Composites Part A 115 (2018) 247–254

Contents lists available at ScienceDirect

Composites Part A

journal homepage: www.elsevier.com/locate/compositesa

Filling natural microtubules with triphenyl phosphate for flame-retarding polymer composites

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ARTICLE INFO

Keywords:
Flame retardant
Epoxy
Kapok microtubules
Triphenyl phosphate
Cellulose acetate

ABSTRACT

Phosphorus flame retardants can provide polymers with flame retardancy, but they often compromise the polymers' mechanical performance due to plasticization. This problem is addressed in this study by filling and sealing triphenyl phosphate into natural microtubules of ∼100 μm in length, 10–20 μm in diameter and 0.5–1.0 μm in wall thickness. We investigated the sealing mechanisms through morphological observation and X-ray photoelectron spectroscopy. An appropriate mixture of triphenyl phosphate and cellulose acetate at mass ratio of 97:3 created an encapsulation effect which prevented triphenyl phosphate from flowing out of the tubules during curing, which resulted in an encapsulation ratio of 56%. Adding the filled tubules into an epoxy resin showed no obvious compromise on the stiffness and strength of the matrix. The tubules proved effective in increasing char and reducing smoke release during combustion. This self-sealing method may be used in other applications such as self-healing composites.

1. Introduction

Hydrocarbon polymers are extensively utilized in various industries, but their applications are limited by inherent flammability. When subjected to an external heat source, these polymers absorb heat, followed by endothermic pyrolysis reactions, resulting in the production of non-combustible gases, combustible gases and liquid. The enormous heat released can cause sequential processes that often lead to a fire disaster [1–5]. The International Association of Fire and Rescue Services reported 3.5 million fires, 18.5 thousand civilian fire deaths and 45.0 thousand civilian fire injuries that occurred in 2015 for 31 countries representing 14% of the World's population [6]. The three most dangerous hazards in fire are high temperature, choking gas and falling structures due to the combustion of inflammable materials [7]. Since it is indispensable to prolong response time for people to escape as well as to rescue valuable personal belongings during a fire, combining polymers with flame retardants has become a common practice to render safer engineering materials for various applications.

Traditional inorganic flame retardants such as metal hydroxides or layered double hydroxides can effectively reduce the flammability of polymers and suppress smoke release [8,9]. However, they require relatively large fractions to maintain overall flame retardancy, which would adversely affect the mechanical properties of the composite [10]. Organic flame retardants for polymers can be classified according to whether they contain halogen. Since halogen flame retardants release smoke and brominated toxin during combustion, they have been gradually phased out or even banned in some jurisdictions [11–13]. Halogen-free flame retardants have become a new research direction owing to their safety and efficient flame retardancy – phosphorous flame retardants are the most promising in both research and market [5,11].

Phosphorous flame retardants release liquid acids during decomposition and form a protective layer efficiently reducing the smoke release. Under heat, the retardants first decompose into phosphoric acid

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https://doi.org/10.1016/j.compositesa.2018.09.030
Received 22 June 2018; Received in revised form 13 September 2018; Accepted 30 September 2018

and then follow a char-forming process during the condensation phase [14–17]. The acid creates a layer of liquid on the burning surface converting the adjacent polymer into char; the char and liquid collectively work as a protection layer to prevent heat and oxygen from contacting the polymer under the burnt surface. However, these retardants are limited by a severe disadvantage – they plasticize polymers and thereby reduce the mechanical properties [18,19]. A solution for this problem is to use less flame retardant, but this would jeopardize the resulting flame-retardant performance. It remains a formidable challenge to develop flame-retarding, mechanically strong polymer composites. From our perspectives, this challenge may be addressed by sealing flame retardants into microcapsules which are subsequently compounded with polymers.

Previous efforts of encapsulation for this purpose are summarized below. Through *in situ* polymerization, microparticles of ammonium polyphosphate were encapsulated with epoxy to create capsules which have improved water resistance and compatibility with polypropylene [20]. As *in situ* polymerization involving a lot of chemicals may be a challenge to scale up, our solution is to encapsulate flame retardants using inexpensive natural kapok microtubules, which are stiffer and stronger than polymeric capsules and hence would minimize the impact of flame retardants on the mechanical robustness of polymeric matrices. Epoxy is selected as the matrix in this research, because it has been extensively studied for flame retardancy [21–25].

We herein report a new method to fill and seal a flame retardant inside kapok microtubules so as to avoid the direct contact between the flame retardant and the polymer to remove the effect of plasticization. The filled kapok microtubules are so intact during a high-temperature curing process that they contribute much to the performance of the resulting composites. This cost-effective method requires minimum number of steps and benign solvent, and more importantly, it provides the resulting composites with both mechanical strength and flame retardancy.

2. Experimental

2.1. Materials

Triphenyl phosphate (TPP) and cellulose acetate (CA) were purchased from Sigma Aldrich Pty Ltd; their molecular formulae are shown in Fig. 1. Kapok fibers were cut to ~100 μm in length, to produce Kapok microtubules. Diglycidyl ether of bisphenol-A (Araldite-F, 182–196 g per equiv.; denoted DGEBA) and hardener polyetheramine (Jeffamine D-400) were provided by the Huntsman Corporation, Australia.

2.2. Filling tubules and fabrication of epoxy composites

4.00 g of triphenyl phosphate (TPP) was dissolved in 20 mL of acetone to form a solution, into which 1.00 g of kapok microtubules were added. Next, the mixture was stirred by a magnetic bar for 10 min to create a uniform suspension before being placed within a fume hood at room temperature for 6 h to evaporate acetone. Through this process, the dissolved TPP would absorb into the kapok tubules through a capillary effect. The evaporation process left TPP inside the tubules. The mixture was then carefully milled by a mortar and pestle to break up the bonding between the tubules to create TPP-filled kapok tubules (denoted **TPP tubules**).

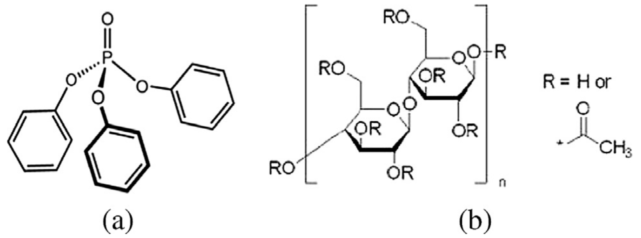

Fig. 1. Molecular formulae of (a) triphenyl phosphate (TPP) and (b) cellulose acetate (CA).

3.88 g of TPP and 0.12 g cellulose acetate (CA) at a mass ratio of 97:3 were dissolved in 20 mL of acetone, into which 1.00 g of kapok microtubules were added. The mixture was treated by the same procedure as described above to produce kapok microtubules filled with both TPP and CA (denoted **TPP-CA tubules**).

DGEBA was blended with a calculated ratio of hardener D400 to form the matrix mixture. A predetermined weight fraction of tubules was then immediately added to the mixture, followed by mechanical stirring for 10 min to obtain a composite blend. It was then poured into a mold for curing by a reported procedure [26]; in specific, a vacuum oven was used at room temperature to remove air bubbles trapped inside the blend, and it was then poured into a polypropylene mold or silicone rubber mold to produce samples with desired geometries, followed by curing at 100 °C for 10 h. The composition for the composites prepared is detailed in Table 1.

2.3. Characterizations

As-received tubules (Kapok microtubules), TPP tubules and TPP-CA tubules were examined by scanning electron microscopy (SEM) using a Philips XL30 FEG. All the composites were also observed with the same setting to examine the dispersion of the tubules and TPP.

TPP, CA and their composites were examined by X-ray photoelectron spectroscopy (XPS) with SPECS SAGE XPS using an Mg Ka source at 10 kV and 20 mA emission. The energy was set to 100 eV and analysis area was 3 mm in diameter. The spectra were analyzed by CASAXPS using a transmission function as advised by the manufacturer.

Tensile testing was conducted according to ASTM D638 at a crosshead speed of 5 mm/min at room temperature using an Instron 5567 equipped with a 40 kN load cell and an extensometer to measure the elongation of the gauge length of each specimen.

Thermal gravimetric analysis (TGA) was performed using a Perkin Elmer TGA 7 under nitrogen atmosphere at a heating rate of 20 °C/min from 40 to 800 °C.

The fire retardancy of neat epoxy and its composites was investigated by cone calorimetry (FTT Limited, East Grinstead, UK) according to ASTM E1354. The specimens were shaped into 100 × 100 × 4 mm at 23 °C under 50% humidity; a heat flux at 50 kW/m^2 was set for all specimens.

3. Results and discussion

3.1. Kapok microtubules filled and sealed with triphenyl phosphate and cellulose acetate

Cellulosic kapok microtubules used in this study were approximately 100 μm in length, 10.0–20.0 μm in diameter and 0.5–1.0 μm in wall thickness [27]; the hollowness was thus calculated to be 81–95%. The microtubules were cut to ~100 μm in length. We found that the microtubules absorbed well acetone-based solution likely due to their hydrophilic nature as well as the capillary effect.

The ratio of the mixture was determined by trial and error. Assuming all of triphenyl phosphate (TPP) being able to fill into the tubules and occupy all the inside space, Eq. (1) was used to calculate the volumetric ratio of TPP to the wall of kapok fibers excluding the hollow cavity,

$$\frac{V_a}{V_b} = \frac{m_a * \rho_b}{m_b * \rho_a} \tag{1}$$

where m_a and m_b refer to the mass of kapok microtubules (1 g) and TPP (4 g), ρ_a and ρ_b indicate the density of kapok fiber wall (1.31 g/m^3) [27] and TPP (1.27 g/m^3). Thus, the ratio of V_{TPP} to $V_{kapok\ wall}$ was ~4:1.

Table 1
The composition of composites prepared.

Specimen	Weight fraction of epoxy	Weight fraction of Kapok tubules	Weight fraction of TPP	Weight fraction of CA
Epoxy	100.00%	Nil	Nil	Nil
Epoxy/tubules, 1.5%	98.50%	1.50%	Nil	Nil
Epoxy/TPP, 6.0%	94.00%	Nil	6.00%	Nil
Epoxy/TPP tubules, 7.5%	92.50%	1.50%	6.00%	Nil
Epoxy/TPP-CA tubules, 7.5%	92.50%	1.50%	5.82%	0.18%
Epoxy/TPP-CA tubules, 10.0%	90.00%	2.00%	7.76%	0.24%

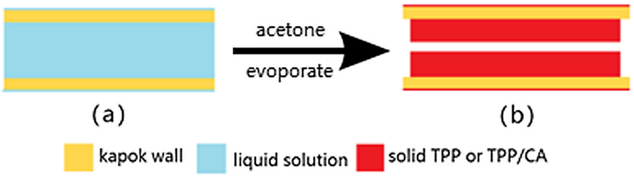

Fig. 2. Schematic of (a) a kapok tubule absorbing acetone solution where triphenyl phosphate (TPP) and cellulose acetate (CA) were dissolved and (b) a tubule where TPP and CA precipitated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Our experiment revealed that during the filling process described in Section 2.2, the tubules would ideally absorb 10 mL of a mixture which contained 3.88 g of TPP and 0.12 g of cellulose acetate (CA) dissolved in acetone. Through evaporation of acetone, TPP and CA should precipitate onto both the inner and outer wall of the tubules, as schematically illustrated in Fig. 2. The middle white zone represents a void left by the evaporation of acetone and the solidification of TPP and CA. Excluding acetone, the total mass of the system was reduced by 4% (0.2 g) through this process (Table 2); the loss was mainly caused by the residues left on the container wall during the milling process.

As the hollowness of kapok microtubules ranges 81–95%, the average hollowness is taken as 88%, implying that 88% volume of kapok is empty. Thus, the ratio of $V_{kapok\ wall}$ to $V_{kapok\ cavity}$ is 144 vol% of kapok. By closely examining SEM micrographs in Fig. 3b and c, it was found that the TPP formed on the outer wall of the tubules was low and can be ignored. From Eq. (1), V_{TPP} to $V_{kapok\ wall}$ was calculated as approximately 4:1. Taking into account the ratio of $V_{kapok\ wall}$ to $V_{kapok\ cavity}$ being 0.14, the encapsulation ratio of V_{TPP} to $V_{kapok\ cavity}$ was calculated to be 56%.

The TPP-filled kapok tubules were verified by SEM. Fig. 3 compares kapok tubules, TPP tubules and TPP-CA tubules. In Fig. 3a, some flattened tubules are seen, as indicated by a red arrow; this may be caused by the vacuum applied during SEM observation because these tubules were empty. As long as the tubules are filled with TPP to produce TPP tubules, no flat tubules could be seen in Fig. 3b where some filled content is marked by a red circle. A similar phenomenon is observed for tubules filled with TPP-CA. The SEM observation provides solid evidence that TPP and TPP-CA can be filled into the tubules.

The tensile-fractured surfaces of neat epoxy and its composites were observed by SEM. In Fig. 4a, neat epoxy shows a flat, featureless surface. The epoxy/TPP composite in Fig. 4b has a relatively rough surface with somewhat sea-island structure as pointed out by a red circle. Flame-retardant TPP has a melting point of 48.5 °C and before reaching the curing temperature of 100 °C, it would melt completely and may flow out of the tubules; once the crosslinking of epoxy occurred, TPP would form sea-island structure inside the matrix epoxy as a result of phase separation due to its low molecular weight and volume fraction.

No structural damage is seen for the tubules in the epoxy/tubule composite as shown in Fig. 4c, which implies that the compounding and curing processes caused no damage to kapok tubules. The sea-island structure observed for the epoxy/TPP tubule composite (Fig. 4d) is similar to what is found for the epoxy/TPP composite (Fig. 4b); this means that TPP was filled into the tubules prior to curing, but it flowed out during curing owing to its low melting point, hence creating the sea-island structure. These results indicate the necessity of sealing TPP inside the tubules.

No sea-island structure can be seen for the epoxy/TPP-CA tubule composite at 7.5 wt% in Fig. 4e, and a similar phenomenon is seen for the 10.0 wt% composite in Fig. 4f. This result demonstrates that TPP-CA can be firmly sealed inside the tubules to create the encapsulated tubules. Therefore, the following sealing mechanism is proposed.

3.2. TPP-CA encapsulation mechanism

With increase in temperature, TPP changes from solid to liquid state at ~50 °C, whilst CA remains solid up to 120 °C. To identify the potential encapsulation mechanism of TPP-CA microtubules, we designed, prepared and observed the following samples:

1. A mixture of TPP and CA at mass ratio of 1:1 was found to be solid below 120 °C.
2. With increase in temperature, a mixture of TPP and CA at 97:3 changed from solid to semi-solid state at ~48.5 °C, and the semi-solid state remained constant even with further increase in temperature. When a filled tubule was cut open, the internal structure was found to resemble gel.

TPP is an organic compound [$(C_6H_5O)_3PO$] with a molecular weight of 326 g/mol, while CA is a polymer of high molecular weight over 10,000 g/mol. Their respective molecular formulae are shown in Fig. 1. In this study, both were dissolved and mixed in acetone, creating a clear solution. During the evaporation of acetone, phase separation should occur, and as a result, low-molecular-weight TPP should form a dispersion phase, while CA would form a continuous phase due to its high molecular weight and excellent capability to form films or membranes [28,29]. With increase in temperature, TPP-CA would behave like a gel – TPP should melt but not flow around as it is wrapped by the CA film.

Fig. 5 contains the XPS spectra of TPP, CA and their two mixtures respectively at 1:1 and 97:3 mass ratios; the concentrations of carbon

Table 2
Ingredients and total mass of kapok tubules, TPP tubules and TPP-CA tubules.

Names	Kapok (g)	Acetone (ml)	Triphenyl phosphate (g)	Cellulose acetate (g)	Total mass before process (g)	Total mass after process (g)
Kapok tubules	1.00	Nil	Nil	Nil	1.00	1.00
TPP tubules[a]	1.00	10.00	4.00	Nil	5.00	4.80
TPP-CA tubules[a]	1.00	10.00	3.88	0.12	5.00	4.80

[a] See the naming in Section 2.2.

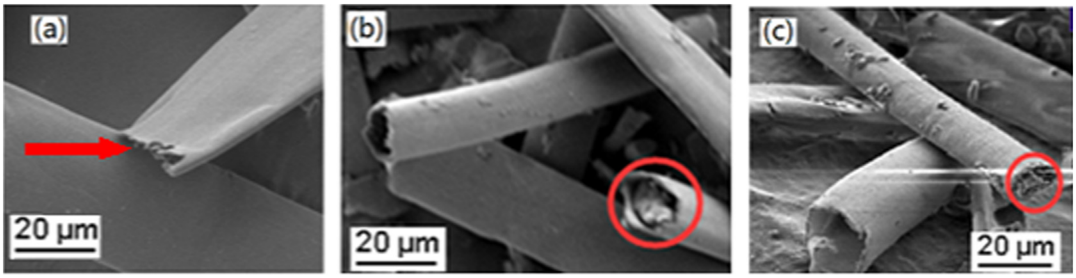

Fig. 3. SEM micrographs of (a) as-received tubules, (b) TPP tubules and (c) TPP-CA tubules. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(C), oxygen (O), and phosphorus (P) elements of these mixtures are presented in Table 3. XPS measured the equivalent surface P concentration by scanning the sample surface. The measurement shows that P takes 5.19 wt% for neat TPP and 2.60 wt% for the TPP/CA mixture at the mass ratio of 1:1; this means that TPP and CA are uniformly dispersed within each other on the surface at such a mass ratio. A TPP/CA mixture at a mass ratio of 97:3 should have 5.03 wt% of P by calculation using the XPS data, if TPP and CA are uniformly dispersed within each other. However, the surface P concentration was measured as 4.23 wt%, which by calculation relates to mass ratio of TPP/CA = 82:18 which is a lot lower than the actual 97:3. The difference indicates that TPP and CA cannot be uniformly dispersed within each other on the surface. As the surface P concentration is lower than the bulk material, CA must be richer in surface and it should have formed a chemically stable layer to seal TPP.

This result confirms that CA at a low concentration would encapsulate TPP inside the tubules preventing TPP from flowing out during curing. This makes a contrasting difference on the mixture morphology. Without encapsulation, TPP flowed out of the tubules, forming a sea-island structure as shown in Fig. 4d for the epoxy/tubule composite; upon encapsulation, such a structure disappears on the fracture surface of epoxy/TPP-CA tubule composite as shown in Fig. 4f.

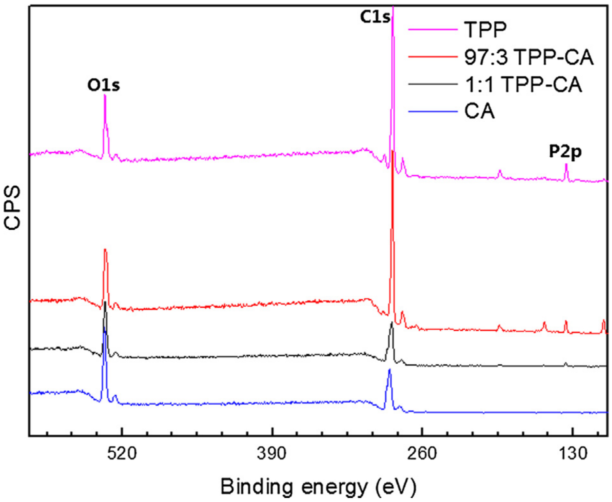

Fig. 5. Binding energy for triphenyl phosphate (TPP), cellulose acetate (CA) and their two mixtures from XPS analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

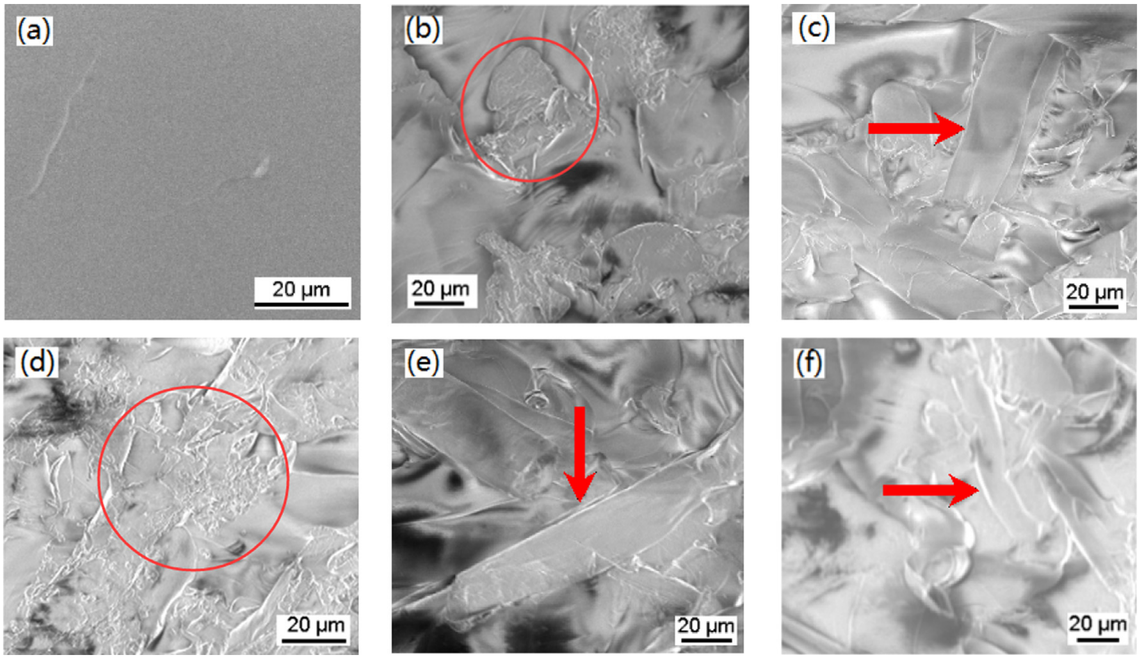

Fig. 4. SEM micrographs of fractured surface of (a) epoxy, (b) epoxy/TPP at 6 wt%, (c) epoxy/tubules 1.5 wt%, (d) epoxy/TPP tubules 7.5 wt%, (e) epoxy/TPP-CA tubules 7.5 wt%, and (f) epoxy/TPP-CA tubules 10.0 wt%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Concentrations of carbon (C), phosphorus (P) and oxygen (O) elements for triphenyl phosphate (TPP), cellulose acetate (CA) and their mixtures.

Specimen	Designed TPP:CA ratio	C concentration (%)	P concentration (%)	O concentration (%)	Measured TPP:CA ratio on surface
Neat TPP	N/A	80.38	5.19	14.43	N/A
Neat CA	N/A	65.18	N/A	34.82	N/A
TPP-CA	1:1	70.46	2.60	26.94	1:1
TPP-CA	97:3	78.31	4.23	17.46	82:18

[a] See the naming in Section 2.2.

Table 4
Mechanical properties of epoxy and its composites (see naming in Section 2.2).

The specimen, weight fraction	Young's modulus (GPa)	Tensile strength (MPa)	Tensile strain (%)
Epoxy	0.95 ± 0.03	37.5 ± 1.2	4.80 ± 0.35
Epoxy/tubules, 1.5%	1.00 ± 0.01	38.4 ± 1.4	4.98 ± 0.18
Epoxy/TPP, 6%	0.73 ± 0.04	29.5 ± 2.2	5.05 ± 1.20
Epoxy/TPP tubules, 7.5%	0.57 ± 0.04	23.2 ± 1.0	5.43 ± 0.54
Epoxy/TPP-CA tubules, 7.5%	0.81 ± 0.04	34.6 ± 2.8	5.00 ± 0.18
Epoxy/TPP-CA tubules, 10.0%	0.89 ± 0.04	32.4 ± 0.5	5.37 ± 1.07

3.3. Mechanical performance of epoxy and its composites

The mechanical properties of neat epoxy and its various composites are listed in Table 4. Neat epoxy has Young's modulus of 0.95 ± 0.03 GPa and tensile strength of 37.5 ± 1.2 MPa, both of which are not as high as those reported [26,30], because the epoxy used in this study was cured by a hardener consisting of flexible long-chain molecules. Adding 1.5 wt% kapok microtubules poses no observable effect on the modulus and tensile strength of epoxy, likely because of the low tubule content. After adding TPP into epoxy, the modulus and strength are reduced respectively to 0.73 ± 0.04 GPa and 29.5 ± 2.2 MPa; this is caused by the low molecular weight of TPP as discussed in the encapsulation mechanism. TPP is well known as a plasticizer [18]. For the epoxy/TPP tubule composite containing 6 wt% TPP and 1.5 wt% tubules, both modulus and strength were further reduced. The reason for the reduction can be explained by the processing and morphology of the composite. TPP that was filled into the tubules beforehand would flow out into the matrix during the curing process to form an island-sea structure (Fig. 3d). Then, TPP stays adjacent to the tubules rather than stays inside, acting as a plasticizer, which reduces the mechanical properties. The moduli of epoxy/TPP-CA tubule composites at 7.5 wt% and 10.0 wt% are 0.81 ± 0.04 and 0.89 ± 0.04 GPa, respectively. Both are close to but still lower than that of neat epoxy 0.95 ± 0.03 GPa. The slight difference is because TPP as a low molecular weight material has a lot lower modulus than epoxy and the tubules. TPP is filled into the tubules and sealed inside, and this would result in the lower moduli.

To prevent TPP from flowing out of the tubules in the curing process, CA was mixed with TPP for sealing; this strategy proved successful in the previous discussion. For the epoxy/TPP-CA tubule composite containing 6.0 wt% TPP-CA and 1.5 wt% tubules, the modulus reaches 0.81 ± 0.04 GPa and tensile strength 34.6 ± 2.8 MPa, both of which are far higher than those of epoxy/TPP tubule composite; this result confirms the positive effect of sealing flame-retarding chemicals inside the tubules on the mechanical performance of the resulting composites. At 10.0 wt%, the composite modulus increases further. The fracture strain does not change notably for these samples.

Composites with higher TPP-CA tubule fraction were also prepared for characterization, but no success in obtaining usable data due to the processing difficulty.

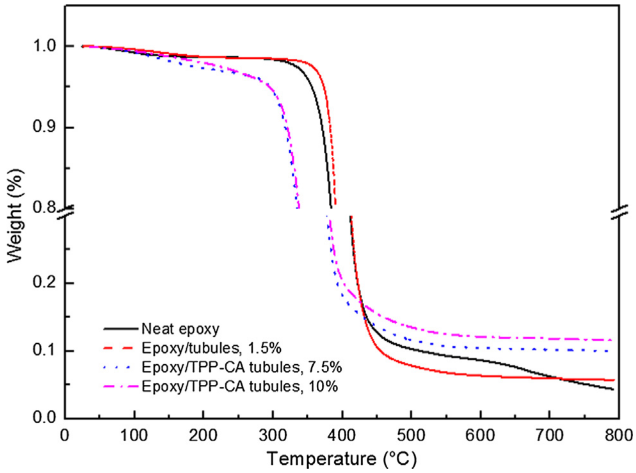

Fig. 6. Thermal gravimetric graphs of epoxy and its composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Thermogravimetric analysis

Thermal gravimetric analysis was undertaken to analyze the thermal properties of neat epoxy and its composites. All samples were heated from room temperature to 700 °C at 20 °C/min under nitrogen atmosphere, where degradation occurred with no combustion.

In Fig. 6 and Table 5, epoxy shows an onset temperature of 350 °C and a significant weight loss is nearly completed at 450 °C. T_{onset} refers to a temperature at which the sample weight starts to drop, T_{major} indicates a temperature at which the sample loses its majority of weight, and T_{finish} is a temperature at which the sample weight loss is completed. The addition of 1.5 wt% tubules does not apparently change the thermal behavior of epoxy, possibly due to the low fraction. For all epoxy/TPP-CA tubule composites, the onset temperature is reduced to 190 °C, where TPP starts pyrolyzing to initiate a chain reaction producing phosphoric acid [15]. The acid should first dehydrate the tubules and CA, and when the tubule wall breaks, it would dehydrate the epoxy resin. At T_{major}, neat epoxy shows a minor weight loss, and the actual weight loss of the epoxy/TPP-CA tubule composites is higher

Table 5
Thermal properties of epoxy and its composites (see sample naming in Section 2.2).

Specimen, weight fraction	T_{onset} (°C)	T_{major} (°C)	T_{finish} (°C)	Residue remaining (%)
Epoxy	325	350	425	4.35
Epoxy/tubules, 1.5%	325	350	425	5.73
Epoxy/TPP-CA tubules, 7.5%	185	300	400	9.98
Epoxy/TPP-CA tubules, 10.0%	185	300	400	11.58

T_{onset} = the temperature at which weight starts to drop; T_{major} = the temperature at which a major drop starts; T_{finish} = the temperature at which mass drop is over.

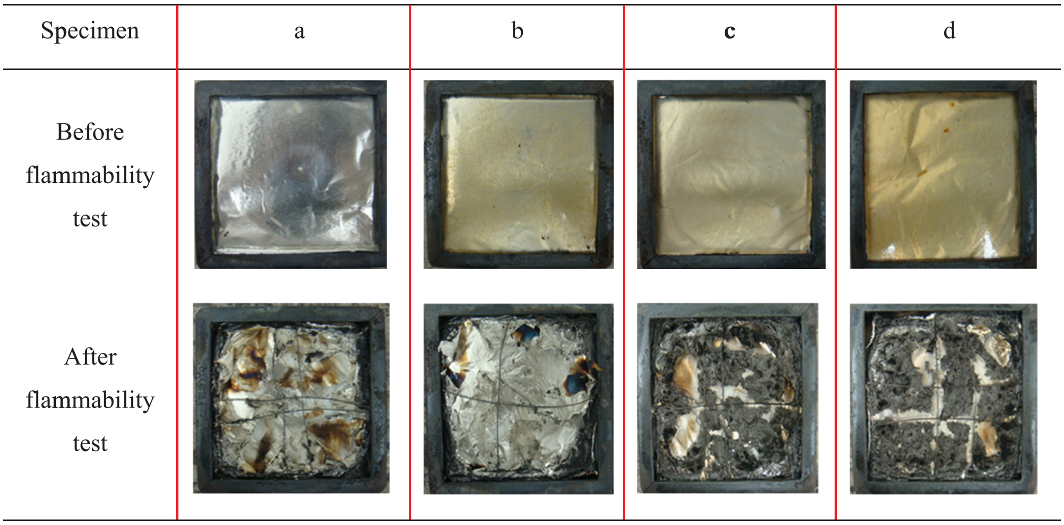

Fig. 7. Optical images of (a) epoxy, (b) epoxy/tubules at 1.5 wt%, (c) epoxy/TPP-CA tubules at 7.5 wt% and (d) epoxy/TPP-CA tubules at 10.0 wt%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

than the exact fractions of TPP; this means that TPP-CA tubules pose a remarkable effect on the thermal degradation of epoxy. T_{major} for epoxy/TPP-CA tubules occurs at 300 °C, being 50 °C lower than that of neat epoxy; this is because of the condensed phase char formation process at the temperature, as to be discussed later. T_{finish} reduces further with increase in the TPP-CA tubule fraction because of more acid accelerating the char-forming process. The addition of 1.5 wt% tubules causes an increase in residue remaining, indicating that tubules have positive effect in char formation. Epoxy/TPP-CA tubules demonstrate more char than the epoxy/tubule composite, and the more TPP-CA tubules, the higher char yield.

3.5. Flame retardancy of epoxy and its composites

It is well-known that phosphoric-based flame retardants such as triphenyl phosphate (TPP) work mainly during the condensed phase, promoting char formation for polymers [14,15,31]. The specimens before and after cone calorimeter test are presented in Fig. 7. Both neat epoxy and epoxy/tubule composites have no char formed. Obvious char is seen for epoxy/TPP-CA tubule composites; the quantity of char increases with the fraction of TPP-CA tubules.

Fig. 8 contains heat release rate (HRR), total heat release (THR), oxygen consumption rate (OCR) and total oxygen consumed (TOC), with their critical values reported in Table 6. Adding 1.5 wt% kapok microtubules has an adverse effect on the heat released and oxygen consumed, probably because the microtubules consisting of carbon and hydrogen should support the composite combustion and yield more heat. However, the addition of 7.5 wt% TPP-CA tubules into the composite reduces both the heat released and oxygen consumed in comparison with the composite having 1.5 wt% kapok microtubules, owing to the flame retardation of the encapsulated TPP which can inhibit the combustion by forming char in the condensed-phase [14,15]. The flame retarding effect of TPP-CA tubules is confirmed by further reduction of the heat released and oxygen consumed for the composite at 10.0 wt%. In comparison with neat epoxy, epoxy/TPP-CA tubule composites have demonstrated the following characteristics:

- increments in peak heat release rate (HRR_{peak}) and heat release rate within 60 s (HRR_{60})
- reduction in time of peak heat release (T_{peak}), total heat release (THR) and heat release rate within 180 s (HRR_{180})

These characteristics are anticipated for all phosphorous-based flame retardants. The retardants under fire transform into phosphoric acid as a key decomposition product, which reacts with polymeric matrices to form char on the burning surface. The char layer can reduce the amount of oxygen and heat transferred to fuel, suppressing the combustion. In addition, the char layer is formed from the fuel, which reduces the total amount of fuel that enrolled in combustion [15]. In this study, TPP decomposed to form phosphoric acid which then reacted with epoxy to form char. The char formation sped up the decomposition process of the composite as shown in Section 3.4, accelerating the combustion process and resulting in the increase of peak heat release and the earlier time of peak heat release. Neat epoxy was burned completely leaving no residue. When epoxy/TPP-CA tubule composites were under fire, TPP formed phosphoric acid which then reacted with epoxy to create char, reducing the quantity of epoxy for combustion.

Another critical factor of flame retardancy is the smoke released; dense smoke causes suffocation in a closed environment. Thus, reduction in the smoke released contributes to life-saving. During combustion, TPP helps inhibit the smoke released by forming a barrier of char layer on the burning surface; the char layer would separate the polymer from air and trap the smoke. Fig. 8e and f shows the smoke release rate (SRR) and the total smoke release (TSR) for epoxy and its composites. Adding 1.5 wt% microtubules shows adverse effects on both the smoke release rate and total smoke release in comparison with neat epoxy, because the tubules are rich in carbon – 50.7 wt% as calculated from their chemical formula $(C_6H_{10}O_5)_n$ – that may lead to insufficient combustion to generate more carbon-based smoke once ignited.

By adding 7.5 wt% TPP-CA tubules into the epoxy, the total smoke release decreases obviously. The char barrier layer efficiently traps some of the smoke to be emitted into the air [15]. With TPP-CA tubules increasing to 10.0 wt%, more char layer would form as shown in Fig. 7, and it would more efficiently separate the polymer from air and trap the smoke, causing further reduction in both smoke release rate and total smoke release. These results indicate that TPP-CA tubules are effective in smoke suppression.

4. Conclusion

Triphenyl phosphate (TPP) and cellulose acetate (CA) were filled into kapok microtubules to create encapsulated flame-retarding tubules that were used to develop mechanically resilient, flame-retarding polymer composites. The SEM and tensile testing results showed that this encapsulation method addressed a serious limitation – the

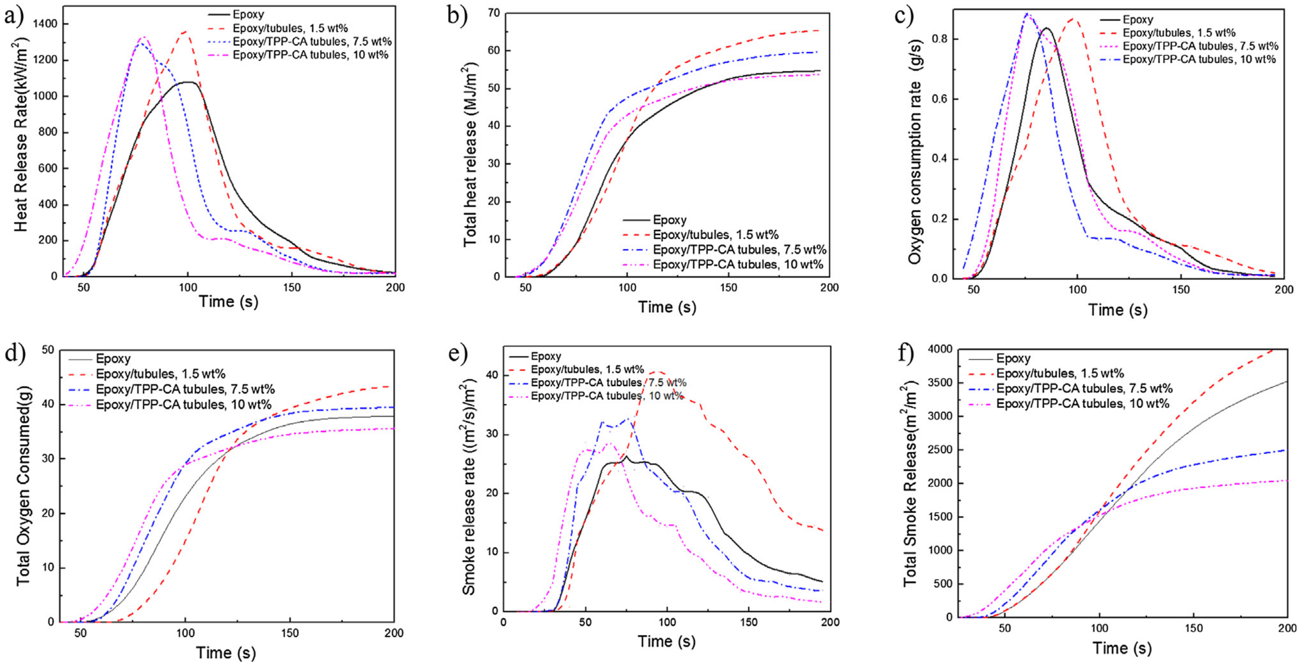

Fig. 8. Flame-retardant properties for neat epoxy and its various tubule composites: (a) heat release rate, (b) total heat release, (c) oxygen consumed rate, (d) total oxygen consumed, (e) smoke release rate and (f) total smoke release. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 6
Key data from the cone test (see the naming in Section 2.2).

Specimen, weight fraction	HRR_{peak} (kW/m^2)	T_{peak} (s)	THR (MJ/m^2)	HRR_{60} (kW/m^2)	HRR_{180} (kW/m^2)
Epoxy	1084.90	105	56.51	548.44	356.93
Epoxy/tubules, 1.5%	1408.81	100	67.46	743.76	342.21
Epoxy/TPP-CA tubules, 7.5%	1313.57	75	62.87	723.74	333.88
Epoxy/TPP-CA tubules, 10.0%	1363.98	80	56.60	550.73	300.27

plasticization effect of TPP; the composites showed minimum reduction of stiffness and strength. Thermogravimetric analysis and cone calorimetry analysis revealed that the encapsulated tubules reduced the smoke released, because these filled tubules helped to form a layer of protection char on the burning surface. This TPP-CA encapsulation technique may be applied to produce functional microtubules for many other applications.

Acknowledgement

The authors appreciate the financial support by the Australian Research Council (LP140100605).

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