In order to overcome the weakness of the epoxy-amine network, the acrylic tri-block copolymer (BMG) and the functionalized multi-wall carbon nanotubes (MWCNTs) were prepared in this article. The curing reaction, rheology, thermal and mechanical performance of epoxy-based composites with BMG and MWCNTs were respectively investigated in this study. The curing schedule of the epoxy-based composites was ascertained by using non-isothermal DSC analysis. The rheological analysis showed that the processing time of composites was over 60 min under the processing temperature window from 75 to 200 °C. The mechanical performance of the epoxy-amine network was improved after introducing the dispersed MWCNTs and BMG. In comparison with the neat epoxy-amine network, the tensile strength and impact strength of the composites with the addition of 7.1 wt.% BMG and 0.4 wt.% MWCNTs increased by 11.25 and 36.4%, respectively.
the side chains of the BMG also increased the compatibility between BMG and epoxy resins.

Multi-wall carbon nanotubes (MWCNTs) have been identified as a promising reinforced material of composites since it was discovered in 1991 [16]. Numerous studies also tried to use the MWCNTs through different treatments to reinforce the strength of the epoxy matrix [17–19]. For example, Lee et al. [20] prepared the epoxy-based composites with fluorinated multi-walled carbon nanotubes. The mechanical properties and fracture surface morphologies were evaluated for epoxy matrices. The tensile strength of the MWCNTs/epoxy composites improved by 31% with treated MWCNTs compared to the epoxy composites with untreated MWCNTs. However, the un-treated MWCNTs are difficult to disperse well into the epoxy matrix. Therefore, the MWCNTs were functionalized by using acid oxidation in the previous work [17]. The hydroxyl and carboxyl groups were successfully formed on the surface of MWCNTs.

The synthesized tri-block copolymer (BMG) and acid-treated MWCNTs were used to prepare epoxy-based composites to overcome the weakness of the epoxy-amine network by using the hot melt blending process. In order to investigate the effects of BMG and acid-treated MWCNTs on epoxy-amine curing systems, the curing reaction, rheology, thermal and mechanical performance of epoxy-based composites and neat epoxy curing networks were compared.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, technical grade, epoxide equivalent weight: 191 g/mol) was purchased from Wuxi Epoxy Resin Plant, China. Diaminodiphenyl sulfone (DDS, chemical pure) was purchased from Sinopharm Group Chemical Reagent Co., Ltd, China. Technical grade MWCNTs was purchased from Beijing Boyu Gao Ke New Material Technology Co. Ltd, China. The lengths and diameters of MWCNTs were ranged from 10–50 μm and 20–80 nm, respectively. The methyl methacrylate block copolymer (BMG) [10] was synthesized by the Institute of Petrochemistry, Heilongjiang Academy of Sciences, China. The synthetic route is shown in Figure 1. The number average- (Mn) and weight average molecular weight (Mw) of BMG as shown in Table 1 was 3,43,600 and 4,70,000, respectively. From the molecular weight and distribution, it can be confirmed that the synthesized BMG has a controlled molecular weight and a narrow molecular distribution.

2.2. Preparation of epoxy-based composites

The epoxy-based composites with MWCNTs and BMG were prepared according to the formula
shown in Table 2 by using a hot melt blending process. Firstly, the BMG was completely mixed up with the preheated DGEBA. Secondly, the acid-treated MWCNTs were evenly mixed up with the above the blends. Thirdly, the curing agents (DDS) were dissolved into the blends. Finally, the blends were degassed under vacuum to eliminate the nonuniformity and air bubbles. The mixtures were diverted into the preheated mold. In order to ensure the curing reaction process to be finished completely, the curing schedules were carefully performed at 150 °C for 1 h followed by 180 °C for 3 h (Figure 2).

2.3. Characterization
The curing characteristics of DGEBA/BMG/MWCNTs composites were obtained by using differential scanning calorimeter analysis (DSC, Q20, TA Instruments, New Castle, DE). The non-isothermal heating rates were performed at 5, 10, 15, 20 °C/min, respectively. The curing temperature was 25 to 250 °C in the nitrogen (N2) atmosphere.

The thermal property of DGEBA/BMG/MWCNTs composites were characterized by thermal gravimetric analysis (TGA, Q50, TA instruments). The heating rate was 5 °C/min from 25 to 800 °C in the N2 atmosphere.

The mechanical performance of DGEBA/BMG/MWCNTs composites were characterized by cantilever pendulum impact tester (XJU-5.5, Chengde Jinjian Testing Instrument, China). According to ISO 180:2000, the dimensions of the samples were 80 × 10 × 4 mm3.

The fracture surface morphology of samples was observed by Scanning Electron Microscopy (SEM, XL20). The fracture surface was prepared by cold fracturing in liquid N2. The fracture surfaces were sputter coated with gold in argon by an SC7620 sputter coater.

The rheology of DGEBA/BMG/MWCNTs composites were investigated by discovery hybrid rheometer (DHR, TA Instruments). A temperature-ramp sweep was conducted at 4 °C/min from 25 to 200 °C at 1 Hz. The mode of the temperature-time sweep was conducted at 150 °C and 1 Hz.

3. Results and discussion
3.1. Curing characteristics
The non-isothermal DSC analysis was performed to investigate the curing characteristics of the DGEBA/BMG/MWCNTs blends as shown in Figure 3. The initial-, peak- and finish temperature of the curing reaction could be obtained from each of the DSC curve. These were defined as Ti, Tp and Tf, respectively. With the increment of heating rates, the characteristic temperatures moved towards higher temperature. This is due to the thermal effect unit time which increases with heating rates. The
response time of the unit mass of the sample is shortened [21–23].

The Kissinger and Ozawa equation were performed to calculate the parameters of the curing reaction. According to Kissinger analysis [24], the equation was given as:

\[
\ln \left( \frac{\beta}{T_p^n} \right) - \ln \left( \frac{AR}{E} \right) = \frac{E_a}{R} \frac{1}{T_p} \quad (1)
\]

\[
\frac{d \ln \left( \frac{\beta}{T_p^n} \right)}{dt} = \frac{E_a}{R} \quad (2)
\]

The Ozawa [25] equation is shown as:

\[
E_0 = \frac{R}{0.4567} \cdot \frac{d \ln(\beta)}{d \left(1/T_p \right)} = - \frac{R}{1.052} \cdot \frac{d \ln(\beta)}{d \left(1/T_p \right)} \quad (3)
\]

The curing kinetic parameters are calculated by Equations (1–3), (2) as shown in Table 3. The values of activation energy \(E_a\) and \(E_0\) are 57.8 and 63.1 kJ/mol, respectively. Taking BMG/MWCNTs/DDS/DGEBAs as an example, the value of \(E_a\) is lower than that of DDS/DGEBA system (around 63–69 kJ/mol).

In order to calculate the theoretical curing schedule, the extrapolation method was constantly performed using DSC measurement. Therefore, the equation of fitted curves [26] is given as:

\[
T = A\beta + B \quad (4)
\]

where \(T\) is the characteristic temperature of curing reaction, \(B\) is the onset temperature of the DSC curves deviates from the baseline, \(\beta\) is the heating rate and \(A\) is the slope of fitted curves. Three fitted lines of \(T_\beta\), \(T_p\), and \(T_f\) are shown in Figure 3(B). The gelation-, curing- and post-curing temperature of the curing reaction was obtained by extrapolating the three lines to zero. These were \(T_{gel} = 145\,^\circ\mathrm{C}\), \(T_{cure} = 198\,^\circ\mathrm{C}\) and \(T_{post} = 303\,^\circ\mathrm{C}\), respectively.

Combined with the actual curing experience and theoretical values, the curing schedule was finally determined as 150 °C for 1 h followed by 180 °C for 3 h.

3.2. Rheology characteristics

The viscosity versus temperature scan was performed to investigate the processing window before gelation as shown in Figure 4(A). It was observed that the viscosity of the DGEBA/BMG/MWCNTs

![Figure 4. The rheological parameters of the DGEBA/BMG/MWCNTs composites. The sample 1–4 stand for the content of MWCNTs in epoxy-based composites that is (0.2, 0.4, 0.6 and 0.8 wt.%, respectively).](image-url)
blends in change with temperature. Firstly, the initial viscosity of the blends was over 10000 Pa\cdot s at room temperature. With temperature increasing up to 100 °C, the viscosity of the blends gradually decreased to a liquid state. The temperature increasing from 100 to 200 °C, the viscosity of the plateau was maintained within 10 Pa\cdot s. This minimum plateau viscosity was defined as the processing window of the blends. The temperature range of processing window is shown in Figure 4(B). It is clear from this figure that the temperature range of the processing window gradually narrowed with the increasing addition of MWCNTs. With the temperature increasing up to over 200 °C, the viscosity dramatically increased to 10,000 Pa\cdot s [27,28]. With the polymerization and crosslink reactions leading to a dramatic increase in viscosity.

The viscosity versus time scan was performed to investigate the processing time before gelation as shown in Figure 4(C). It is observed that the processing time was slightly narrowed with the increment of MWCNTs. When MWCNTs were added to over 0.4 wt.%, the processing time was less than 60 min. This is due to the amount and size of the MWCNTs that are leading to a decrease in processing time [29].

3.3. Thermal characteristics

The TGA analysis was performed to investigate the thermal performance of the DGEBA/BMG/MWCNTs network as shown in Figure 5. The temperature of the initial decomposition ($T_{d5\%}$) decreased with the increment of acid-treated MWCNTs. The maximum thermal degradation also decreased with the increment of acid-treated MWCNTs as shown in Figure 5(B). The carbon residue rate of the epoxy network increased after introducing the acid-treated MWCNTs and BMG.

This phenomenon indicated that the thermal stability of the composites is weakened by incorporating the BMG and acid-treated MWCNTs. The surface of MWCNTs formed the functional groups (-OH, -COOH) after the acid oxidation treatment. The thermal stability of acid-treated MWCNTs are rapidly declined in comparison with the MWCNTs without any treatment. In addition, the acrylate chain of BMG is another reason for the decrease of thermal stability of the epoxy-based composites [30,31].

3.4. Mechanical characteristic

The tensile and un-notched impact tests were performed to investigate the mechanical properties of the DGEBA/BMG/MWCNTs network as shown in Figure 6. The storage modulus and elongation at break increased by 18.7 and 15.8%, respectively. The change tendency of impact strength was similar to the tensile strength. The maximum tensile and impact strength of epoxy-based composites with 0.4 wt.% acid-treated MWCNTs and 7.1 wt.% BMG was 89 MPa and 19.5 kJ/m², respectively. The mechanical performance of epoxy-based composites with suitable acid-treated MWCNTs and BMG was enhanced due to the unique structure of MWCNTs and BMG. When the addition of MWCNTs increasing to over 0.4 wt.%, the impact strength of composites gradually decreased. This is due to the agglomeration that is prone to form during the curing process resulting in the decrease of mechanical strength. Moreover, a large number of air bubbles from stirring remain in the blends resulting in massive defects forming in the cured epoxy networks [32,33].
3.5. Micromorphology

The micromorphology of epoxy-based composites was observed by using SEM analysis as shown in Figure 7. All samples were first cold fractured in liquid N₂ and then were broken under external force. The fracture surfaces were sprayed with gold before the test. The fracture surface of the neat epoxy-amine network is shown in Figure 7. This was a typical fracture of brittleness with no cracks. The fracture surface of the epoxy-amine network changed into a typical fracture of toughness after introducing the BMG and acid-treated MWCNTs. The river-like cracks started to form in 0.2 wt.% MWCNTs. With the addition of 0.4 wt.% MWCNTs, some holes were observed in the epoxy-network matrix. These suitable river-like cracks and holes can absorb the energy generated during the fracture process. In addition, the extension of cracks also is hindered by these structures. With the addition of the 0.6 wt.% MWCNTs, excessive nail anchors were formed in the epoxy-network matrix. With the 0.8 wt.% MWCNTs, the excessive nail anchors gradually turned into cracks. However, the excessive cracks and anchors in the samples with over 0.4 wt.% MWCNTs apparently leading to more defects to decline the performance of the composites.

4. Conclusion

In order to overcome the weakness of the epoxy-amine network, the acrylic tri-block copolymer (BMG) and the functionalized multi-wall carbon nanotubes were used to prepare the epoxy-based composites. The curing kinetics, rheology, the thermal and mechanical performance of epoxy-amine composites with BMG and acid-treated MWCNTs were respectively investigated. The detail conclusions are summarized as follows:

![Figure 6](image-url) **Figure 6.** The mechanical performance of the DGEBA/BMG/MWCNTs composites. The sample 1–4 stand for the content of MWCNTs in epoxy-based composites that is 0.2, 0.4, 0.6 and 0.8 wt.%, respectively.

![Figure 7](image-url) **Figure 7.** The SEM photos of the DGEBA/BMG/MWCNTs composites. The sample 1–4 stand for the content of MWCNTs in epoxy-based composites is 0.2, 0.4, 0.6 and 0.8 wt.%, respectively.
1. Combining the curing reaction parameters and actual experience in production, the curing schedule was determined as 150 °C for 1h followed by 180 °C for 3h for the current system.

2. The epoxy-based composites possessed an appropriate processing viscosity and processing window. The rheological analysis showed that the processing time of composites was over 60 min under the processing temperature window from 75 to 200 °C.

3. The maximum tensile and impact strength of epoxy-based composites with the addition of 7.1 wt.% BMG and 0.4 wt.% acid-treated MWCNTs was 89 MPa and 19.5 kJ/m², respectively.

4. The thermal stability of epoxy-amine network was decreased after introducing the BMG and acid-treated MWCNTs. The introduction of the acrylate segment in the epoxy-based composites is the main reason for the slight decrease of the heat resistance.

Disclosure statement

No potential conflict of interest was reported by the authors.

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