitable thickness for analysis. The formulations are given in Table 1.

Measurements

XPS spectra

The X-ray photoelectron spectroscopy spectra were recorded with a VG ESCALAB MK II spectrometer using Al K α excitation radiation ($h\nu = 1253.6$ eV).

Limiting oxygen index

Limiting oxygen index was measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 100 × 6.5 × 3 mm³.

UL 94 testing

The vertical test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL 94 test standard. The specimens used were of dimensions 100 × 10 × 3 mm³.

Cone calorimeter test

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen of dimensions 100 × 100 × 3 mm³ was put on an aluminium tray and exposed horizontally to an external heat flux of 35 kW m⁻².

Thermogravimetry

Each sample was examined under air flow on a STA 409C TG apparatus (Netzsch Company, Germany) with crucible sample holders, at a heating rate of 10 °C min⁻¹.

Microscale combustion calorimeter

Approximately 4–8 mg of each sample was weighed with a microbalance and placed in a Pyroprobe (CDS Analytical Model 2000) for pyrolysis in a pyrolysis-combustion flow calorimeter. A special probe was placed into a heated interface continuously purged with pure nitrogen. Then programming the system to heat at $1\text{ }^{\circ}\text{C s}^{-1}$ from 90 to $600\text{ }^{\circ}\text{C}$ and held there for 30 s. During pyrolysis, the volatilized decomposition products are transferred in the stream of nitrogen to a high-temperature combustion furnace where pure oxygen is added and the decomposition products are completely combusted. The amount of oxygen consumed is measured with an oxygen analyzer and used to calculate a HRR.

Determination of water resistance of the TPU composites

The specimens of the TPU composites were put in distilled water at $75\text{ }^{\circ}\text{C}$ and were kept at this temperature for 7 days. The treated specimens were subsequently taken out and dried to constant at $105\text{ }^{\circ}\text{C}$. The water resistance of the composites was evaluated by the change of LOI values, UL 94 ratings after the water treatment.

Results and discussion

Characterization of MAPP by XPS

Figure 1 shows the XPS spectra obtained from MAPP sample. It can be seen that for APP, the four peaks at 134.4, 190.3, 284.7, 401.1, and 532.1 eV were clearly seen, which were attributed to $\text{P}_{2\text{P}}$, $\text{P}_{2\text{S}}$, $\text{C}_{1\text{S}}$, $\text{N}_{1\text{S}}$, and $\text{O}_{1\text{S}}$, respectively. After the microencapsulation of the APP with hydroxyl silicone oil, the $\text{P}_{2\text{P}}$, $\text{P}_{2\text{S}}$, and $\text{N}_{1\text{S}}$ peaks of MAPP are

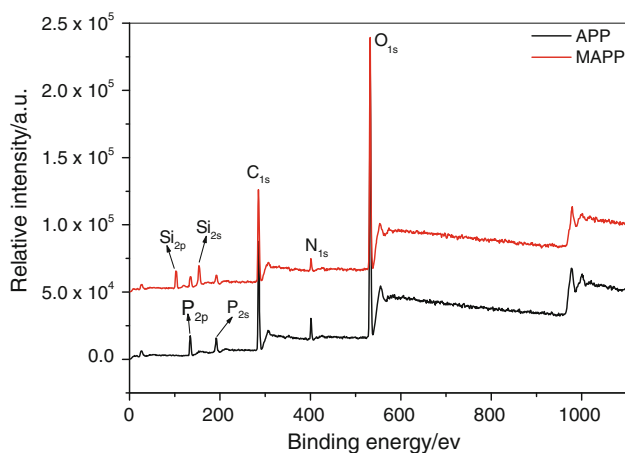


Fig. 1 XPS spectra of MAPP

greatly decreased, and the intensity of the $\text{O}_{1\text{S}}$ peak (532.1 eV) increases compared with that of APP. Furthermore, there are two new peaks at 153.7 and 102.7 eV, which are attributed to $\text{Si}_{2\text{S}}$ and $\text{Si}_{2\text{P}}$, respectively. The results indicate that the surfaces of APP particles were well covered by the hydroxyl silicone oil.

Effect of microencapsulation on the flame retardation of the IFR additives

LOI and UL 94 test

The LOI values and UL 94 testing results of the flame retardant TPU composites are presented in Table 1. It can be seen that the LOI value of the composite containing 10% (or 20%) MAPP is 25.5 (or 29.3), whereas the values of the composite containing APP at the corresponding additive level are only 25.1 and 28.0, respectively. The LOI value of the composite containing MAPP is higher compared with the TPU/APP composite at the same loading level of APP. Moreover, the microencapsulation can raise UL 94 ratings for TPU-2 and TPU-4 to V-1 and V-0, respectively. From this data, conclusion can be drawn that the microencapsulation can enhance the flame retardant properties of APP remarkably.

Cone calorimeter test

Cone calorimetry is an effective approach to compare the combustion behavior of flame retardant polymers. HRR results are shown in Fig. 2, and the co-related data are listed in Table 2. The presence of APP or MAPP in TPU decreases the HRR values significantly compared with pure TPU (the HRR peak value of TPU is 740.7 kW m^{-2}). In the case of TPU/APP composite, its HRR peak is before

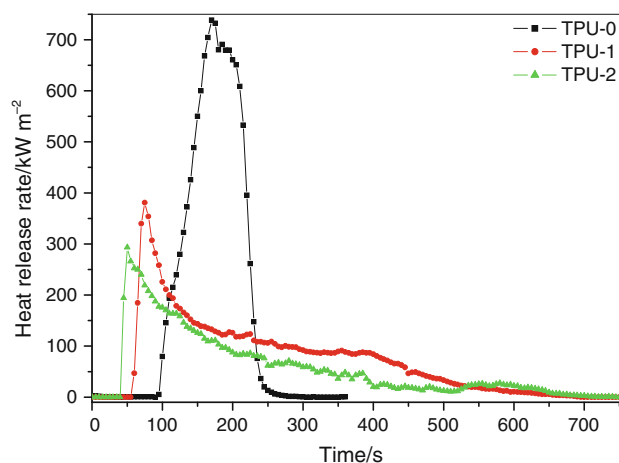


Fig. 2 Heat release rate curves of flame retardant TPU at a flux of 35 kW m^{-2}

Table 2 The data from cone calorimeter test of the flame retardant TPU composites

Sample code	TTI/s	PHRR/kW m ⁻²	Time to PHRR/s	THR/MJ m ⁻²	TSR/m ² m ⁻²
TPU-0	90	738.9	170	64.7	373.7
TPU-1	50	382.6	75	51.9	322.5
TPU-2	35	292.8	50	42.9	215.0

that of pure PP, and its peak value is a much lower (382.4 kW m⁻²) compared with TPU. Furthermore, it is noted that the ignition time (IT) of the PP/APP composite is less than that of TPU. The reason may be due to the fact that APP decomposes earlier than pure TPU, and it initiates degradation of TPU after the cone heater irradiated the surface of the composite, and some small volatile molecules are produced. The HRR curve of TPU/MAPP is very flat, and the values of HRR decrease further compared with that of TPU/APP. However, the IT of the PP/MAPP decreased a lot from the sample TPU-1. This phenomenon can be illustrated by the flammable hydroxyl silicone oil which can migrate onto the surface of the sample when it was heated. Moreover, addition of MAPP strongly prolongs the process of combustion compared with APP in TPU. From the above results, it can be concluded that the microencapsulation can remarkably enhance the flame retardant properties of APP in TPU.

The primary parameter which was responsible for HRR of the samples filled with flame retardant is the MLR during combustion, which was significantly reduced compared with those values observed for the pure polymer. Figure 3 shows that the MLR decreased in the order of TPU-2 > TPU-1 > TPU-0, this trend is the same as those of the HRR in the cone calorimeter (Fig. 2). These similarities indicate that the mechanism of the observed reduction in HRR and also in MLR depends mainly on the condensed phase process instead of the gas phase process.

Figure 4 presents the THR for all samples. The slope of THR curve can be assumed as representative of fire spread. From Fig. 4, it can be seen that the THR is decreased by the flame retardants. It is very clear that the flame spread of samples (TPU-1 and TPU-2) has decreased. It should be figured out that the THR of TPU-2 is higher than that of TPU-1 between 0 and 400 s. However, the flame spread of sample TPU-2 becomes much lower than that of TPU-1 when the time exceeds 400 s. This phenomenon can be explained by hydroxyl silicone oil which can lead flame spread large at the fire beginning. In this process, there is condense and compact char residue formed, which can isolate heat from the outside and combustible gases from the inside. For TPU-1, the structure of char is not good enough to stop flame spread. It is also suggested there is a synergistic effect of flame retardance between APP and hydroxyl silicone oil.

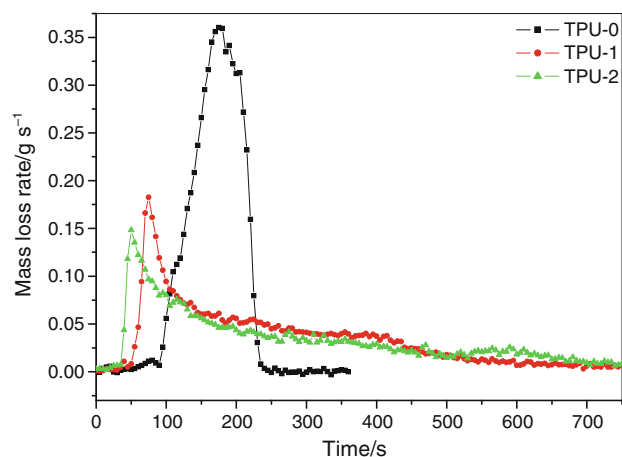
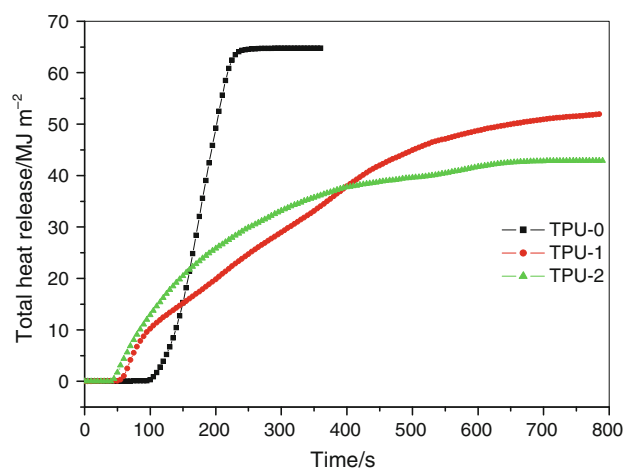
**Fig. 3** Mass loss rate curves of flame retardant TPU at a flux of 35 kW m⁻²**Fig. 4** Total heat release curves of flame retardant TPU at a flux of 35 kW m⁻²

Figure 5 shows the weight of the char residues. It can be seen from Fig. 5, the char residue weight of TPU-2 containing MAPP is higher than that of TPU-1 containing APP. In case of TPU/MAPP, SiO₂ will be formed during combustion. SiO₂ may occur on the surface of the burning composite creating a physical protective barrier on the surface of material [22, 23]. The physical process of the layers reassembling would act as a protective barrier in addition to the intumescent shield and can thus limit the oxygen diffusion to the substrate or give a less disturbing low volatilization rate.

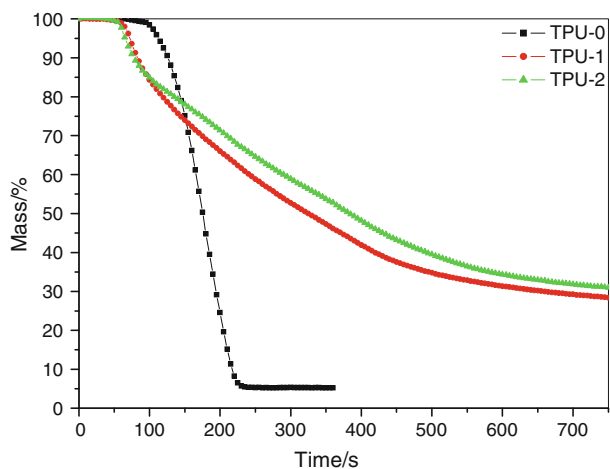


Fig. 5 Mass curves of flame retardant TPU at a flux of 35 kW m^{-2}

Figure 6 is digital photos of residues of the series of samples. It can be seen that a more coherent and dense char can be formed with the addition of flame retardant. From the char structure, we can explain the combustion phenomenon of the flame retardant TPU composites. The formation of the efficient char can prevent the heat transfer between the flame zone and the burning substrate, and thus protect the underlying materials from further burning and retard the pyrolysis of polymers. As a result, HRR values are strongly reduced, as shown in Fig. 2. The intumescent residue of TPU-1 was tighter, denser, and higher than TPU-0, at the same time the residue of the sample with MAPP was more compact than TPU-1. The results are in accordance with the order in Fig. 2. This can be explained that the hydroxyl silicone oil can lead to the transformation of durable and deformable ceramic-like material with a homogeneous surface which will protect the material throughout combustion and also to a mechanical reinforcement of the charred layer which would lead to a better accommodation of strains [24]. However, the micro composite may lead to the formation of an inhomogeneous and thus brittle surface material. The different char residues also contribute to the FR performance. For the above reasons, the HRR of the sample with MAPP is lower than that of TPU-1.

Fig. 6 Char residue of flame retardant TPU, **a** TPU-0; **b** TPU-1; **c** TPU-2

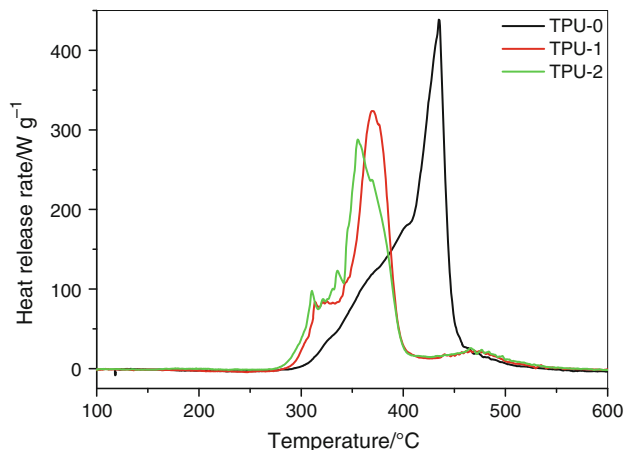
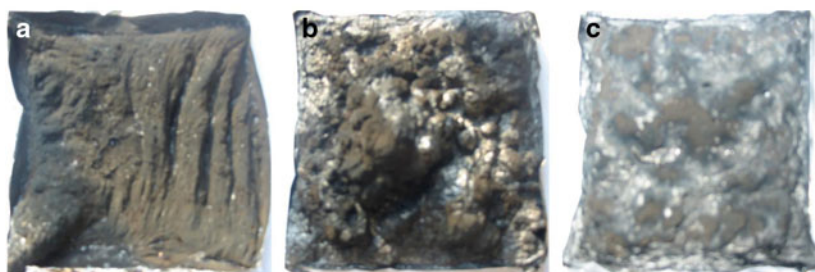


Fig. 7 Heat release rate curves of TPU and flame retardant PU composites from MCC

Microscale combustion calorimeter

The dynamic flammability data detected by MCC of TPU and flame retardant TPU samples are shown in Fig. 7. Compared with TPU, the peak HRR values decrease dramatically with addition of APP or MAPP, which also prolong the process of combustion. In the case of TPU-1, its peak HRR value is 322.4 J g K^{-1} , which is much lower than that of TPU (446.5 J g K^{-1}) as shown in Fig. 7. As for TPU-2, peak HRR value is 286.4 J g K^{-1} , lower than that of TPU-1. It is believed that stable char forming by MAPP and TPU matrix is responsible for the improvement of flame retardant. The shape of the HRR curves for TPU-1 and TPU-2 are very similar, but the IT of TPU-2 is less than that of TPU-1 and TPU, which also means silicone decompose at low temperature. It should be figured out the MCC evaluation of the materials shows less difference between the effect of coated and uncoated APP than the cone results probably because of the lower heating rate, which allows the silicone to decompose during the slow heating up.

Thermal stability of TPU composites

The thermal stability of TPU and TPU composites was studied by thermogravimetry (TG). The TG and DTG curves of TPU-0, TPU-1, and TPU-2 are shown in Fig. 8.

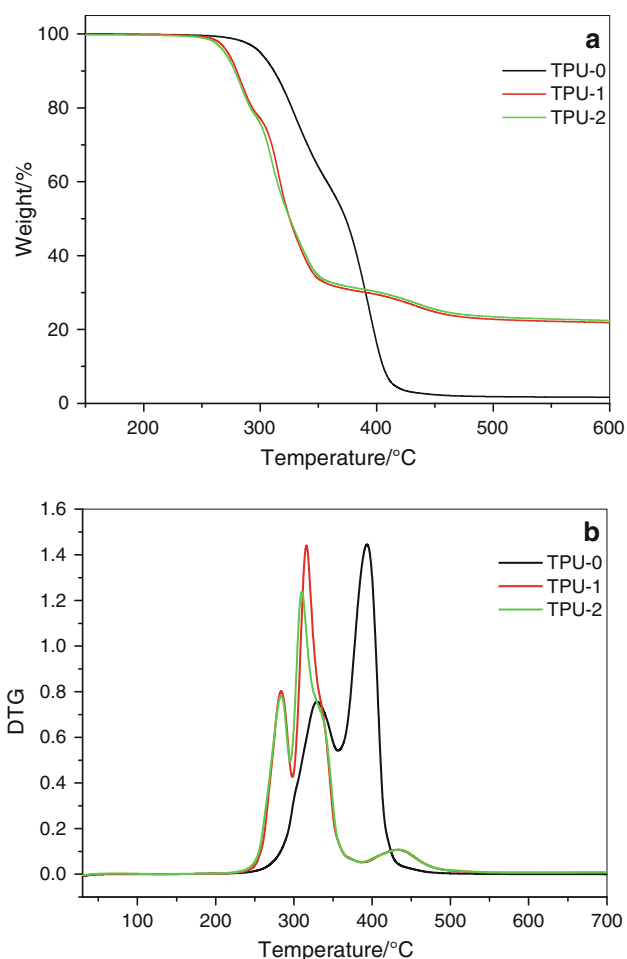


Fig. 8 Thermal analysis curves of flame retardant TPU

It is clearly seen that the thermal decomposition of the TPU resin in air occurs in two steps. The first step of decomposition for pure TPU is between 270 and 350 °C as shown in Fig. 8, which attributes to depolycondensation reaction [25]. At next step from 350 to 440 °C, The T_{\max} value of TPU is 329.6 and 392.4 °C. Then the material decomposes slightly to leave 1.62 wt% residues at 600 °C.

It is obvious that the thermal-oxidized decomposition of TPU-1 and TPU-2 show three-step process. The initial decomposition temperature for TPU-1 and TPU-2 is lower than that of TPU. This may be assigned to acid catalysis by decomposers of APP, which accelerate the depolycondensation of PU matrix [26]. The second step of mass loss forms a carbonaceous material between 290 and 380 °C. The T_{\max} for TPU-1 at second steps is 316.0 °C, while T_{\max} for TPU-2 is 308.7 °C. It is found that flame retardant TPU formulation has higher thermal stability compared with PU up to 390 °C, which suggests that addition of APP and MAPP in TPU lead to form a thermally stable material and postpone the decomposition of TPU matrix.

The TG results show again less difference between the effect of coated and uncoated APP than the combustion test because the lower heating rate allows the silicone to decompose instead of transforming to ceramic-like material. Despite the similar thermal decomposition behaviors between TPU-1 and TPU-2, there are still some differences. From Fig. 8, it can be seen that TPU-2 is more thermally stable than TPU-1, especially during 350 to 600 °C. Meanwhile, because the char residue lies on the structure of TPU [27], the char residue of TPU-2 is 22.7 wt%, which is higher than that of TPU-1.

Effect of microencapsulation on the water resistance of TPU composites

To investigate the effect of the microencapsulation on the water resistance of the TPU composites containing the non-microencapsulated APP additive or microencapsulated ones, the composites were immersed into 75 °C water for 7 days to evaluate the changes of their flame retardant properties. Table 1 lists the LOI and UL 94 testing results of the TPU composites before and after the water treatment. It can be seen that after the treatment, the LOI value of the composite containing non-microencapsulated APP additive decreases. The composites containing non-microencapsulated APP additives cannot pass the UL 94 tests after the water treatment. Furthermore, the UL 94 ratings decrease greatly after the water treatment.

In the case of the TPU composites containing the microencapsulated additives, the hot water treatment has a little effect on the LOI value as shown in Table 1. The LOI values of the composites containing microencapsulated additives decrease slightly via the treatment. And, the treatment does not change their UL ratings. The above results imply that the APP additive via the microencapsulation with the hydroxyl silicone oil can greatly reduce their exudation from the polymer composites.

Conclusions

In this study, microencapsulated APP (MAPP) was successfully prepared using hydroxyl silicone oil by in situ polymerization method. It is found that the microencapsulation of APP leads to an increase in flame retardance and water resistance.

In comparison with the TPU/APP composite, the LOI values and UL 94 ratings of the TPU composite containing MAPP microcapsules are greatly improved. The microencapsulation with hydroxyl silicone oil can obviously improve the water resistance properties of TPU composite. The TG results indicate that the TPU/MAPP composite has higher thermal stability than the TPU/APP composite. The

HRR from cone calorimeter and MCC is decreased greatly by the microencapsulation.

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