1 Introduction
Epoxy resin exhibited excellent processing property, mechanical and physical properties compared to other competitive resins. The use of epoxy resin for composite preparation allowed considerable cost saving and could form ideal adhesive bond with high performance fibers [1-3]. Thus, epoxy resin was the preferential candidate for high-performance composites. However, shortcomings of general epoxy resin such as poor thermal behavior and brittleness limited its application in many special fields [4-5]. So, numerous scientific efforts have been devoted to promote the comprehensive performance of epoxy resin by a variety of methods. Layered nanomaterials as interlayer had large space that allowed the entry of epoxy resin. Using layered nanomaterials modified by organic treatment, both intercalated and exfoliated epoxy/clay nanocomposites could be obtained [6]. Large specific surface area and strong interaction of layered nanomaterials led to high strength, modulus, toughness and thermal properties of the final composites [7]. Coarse multi-scale interface played a positive role in enhancing mechanical and thermal behavior of nanocomposites. On the other hand, heat-insulating property of multi-scale composite was reported to be improved owing to good barrier properties of layered nanomaterials [8].

In this paper, the montmorillonite (MMT) was treated by long chain alkyl quaternary ammonium salts. The MMT/epoxy resin nanocomposite and MMT/epoxy/carbon fiber multi-scale composite were prepared. Intercalation and exfoliation state of organo-clays in epoxy resin were analyzed by X-Ray diffraction (XRD). The mechanical, thermal properties of MMT/epoxy and MMT/epoxy/carbon fiber composites were evaluated, and their failure mechanism was analyzed through fracture surfaces of damaged samples.

2 Experimental

2.1 Materials
Three types of epoxy resins were used in this work. The diglycidyl ether of bisphenol A (E-51) type epoxy resin was supplied by Lan Xing new chemical material Co.LTD China (epoxy value, 0.51). The diglycidyl ester of aliphatic cyclo (TDE-85) type was provided by Tianjin Jindong chemical factory (epoxy value, 0.85). Reactive diluent was supplied by Jiangsu Sanmu Co, and amine curing agents were home-made. Sodium montmorillonite (Na+-MMT) was obtained from Zhejiang Feng Hong Clay chemical industry Co.LTD. Hexadecyl trimethyl ammonium bromide was bought from Shanghai San Pu chemical Co. LTD. T-700 carbon fiber (CF) was obtained from Toray Co. The chemical structures of the resins and diluter were shown in Table 1.

![Table 1: Chemical structures of the materials](image-url)
2.2 Specimen preparation and testing

2.2.1 MMT organic modification
A certain amount of Na⁺-MMT clay was dispersed in de-ionized water. Although the clay can be exfoliated in water almost instantaneously to form a stable dispersion, the mixture was still stirred for 3 h at 5000 rpm to ensure uniform dispersion of the clay in water. Certain amount of hexadecyl trimethyl ammonium bromide was mixed with dispersion mentioned above, then the mixture was stirred for 6 h at 70°C. The MMT nanoplatelets formed a gel after deposition, and supernatant was easily removed. After removing the supernatant, the precipitation was filtered, then washed three times by de-ionized water, and subsequently dried under vacuum at 80°C for 24 h, finally crushed in a mortar. As organic MMT powder was then obtained.

2.2.2 MMT/epoxy resin system
Some amount of E-51 and TDE-85 epoxy resin was poured into a glass vessel at 80°C and then a certain amount of org-MMT was added. Both ultrasonication and magnetic stirring were applied to the mixture to achieve good dispersion. Then, the amine curing agents and diluter were added into the dispersion. After degassed under vacuum at 90°C, the mixture was poured into a preheated metal mold. The resin mixture was then cured in an oven at 90°C for 2 h, 120°C for 2 h, followed by 4 h at 150°C. For comparison, a neat epoxy panels were also prepared via the same procedures described earlier. The cure cycles were the same as that of the unidirectional composite laminates. The tensile strength of the NOL-ring was tested on an Instron-1196 universal testing machine at a rate of 5 mm/min [11].

2.2.3 Composite samples
Resin system was poured into a dip tank. Naval Ordnance laboratory (NOL) rings, as shown in Fig. 1, one kind of filament wound composite samples were prepared. Not only can it reflect the capability of the composite to transfer load, but also assess the interfacial adhesion of the composite [9-10]. In this work, NOL-rings were produced on a filament winding machine with a winding tension of 25 N. The cure cycles were the same as that of the unidirectional composite laminates. The tensile strength of the NOL-ring was tested on an Instron-1196 universal testing machine at a rate of 5 mm/min [11]. It should be noted that the tensile strength (σ) could be determined as

\[
\sigma = \frac{p}{2tw},
\]

Where p is the ultimate burst force recorded in Newton (N), t and w are the thickness and width of the NOL-ring in millimeter (mm), respectively. According to GB/T1458-1988, short-beam-shear test of the unidirectional composites was carried out on an Instron-1196 universal testing machine at a span-to-depth ratio of 6/1. More than six composite specimens with dimensions of 20 mm×6 mm×3 mm were selected for each ILSS test.

2.3 Analysis and characterization
X-ray diffraction (XRD) patterns were recorded by monitoring the diffraction angle 2θ from 1.5 to 10° on a Rigaku-D/max-γA X-Ray diffractometer. The diffractometer was equipped with a CuKα (λ=0.154 nm) radiation source operated at 40 kV and 100 mA. The scanning speed and the step size were 2°/min and 0.02°, respectively. Fourier-transform infrared spectroscopy (FT-IR) spectra were taken with a Magna IR TM Spectrometer 550 (Nicolet) in the reflectance mode. Data acquisition was performed automatically using an inter-faced computer and a standard software package. Solid samples after grinding with KBr were compressed into sheets, and liquid samples smeared on the KBr slide directly. The samples were observed with Cambridge Stereoscan 250MK3 scanning electron microscope (SEM). All samples were coated with gold to avoid the electric charge.
3 Results and discussion

3.1 MMT organic modification

MMT was a kind of hydrophilic layered silicate material. An idealized structure of MMT unit layer was given in Figure 2[12]. It could be modified for lipophilicity and the layer spacing might be increased, which were beneficial for resin to enter the piece of interlayer. In this work, cetyl trimethyl ammonium bromide was selected to modify sodium MMT to replace inorganic cations on the unit layer with organic cations by ion exchange mechanism, and thus make the clay develop affinity with an organic phase such as polymer. As a result, the affinity between laminar and molecular chain could be enhanced and the layer spacing could be increased. Accordingly, MMT was easy to be intercalated by epoxy resin.

![Fig. 2 Structure of MMT](image)

**Fig. 2 Structure of MMT**

Fig. 3 showed the XRD patterns of MMT and organic MMT. The layer spacing of MMT was 1.46nm and that of organic MMT was 2.34nm which could be calculated by the Bragg diffraction equation ($2d\sin\theta=n\lambda$). It indicated that organic-treatment made the layer spacing of MMT greater. The FT-IR was used to detect the stretching and bending vibrations of molecules in organic-MMT. When long-chain alkyl ammonium ions were intercalated in the clay galleries, new peaks could be found. Results were shown in Fig.4. The downward convex bands in 1300cm$^{-1}$ were due to the vibration of $\text{Si} - \text{O} - \text{Si}$ and that in 800-400cm$^{-1}$ were due to the vibration of silica tetrahedron and alumina octahedron, which belong to the MMT. New absorption peaks at 2921–2851cm$^{-1}$, 1488cm$^{-1}$ and 1371cm$^{-1}$ for organic-MMT could be identified. These peaks were attributed to the vibration of $-\text{CH}_3 -\, -\text{CH}_2 -$ of quaternary ammonium salt, indicating that long-chain alkyl ammonium ions had intercalated within the clay galleries.

3.2 Intercalation and exfoliation of organic MMT in epoxy resin

As depicted in Fig.5, when epoxy resin with content of MMT less than or equal to 4 wt%, diffraction peak was reduced to wide-angle X-ray diffraction observation under the limit of 1.5$\degree$ and the layer spacing expanded to more than 5.88 nm for most MMT layer. MMT was considered to be exfoliated when the MMT layer spacing of the layered silicate nanocomposites expands to more than 4.4 nm [13].

![Fig. 5 Intercalation and exfoliation of organic MMT in epoxy resin](image)
Therefore, MMT was fully exfoliated. When content of MMT increased to 6 wt%, XRD diffraction peak of the MMT/epoxy occurred at apparently 2.5°, which indicated that parts of exfoliated and intercalated epoxy resin system was formed.

3.3 Properties of MMT/epoxy resin

3.3.1 Mechanical properties
Tab.2 showed the properties of MMT/epoxy nanocomposites with different content of MMT. It could be found that tensile, flexural and compression properties of epoxy resin, in general, were increased with increasing amount of MMT. When content of MMT was 2 wt% and 3 wt%, mechanical properties showed a higher value. That was attributed to MMT layers dispersed in the epoxy resin as nanophase causing strong combination. Thus, a number of physical crosslink points between MMT and epoxy resin were formed. When external force was loaded on the sample, MMT slices, which embedded in epoxy resin would be pulled up and broken. Herein, MMT slices played a role resembling short fiber which improved mechanical properties of the epoxy resin [14]. At the same time, higher modulus of MMT, compared to polymeric resin, led to increase of modulus of polymeric matrix. However, when MMT content maintained 6 wt%, the mechanical properties of MMT/epoxy nanocomposites, including tensile, flexural and compression properties, were lower than that of neat epoxy. That was due to higher stress concentration effect of clay agglomerated particle at high clay content. Nonexfoliated clay particles from larger agglomerates, and thus clay-polymer surface interactions decreased as the clay content increases resulting in lower mechanical properties.

The impact strength of MMT/epoxy with different content of MMT was shown in Fig.6. Results suggested that when content of MMT was 2 wt% and 3 wt%, impact strength of epoxy resin increased by 25.1% and 35.3%, and reached to 20.9 kJ·m⁻² and 22.6 kJ·m⁻², respectively. The improvement in the impact strength could be attributed to the good dispersion of nanoclay particles, as well as the intrinsic properties of the modified epoxy resin network [15-16]. Failure section of impact samples for epoxy and MMT/epoxy were shown in Fig.7. It could be found that impact section of the epoxy resin was clear and smooth which belonged to the typical brittle fracture. However, fracture section of MMT/epoxy exhibited more rough surfaces, and fracture directions of MMT/epoxy were dispersed which tended to ductile fracture.
3.3.2 Heat resistance

Fig. 8 represented the Tg curve of MMT/epoxy nanocomposites with different content of MMT. When the content of MMT was 1 wt%, 2 wt%, 3 wt%, 4 wt% and 6 wt%, the corresponding Tg of MMT/epoxy was 113.4 °C, 123.7 °C, 119.5 °C, 115.3 °C, and 113.3 °C, respectively. Additionally, the Tg of MMT/epoxy was higher than that of neat epoxy resin of 110.1 °C. For the epoxy resin with 2 wt% organic MMT, Tg increased by 13.6 °C and reached to the maximum value, compared to neat epoxy resin. The increase of Tg was attributed to the epoxy resin network structure strengthened by the dispersed silicate layers in the matrix. Thus, the mobility of epoxy resin molecular chain was restricted by MMT slices. At the same time, free volume of MMT/epoxy reduced and it was more difficult for mobility of macromolecular chain segments when the MMT/epoxy nanocomposites was heated [17-18].

### Tab. 2 Properties of MMT/epoxy castings with different MMT contents

<table>
<thead>
<tr>
<th>contents of MMT/ wt%</th>
<th>tensile strength /MPa</th>
<th>tensile modulus /GPa</th>
<th>elongation /%</th>
<th>flexural strength /MPa</th>
<th>flexural modulus /GPa</th>
<th>compression strength /MPa</th>
<th>Compression modulus /GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>85.8</td>
<td>3.63</td>
<td>4.10</td>
<td>147.0</td>
<td>3.76</td>
<td>140.0</td>
<td>3.60</td>
</tr>
<tr>
<td>1</td>
<td>88.1</td>
<td>3.74</td>
<td>4.50</td>
<td>154.6</td>
<td>3.76</td>
<td>145.0</td>
<td>3.72</td>
</tr>
<tr>
<td>2</td>
<td>96.1</td>
<td>3.85</td>
<td>3.58</td>
<td>166.6</td>
<td>3.86</td>
<td>156.4</td>
<td>3.69</td>
</tr>
<tr>
<td>3</td>
<td>94.5</td>
<td>4.05</td>
<td>3.86</td>
<td>163.4</td>
<td>4.06</td>
<td>150.4</td>
<td>3.65</td>
</tr>
<tr>
<td>4</td>
<td>88.1</td>
<td>3.91</td>
<td>3.45</td>
<td>150.0</td>
<td>3.70</td>
<td>142.6</td>
<td>3.49</td>
</tr>
<tr>
<td>6</td>
<td>84.1</td>
<td>3.91</td>
<td>3.14</td>
<td>129.0</td>
<td>3.87</td>
<td>143.2</td>
<td>3.29</td>
</tr>
</tbody>
</table>

![Fig. 6](image6.png) Impact strength of MMT/epoxy with different MMT contents

![Fig. 7](image7.png) SEM images of impact section: (a) epoxy resin, (b) epoxy resin with 3% MMT
3.3.3 Heat-insulating properties
Good heat insulation of resin matrix could effectively prevent delivery of heat from external to internal, and protected the internal matrix from decomposition at high temperature. Under the same conditions, material heat insulation was determined by the formula of \( \rho \cdot \lambda /C_p \), Where \( \rho \), \( \lambda \) and \( C_p \) represented the density, coefficient of thermal conductivity and specific heat capacity of the material, respectively. There were not much difference of density and specific heat capacity for resembling materials. Consequently, heat insulation depended primarily on coefficient of thermal conductivity of the material.

The high surface area of MMT clay played an important role in property enhancement of polymer nanocomposites. In both exfoliated and intercalated nanocomposites, dispersed nanoclay platelets created a tortuous structure in polymer matrices. The effective diffusion path for a diffusing molecular was longer. Therefore, polymer nanocomposites exhibited very good diffusion barrier properties for heat flow, liquid and gas as showed in Fig.9 [8, 19-21]. Heat-insulating properties of MMT modified epoxy resin were given in Tab.3. Data showed that thermal conductivity of epoxy resin with 3 wt% MMT reduced by 36.6%, and was 0.202 W·m\(^{-1}\)·K\(^{-1}\).

**Tab.3 Thermophysical properties of epoxy and MMT/epoxy**

<table>
<thead>
<tr>
<th>Material system</th>
<th>coefficient of thermal conductivity /W·m(^{-1})·K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>room temperature</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>0.276</td>
</tr>
<tr>
<td>with 2 wt% MMT</td>
<td>0.220</td>
</tr>
<tr>
<td>with 3 wt% MMT</td>
<td>0.202</td>
</tr>
</tbody>
</table>

Fig.8 Tg curve of MMT/epoxy with different MMT contents

Fig.9 Different diffusion paths in polymer and polymer nanocomposites

3.4 MMT/epoxy/carbon fiber multi-scale composites

3.4.1 NOL rings of composites
As a kind of ring test samples, NOL rings were the simple experimental method to measure performance of winding composite which were based on the netting theory. Winding tests and property measurements of NOL rings could provide valuable process parameters and design parameters for the pressure vessels forming as well as the ability of interface impregnating, adhesive and stress transferring between fiber and resin matrix [22]. Tab.4 showed the properties for the NOL ring of T700 CF/epoxy composites and MMT/epoxy/T700 CF multi-scale composites.
Tab.4 Mechanical properties for the NOL rings of composites

<table>
<thead>
<tr>
<th>Material systems</th>
<th>tensile strength /MPa</th>
<th>tensile modulus /GPa</th>
<th>interlaminar shear strength /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>T700CF/epoxy</td>
<td>2010</td>
<td>121</td>
<td>69.2</td>
</tr>
<tr>
<td>MMT/epoxy/T700CF</td>
<td>2143</td>
<td>130</td>
<td>79.0</td>
</tr>
</tbody>
</table>

Tab.4 showed the Mechanical properties for the NOL rings of T700CF/epoxy composites and MMT/epoxy/T700CF multi-scale composites with 3 wt% MMT, which suggested that the multi-scale composites showed higher mechanical properties, compared to the T700CF/epoxy composites. Particularly, ILSS enhanced by 14% and reached 79.0MPa. The ILSS improvement of multi-scale composites should contribute to the dispersion of clay particles in the matrix which became resin network junction and had a riveting effect to inhibit propagation of micro cracks. Moreover, the high surface energy of MMT might improve the interface binding force between the resin and fibers. Consequently, the resin matrix could take the energy transferring between the fibers to ensure that the damage would not occur at the relatively weak interfaces [23-25].

Fig.10 and Fig.11 showed SEM images of the tensile and shear section of NOL rings. It could be found that the fracture of T700 CF/epoxy composites occurred at interfaces between fibers and matrix, and some carbon fibers were separated from matrix and pulled out which indicated a poor adhesion between fibers and matrix. That indicated the interfacial bonding was poor and the interface structure could not transfer stress effectively for T700 CF/epoxy composites. As a contrast, the image of MMT/epoxy/T700CF multi-scale composites was different. Large quantity of resin matrixes could be observed covering on the fiber surface, which indicated that the nano size clay particles embedded in the matrix were combined with the carbon fibers. The clay particles played a role in increasing the mechanical properties of multi-scale composites.

3.4.2 Heat-insulating properties of composites

Heat-insulating properties of two kinds of composites were given in Tab.5. When 3 wt% MMT were added, the thermal conductivity of MMT/epoxy/T700CF multi-scale composites was 0.341W·m⁻¹·K⁻¹, which was 37.5% lower than that of T700CF/epoxy composites at room temperature.

Tab.5 Thermophysical properties of composites

<table>
<thead>
<tr>
<th>Material systems</th>
<th>coefficient of thermal conductivity /W·m⁻¹·K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>room temperature</td>
</tr>
<tr>
<td>T700CF/epoxy</td>
<td>0.469</td>
</tr>
<tr>
<td>MMT/epoxy/T700CF</td>
<td>0.341</td>
</tr>
</tbody>
</table>

Fig.10 SEM photographs of tensile sample fracture section for composite NOL-rings (a, T700 CF/epoxy composites; b, MMT/epoxy/T700 CF multi-scale composites)
4 Conclusions

Cetyl trimethyl ammonium bromide could be used to modify sodium MMT to replace inorganic cations on the unit layer surface with organic cations by ion exchange mechanism. The layer space of organic MMT could expand from 1.46 nm to 2.34 nm, which was beneficial to allow the intercalation of epoxy resin.

As for MMT/epoxy nanocomposites, certain amount of the organic MMT could improve mechanical and thermal properties. When content of MMT was 3 wt%, compared to neat epoxy resin, impact strength of MMT/epoxy nanocomposites could enhance by 35.3%, and thermal conductivity could decrease by 36.6%. When content of MMT was 2 wt%, Tg could increase by 13.6°C and was 123.7°C. That might attributed to the interaction occurred between MMT slices and epoxy resin.

Compared to properties of T700 CF/epoxy resin composites, ILSS of MMT/epoxy/T700 CF multi-scale composites were enhanced by 14%. The thermal conductivity of MMT/epoxy/T700CF multi-scale composites with 3 wt% MMT could be 37.5% lower than that of T700CF/epoxy composites at room temperature.

References

Preparation and Properties of MMT/Epoxy/Carbon Fiber Multi-scale Composite


