Loading the polyol carbonization agent into clay nanotubes for the preparation of environmentally stable UV-cured epoxy materials

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ABSTRACT: The halloysite nanotubes (HNTs) were loaded with pentaerythritol (PER). The as-prepared composite (HNT-P) and ammonium polyphosphate (APP) was subsequently added to the UV-curable epoxy resins, giving a new flame-resistant system. Loading of the hydrophilic PER into HNT can reduce the moisture absorption in the UV-curable epoxy resins. The flame retardancy was evaluated by means of the cone calorimeter and limit oxygen index test. The results showed that the flame retardancy of the modified epoxy resin was greatly improved with an obvious decrease in both the heat release and smoke release. Moreover, it was revealed that HNT could catalyze the reaction of APP and PER, and the burning surface of the epoxy resin should be covered by the polyphosphoric-HNT intumescent char layer. We have measured the moisture sorption and dynamic mechanical properties of the UV-cured epoxy resins. As compared to the use of the simple mixture of PER and HNT, the use of the HNT-P nearly kept the storage modulus at about 1809 Mpa and reduced the moisture absorption by 58.2 wt % at 40 °C. The results proved that the addition of the HNT-P obtained lower moisture absorption and higher stability of the mechanical properties than adding the simple mixture.


KEYWORDS: clay; degradation; flame retardance; fullerenes; graphene; nanotubes

INTRODUCTION

Intumescent flame retardants, one kind of halogen-free flame retardants have been extensively used for enhancing the flame retardancy of polymers due to high efficiency and low toxicity. In general, the intumescent flame retardants contain the ternary components, called acid source, carbonization source and gas source. Catalyzed by the acid agent and gas source during combustion, the carbonization agent can give the intumescent carbonaceous layer which covers on the surface of the materials. The layer can keep the underlying materials from the flame, oxygen and heat. As the efficient intumescent flame retardant formulations, ammonium polyphosphate (APP) and polyol-type carbonization agents have been usually used for manufacturing the flame retardant plastic parts. In the process of the polymer combustion, the pair of APP and polyol can show a series of esterification reactions which generate the phosphoric acid-polyol intermediates, followed by a formation of the stable carbonaceous layer through cracking and crosslinking reactions. However, the polyol-type carbonization agents such as pentaerythritol (PER) are capable of absorbing moisture due to the presence of the hydrophilic hydroxyl groups and as a result, the plastic parts usually incline to soften with a gradual decay in their durability. At present, there are few works intended to deal with the issue of the moisture absorption when the polyols are employed as the carbonization agents in the intumescent flame retardant plastics.

It has been reported that the halloysite clay is capable of improving the flame retardancy of the polymers. Halloysite nanotubes are a type of the naturally occurred clays made by rolling of aluminosilicate sheets. This kind of nano-clay is available in large amount at a low price. With the unique hollow nanotube structure, halloysite nanotubes (HNTs) have been used as nanocarriers to fabricate the controlled release systems by loading with various chemical reagents such as the antimicrobial agents, inhibitors, metal and antibiotics. For example, the antioxidant has been loaded into halloysite clay for improving the anti-aging properties of rubber. The HNT recently have been used as a kind of inorganic flame retardant in polymers which include polypropylene, acrylonitrile butadiene styrene, soy protein, polyamide, and epoxy resin. It is
of industrial importance that the HNT can be better dispersed in polar polymers without an exfoliating treatment, as compared to other nano-clays like montmorillonite and bentonite. Moreover, the one-dimensional HNT are regarded to construct networks during combustion, which should favor the flame retardancy.

UV-curable epoxy materials have been applied in various fields such as coating, electronic industry and the developing three-dimensional printing technology. However, the high flammability is one of the serious problems for UV-curable epoxy resin to be dissolved. For example, the 3,4-epoxycyclohexylmethyl, which is used as the typical UV-curable monomer, has the limiting oxygen index less than 18. Moreover, during combustion, the photo-initiators which remain in the UV-cured materials can give radicals which accelerate the combustion. There have been some articles addressing the intumescent flame retardant in the epoxy resin. In the process of epoxy combustion, the use of the intumescent flame retardant decreases the heat release rate and also raises the residue mass. However, it should be emphasized that by absorbing moisture, the polyol, which is the typical carbonization agent, always unavoidably affect the mechanical properties and thermostability of the epoxy materials. It is important to enhance the moisture resistance of polyl carbonization agents.

In this study, we prepare an efficient flame-resistant composite consists of the PER-loaded HNT and ammonium phosphate for the UV-curable epoxy resins. The new structure of PER loaded in the hollow nanotubes can alleviate the problem that the polyol-type carbonization agents are sensitive to moisture sensitivity. The new structures of PER loaded in nanotubes protect the epoxide composites from the typical moisture and water sorption of the polyol-type carbonization agents. The structures of the modified nanotubes are analyzed by transmission electron microscopy (TEM) and the Brunauer-Emmett-Teller (BET) test. The properties of epoxide composites are analyzed by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The flammability of the EP composites is measured by using the cone calorimetry (CC) and limit oxygen index (LOI).

**EXPERIMENTAL**

**Materials**

Halloysite nanotubes were supplied by Dongming Tianhe Inc. (Shandong, China); Pentayrithritol was obtained from Sinopharm Chemical Reagent Co., Ltd; Ammonium polyphosphate was purchased from Xingxing flameretard Co., Ltd. (Jiangsu, China); UV-curable epoxy resin was supplied by Royal DSM Inc and used as received. Other reagents and materials were purchased from Sinopharm Chemical Reagent Co., Ltd.

**The Preparation of PER-Loaded HNT**

The modified halloysite tubes (HNT-P) were prepared by using vacuum suction. 0.5 g of pure HNT and 1.2 g of PER were added to 20 mL of water and mixed thoroughly by sonication for 30 min. Then, the water suspension was transferred to a vacuum flask for 1 h. With bubbles out of the suspension and muffled hiss of the flask, the PER solution replaced the air in the lumens of HNT. This process was repeated for five times. After vacuum cycle, the mixture was kept stirring for 3 days to increase the loading efficiency. Then the sample was separated by centrifugation and washed by distilled water for only one time. This process can decrease the amount of the unloaded PER. Finally, the sample was placed in a vacuum oven at 45 °C to dry until recovering powder.

**The Preparation of the EP/HNT-P Composites**

EP/HNT-P was prepared as the following steps: the APP and HNT-P were added into UV-curable epoxy resin (EP) in different ratios. The homogenous mixtures were prepared by stirring continuously. Then the mixtures were exposed to the UV apparatus for 3 h and had postcure process at 45 °C for 6 h. To compare the moisture resistance for the composites with HNT-P and composites in which HNT and PER was added directly, we prepared the EP/HNT/PER composites by adding PER and HNT, respectively.

**Characterization**

The morphology and structure of the sample were observed by transmission electron microscopy (TEM, Tecnai G2 20 TWIN). All samples were prepared by dropping onto carbon-coated copper grid.

TGA measurements were recorded on a TGA 1 (Mettler Toledo, Switzerland) thermogravimeter. The sample was heated from 50°C to 800°C at a heating rate of 20°C/min. The quantitative analysis of PER in HNT-P was measured under nitrogen condition. The content of PER in HNT-P is calculated according to eq. (1):

$$E = \frac{W_{H} - W_{H-P}}{W_{H}} \times 100\%$$

where the \( W_{H} \) is the weight of HNT at 800°C, the \( W_{H-P} \) represents the weight of HNT-P at 800°C and \( E \) represents the content of PER in HNT-P. The tests of flame mechanism were measured under air condition.

The specific surface area and total pore volume of samples were measured via the Brunauer-Emmett-Teller (BET) method. The pore size distribution of nanotubes was performed by the Barrett-Joyner-Halenda (BJH) method.

The flammability of the sample was recorded via a cone calorimeter (Fire Testing Technology, UK). The testing samples have the size dimensions of 100 mm × 100 mm × 3 mm. All the samples were tested at a heat flux of 35 kW/m².

The LOI of samples was measured by a XYC-75 oxygen index instrument (Hebei, China). All samples were tested with the dimension of 120 mm × 6.5 mm × 3.2 mm.

The microstructures of residue surface were analyzed by scanning electron microscope (SEM, Ultra 55). The samples were sputtered with a thin gold layer before test. The accelerating voltage of measurements was 10 kV. The element distribution of the residues surfaces was tested by an energy-dispersive X-ray analysis (EDX). The tests were measured with the accelerating voltage of 10 kV.

The dynamic mechanical properties of samples were performed on a DMA/SDTA 861e (Mettler-Toledo, Switzerland). All
samples were measured at a heating rate of 2 °C/min. The constant frequency of this test was 1 Hz.

The moisture sorption measurements of the samples were measured via an environmental chamber. The samples (20 mm × 20 mm × 0.9 mm) were tested under humidity of 85% RH and at temperatures of 45 and 85 °C, respectively. In the water sorption test, all samples were immersed in the 85 °C water.

RESULTS AND DISCUSSION

Pentaerythritol Loading in the Halloysite Nanotubes
As illustrated in Scheme 1, the modified HNT were prepared by using vacuum suction. This process helped to completely remove the air from halloysite lumen. Figure 1 shows the BET curves of the empty HNT and PER-loaded halloysite tubes (HNT-P), respectively. The data are collected in Table I. It is observed that the isotherm of the pure HNT is of type IV with H3 hysteresis loops, which is a characteristic of mesoporous structure.32 Compared to the HNT with a specific surface area of 36.40 m² g⁻¹, the HNT-P has a lower specific surface area of 19.64 m² g⁻¹. The total pore volume of HNT-P is decreased from 0.25 to 0.067 cm³ g⁻¹, agreeing with the tendency of the specific surface area. Moreover, the pore size distributions of both pure HNT and HNT-P are shown in the inset of Figure 1. The HNT-P having weaker intensity of pore sizes than the pure HNT confirms that the load of PER has blocked the pore channel in HNT. These results show that the PER has been loaded in halloysite nanotubes.

Figure 2 shows the TEM images of HNT and HNT-P. It is estimated that the HNT have a length in the range from 300 to 1000 nm, and the inner diameter in the range from 15 to 25 nm, outside diameter from 50 to 70 nm. Moreover, compared to the HNT, the central channel of HNT-P becomes less lucid. This phenomenon confirms that the PER has been loaded in the halloysite tubes.

Table I. The Pore Characteristics of HNT and HNT-P

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNT</td>
<td>36.40</td>
<td>0.25</td>
</tr>
<tr>
<td>HNT-P</td>
<td>19.64</td>
<td>0.067</td>
</tr>
</tbody>
</table>

Figure 1. Nitrogen gas adsorption–desorption isotherms and pore size distributions of HNT and HNT-P, respectively. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 2. The TEM images of (A,C) empty halloysite nanotubes and (B,D) PER-loaded halloysite nanotubes.

Figure 3. The TGA curves of HNT, HNT-P, and PER. [Color figure can be viewed at wileyonlinelibrary.com]
The TGA curves of HNT, PER, and HNT-P are shown in Figure 3, with the analysis results of TGA shown in Table II. The content of PER in HNT-P is calculated according to eq. (1). Calculated from the data in Table II, the loading content of PER is 41.7 wt %. This result shows that the PER was not only loaded in the tube lumen but also absorbed in the external cavities or on the surface of halloysite clay.

### The Flame Retardancy of EP Composites

The compositions of the EP and its composites are shown in Table III. To evaluate the flame retardant effect of the APP/HNT-P system, we have measured the LOI of the EP and its composites, respectively. The LOI values of all the samples are shown in Table III. The LOI value of EP is only 18, which confirms the combustibility owned by the pure epoxy resin. For UV-curable epoxy resin containing APP/HNT-P (EP/HNT-P), the LOI value increases obviously as more APP/HNT-P is added. When 35 wt % of APP/HNT-P is added, the LOI value of EP/HNT-P reaches to 28.2. Conclusively, the use of APP/HNT-P has increased the LOI values of EP composites. Moreover, the LOI results were also presented in Table III by measuring the EP with only HNT-P and unmodified HNT, respectively. The results show that there is the synergistic effect in the binary flame retardant.

We have measured the CC data of the EP and EP/HNT-P with the aim of evaluating the flame retardant effect of APP/HNT-P system. In the CC experiment, we chose the EP2, which contained 25 wt % of APP/PER, to represent the EP/HNT-P composites. The CC data of EP and EP/HNT-P are shown in Figures 4 and 5 and Table IV. The time to ignition (TTI) of the EP is only 24 s. When 25 wt % of APP/HNT-P is added, the TTI of EP/HNT-P prolongs to 33 s. Moreover, as compared to

<table>
<thead>
<tr>
<th>Samples</th>
<th>EP (%)</th>
<th>HNT (%)</th>
<th>HNT-P (%)</th>
<th>APP (%)</th>
<th>LOI (%)</th>
</tr>
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<tbody>
<tr>
<td>EP</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>18.0</td>
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<tr>
<td>EP1</td>
<td>85</td>
<td>0</td>
<td>6</td>
<td>9</td>
<td>22.2</td>
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<tr>
<td>EP2</td>
<td>75</td>
<td>0</td>
<td>10</td>
<td>15</td>
<td>24.8</td>
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<tr>
<td>EP3</td>
<td>65</td>
<td>0</td>
<td>14</td>
<td>21</td>
<td>28.2</td>
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<tr>
<td>EP4</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>19.2</td>
</tr>
<tr>
<td>EP5</td>
<td>80</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>20.4</td>
</tr>
<tr>
<td>EP6</td>
<td>90</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>20.8</td>
</tr>
</tbody>
</table>

The TGA curves of HNT, PER, and HNT-P are shown in Figure 3, with the analysis results of TGA shown in Table II. The content of PER in HNT-P is calculated according to eq. (1). Calculated from the data in Table II, the loading content of PER is 41.7 wt %. This result shows that the PER was not only loaded in the tube lumen but also absorbed in the external cavities or on the surface of halloysite clay.

### Table II. The TGA Data of PER, HNT, and HNT-P

<table>
<thead>
<tr>
<th>Samples</th>
<th>800°C Residue (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNT</td>
<td>81.1</td>
</tr>
<tr>
<td>PER</td>
<td>0.3</td>
</tr>
<tr>
<td>HNT-P</td>
<td>47.3</td>
</tr>
</tbody>
</table>

### Table III. The Formulations of Flame-Retardant Composites

![Figure 4. The (a) heat release rate and (b) total heat release curves of EP and EP/HNT-P. [Color figure can be viewed at wileyonlinelibrary.com]](image)

![Figure 5. The (a) smoke production rate and (b) total smoke release curves of EP and EP/HNT-P. [Color figure can be viewed at wileyonlinelibrary.com]](image)
the neat EP, it is observed that both the peak of heat release (pHRR) and total heat release (THR) of composites are significantly decreased, as shown by the results in Figure 4. After mixing APP/HNT-P, the pHRR and THR of neat EP decrease from 1002.4 kW/m² and 104.1 MJ/m² to 562 kW/m² and 51.8 MJ/m², respectively. Clearly, the APP/HNT-P system can obviously extend the TTI and decrease the heat release during composites combustion.

Table IV. The Cone Calorimeter Data of EP and EP/HNT-P

<table>
<thead>
<tr>
<th></th>
<th>EP</th>
<th>EP/HNT-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTI (s)</td>
<td>24</td>
<td>33</td>
</tr>
<tr>
<td>PHRR (kW/m²)</td>
<td>1002.4</td>
<td>562.0</td>
</tr>
<tr>
<td>THR (MJ/m²)</td>
<td>104.1</td>
<td>51.8</td>
</tr>
<tr>
<td>TSR (m²/m²)</td>
<td>2506.5</td>
<td>1430.1</td>
</tr>
<tr>
<td>AMLR (g/s m²)</td>
<td>8.4</td>
<td>5.0</td>
</tr>
<tr>
<td>Residue mass (wt %)</td>
<td>2.2</td>
<td>35.7</td>
</tr>
</tbody>
</table>

Figure 6. The digital photographs of (A) EP, (B) EP₃, and (C) EP₇ after the combustion. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 7. The SEM images of the combustion residues of EP/HNT-P at magnification of (a) 200×, (c) 4000×, and (d) 80,000×. The image (b) was the EDX image of the residues at magnification of 200×. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 8. (a) TGA and (b) DTG curves of APP/HNT-P. (1): experimental; (2) calculated. [Color figure can be viewed at wileyonlinelibrary.com]
The smoke release data, such as smoke production rate (SPR) and total smoke release (TSR) are the significant parameters of polymer combustion. Figure 5 shows the SPR and TSR curves of neat EP and EP/HNT-P. When 25% of APP/HNT-P is added, both the SPR and TSR curves have an obvious decrease, similar to the tendency of the HRR and THR curves. Compared to the neat EP, with a TSR of 2506.5 m² m⁻², the EP/HNT-P exhibits a much lower TSR (1430.1 m² m⁻²), decreased by 42.9%. These results indicate that the APP/HNT-P system is capable of inhibiting the smoke release of composites during combustion. We have measured the average mass loss rate (AMLR) and residue mass of EP and EP/HNT-P with the aim of analyzing the combustion process of composites. The data of all the samples are shown in Table IV. The large value of AMLR means the rapid mass loss rate. It is clear to see that the AMLR of EP/HNT-P has an obvious decrease. Compared to the AMLR of the neat EP, the AMLR of EP/HNT-P is decreased from 8.4 to 5.0 g/s m², decreased by 40.5%. Moreover, the residue mass left in the samples is 2.2 wt % of EP and 35.7 wt % of EP/HNT-P. Obviously, according to the change in the residue mass and AMLR value, the flammability of EP composites has been reduced by using APP/HNT-P system.

The Structures of Combustion Residues and the Reactions in the Modified Material

Figure 6 shows the digital photographs of the combustion residues from the LOI test. As shown in Figure 6(A), there is nearly no residue left after the combustion of the neat EP. It is found that the combustion of EP/HNT-P gives the highly intumescent char as shown in Figure 6(B). The observation of the highly intumescent char clearly reveals that PER which is loaded in HNT can react with APP, thus releasing the gaseous products to expand the material. The intumescent char layer has been regarded to prevent the underlying materials from flame, heat and oxygen.

The microstructures of the residues from EP/HNT-P combustion are measured and presented in Figure 7. We still chose the residue of EP₂ to represent the residues of EP/HNT-P composites. It is seen that the combustion residues have the continuous char layer with a flat surface, as indicated by SEM image in Figure 7(a). By using the FESEM-EDX technique, we obtain the map of the silicon and aluminum elements, both of which come from the HNT. It is observed that the silicon and aluminum elements, which are represented by the pink and green dots, are uniformly distributed at the top layer of the residual char [Figure 7(b)]. This result implies that the HNT can keep dispersing during the combustion. In the early stage of polymer combustion, the polymer should be melt, and the degraded gas which is formed in bulk exits through the surface of the melt. As a result, the residues usually have a crack char-layer full of large and irregular holes. In EP/HNT-P here, the HNT should have enhanced the melt strength of polymer, thus avoiding the crack at the surface. As indicated by the SEM images at high resolution, the top layer has small holes with the sizes of lower than 1 μm [Figure 7(c,d)]. This layer with considerable compact
The structure should efficiently inhibit the underlying matter from further heating and flame. Moreover, we have observed that the residues from the EP/HNT-P combustion are much solider than that of the pure EP. It is considered that one dimension HNT may have acted as a supporting frame in the matter during combustion.

The inset images are the digital photograph of APP/HNT-P mixture at different temperatures. To probe the reaction between PER and APP components in the modified material, TGA and FTIR analysis has been carried out. Figure 8 shows the TGA and derivative thermogravimetry (DTG) curves obtained from the mixture of APP and HNT-P. Moreover, we have measured TGA curves from the pure HNT and mixture of APP and PER, respectively (Supporting Information Figure S1). From their TGA data, a curve (APP/HNT-P THEO) is calculated out to predict the temperature-dependent weight loss for comparison. In the calculated curve shown in Figure 8(b), the DTG peak at about 220 °C is caused by the esterification reaction of APP and PER, which should release the ammonia gas and water vapour. As for the mixture of APP and HNT-P, the reaction of PER and APP also takes place with the DTG peak being measured at 211 °C. Figure 9 gives the FTIR spectra of APP/HNT-P mixture heated at different temperatures. It is observed that the H-N vibration (at 3250 cm\(^{-1}\)) of APP and C–H vibration (at 1430 cm\(^{-1}\)) of PER commence declining at about 220 °C, both of the peaks nearly completely disappear when the temperature increases to 420 °C. Consequently, PER can release from the loaded HNT and then reacts with APP during heating the material. It is noted that as for the predicted TGA curve, the reaction of APP and PER occurred alone, independent of HNT. In comparison to this curve without HNT influence, the reaction of APP and PER in APP/HNT-P mixture brings about stronger DTG peak, and it causes larger mass loss in the same temperature range. Meanwhile, the DTG peak of this reaction shifts to lower temperature obviously due to HNT [Figure 8(b)]. These results indicate that HNT can catalyze the reaction of APP and PER. In the case without HNT influence, the char formation of APP and PER occurs with the peak temperature at 614 °C. When HNT is used, the rate of decomposition is slow in the identical temperature range. It is most likely that the presence of HNT accelerates the charring reaction at low temperature and as a result, the residues are thermally stabilized. As indicated by the inset photograph in Figure 8(b), the intumescent char keeps almost complete cylindrical shape even at the high temperature of 600 °C. According to the results mentioned above, the possible reactions involved in the combustion process are shown in Scheme 2. The use of HNT potentially provides an efficient approach for further improving the traditional flame retardant containing APP and PER.

The Moisture Resistance of the EP Composites

We have measured the moisture sorption of EP/HNT-P and EP/HNT/PER at 40 °C, respectively. As shown the results in Table V, it is found that the moisture resistance of the composites with HNT-P is much better than the composites containing a simple mixture of HNT and PER was added directly. Figure 10 shows the moisture sorption curves of EP/HNT-P and EP/HNT/PER at 85 °C. The unit of water and moisture sorption content is % by weight.

### Table V. The Gravimetric Measurement Results of EP/HNT-P and EP/HNT/PER

<table>
<thead>
<tr>
<th>Samples</th>
<th>HNT-P (%)</th>
<th>HNT (%)</th>
<th>PER (%)</th>
<th>(M_{\text{max-m}}) at 40 °C</th>
<th>(M_{\text{max-m}}) at 85 °C</th>
<th>(M_{\text{max-w}}) at 85 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP/HNT-P</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0.87</td>
<td>2.90</td>
<td>6.42</td>
</tr>
<tr>
<td>EP/HNT/PER</td>
<td>0</td>
<td>5.80</td>
<td>4.20</td>
<td>2.08</td>
<td>5.68</td>
<td>7.83</td>
</tr>
</tbody>
</table>

*The unit of water and moisture sorption content is % by weight.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Storage modulus at 30 °C (Mpa)</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before aging</td>
<td>After aging</td>
</tr>
<tr>
<td>EP/HNT-P</td>
<td>1896.8</td>
<td>1891.1</td>
</tr>
<tr>
<td>EP/HNT/PER</td>
<td>1883.7</td>
<td>1691.8</td>
</tr>
</tbody>
</table>

Figure 11. The water sorption curves of EP/HNT-P and EP/HNT/PER at 85 °C. [Color figure can be viewed at wileyonlinelibrary.com]
and PER. As compared with the maximum ratio of moisture sorption ($M_{\text{max,m}}$) of the EP/HNT/PER at 40°C, the $M_{\text{max,m}}$ of EP/HNT-P drops from 2.08 wt % to 0.87 wt %, decreased by 58.2%. When the temperature rises to 85°C, the $M_{\text{max,m}}$ is 5.68 wt % for EP/HNT/PER and 2.90 wt % for EP/HNT-P. Obviously, the use of HNT-P has decreased the $M_{\text{max,m}}$ by 48.9%. Figure 11 presents the water sorption curves of EP/HNT-P and EP/HNT/PER at 85°C. The water resistance of EP/HNT-P is better than EP/HNT/PER, just as the results of moisture resistance. Compared to the maximum ratio of water sorption ($M_{\text{max,w}}$) of the EP/HNT/PER, the $M_{\text{max,w}}$ of the EP/HNT-P is decreased from 7.83 wt % to 6.42 wt %. These above results indicate that the EP/HNT-P composites have the better moisture and water resistance than the EP/HNT/PER composites.

To examine the moisture resistance of composites, the DMA was carried out about the EP/HNT-P and EP/HNT/PER composites before and after moisture aging. Table VI presents the dynamic mechanical properties of two kinds of composites before and after aging at 85°C, 85% RH. Compared to the EP/HNT/PER, the EP/HNT-P has the higher storage modulus and glass transition temperature. As we all know that the PER is a kind of polyol-type carbonization agent, which can absorb moisture due to the presence of the hydrophilic hydroxyl groups. For EP/HNT/PER, the PER affects the epoxy materials by decreasing the moisture resistance and as a result, the composite usually becomes soften with a gradual decay. However, for EP/HNT-P, the hydrophilic PER has been loaded in HNT and therefore, the softening influence is reduced. These results show that the use of HNT-P has restrained the moisture sorption of PER.

CONCLUSIONS

The new flame retardant system for the UV-curable epoxy resins was prepared by using APP and PER which was loaded in HNT. Loading hydrophilic PER in HNT was intended to reduce the moisture absorption in the modified epoxy resins. The TEM and BET tests were used to analyze the physical structures of the HNT-P. The effect of the new flame retardant system on the UV-curable epoxy resin was studied by CC test and LOI. The results of this study showed that the flame-resistant composites exhibited excellent flame retardancy with a significant decrease in pHRR, THR, TSR, and AMLR, respectively. As for composites including 25% flame retardants, in particular, the residue mass was increased from 2.2 wt % to 35.7 wt %. The retardant mechanism investigation revealed that HNT can catalyze the reaction of APP and PER, the resulting polyphosphoric-HNT intumescent char layer covers on the burning surface of the epoxy materials. The DMA and moisture sorption results showed that as compared to the use of the simple mixture of PER and HNT, the use of the HNT-P composite obtained the better moisture resistance and more stable mechanical properties. This method here may be used to enhance the flame retardancy of UV-curable epoxy resin in the future.

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