

EFFECTS OF MULTI-WALLED CARBON NANOTUBE (MWCNT) ON RAMIE FIBER-REINFORCED EPOXY RESIN COMPOSITES

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The effects of multi-walled carbon nanotube (MWCNT) on thermal stability and mechanical properties of ramie fiber reinforced epoxy resin composites were studied. In this paper, MWCNT was used as the nano-sized reinforced material. The epoxy resin composites with different MWCNT contents were prepared by vacuum aided resin infusion process (VARI). The influence of MWCNT contents on thermal stability and mechanical properties of the composite was analyzed by experimental methods. The results showed that the vicat softening temperature, bending strength and impact strength of epoxy resin composite with MWCNT and ramie fiber was improved greatly. Moreover, the morphology of fracture surface evaluated by scanning electron microscopy (SEM) showed that adding of MWCNT is helpful to get better interface adhesion between ramie fiber and epoxy resin matrix.

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1. Introduction

The ramie-reinforced epoxy resin composites have been widely used in aerospace, automobile, watercraft, wind electricity, micro-electronic packaging, electromagnetic shielding, electronic information and other fields^[1-2]. For this, it has become an irreplaceable material in modern industry and life^[3]. However, the ramie-reinforced epoxy resin composites are easy to be bent, have lower yield point and are water-absorbent^[4]. A way to improve the thermal stability and mechanical properties of is the addition of multi-walled carbon nanotube (MWCNT)^[5].

MWCNT are considered as one of the most important nano reinforcing materials and functional materials in polymer materials due to their excellent mechanical properties and specific physical properties^[6]. The common modification methods are physical and chemical treatment^[7-9]. Hepworth, et al.^[10] obtained excellent interface bond in composite and improved stiffness and mechanical property of the materials by permeating epoxy resin into cell wall of flax. The researches of Fan, et al.^[11, 12] showed that mechanical property of the composite obtained by impregnating the fiber fabric in resin system containing MWCNT was improved significantly. During molding of WMCNT/epoxy resin-based composite, how to disperse the MWCNT uniformly is especially crucial. For this, the molding process and dispersion method are the points

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which are worthy of thoroughly studying^[13-14].

In the experiments, a small quantity of MWCNT was uniformly dispersed in epoxy resin system by combining mechanical mixing and ultrasonic dispersion, and the MWCNT-ramie fiber/epoxy resin-based composite was obtained by infusing MWCNT-epoxy resin into fiber preform by vacuum infusion. The mass fraction of MWCNT used was 0%, 0.05%, 0.1%, 0.3% and 0.6% respectively. In this paper, thermal resistance, mechanical property, hydrophobic property and micro morphology changes, etc. of the composite were characterized by some experiments made on the composite laminate.

2. Experiments

2.1 Materials

Epoxy resin (E-51) (epoxy equivalent 184-200, epoxy value 0.50-0.54) produced by Nantong Xingchen Synthetic Material Co. Ltd., china; methyl tetrahydrophthalic anhydride (MeTHPA) (content of acid anhydride $\geq 40\%$, neutralization equivalent 81-85) produced by Puyang Huicheng Electronic Material Co., Ltd. china; 2,4,6-tri(dimethylamiomethyl) phenol (DMP-30) (a faint yellow transparency liquid, amine value is 600-630mg KOH/g) produced by Puyang Huicheng Electronic Material Co., Ltd. china; multi-walled carbon nanotube/epoxy resin composite (TNM8) (content of MWCNT is 4.5% and content of epoxy resin is 93.5%) provided by the Business Division in Zhongke Era Nano Center of China Sciences Academy Chengdu Organic Chemical Co., Ltd. china; and ramie fiber plain weave fabric (surface density is 2,100 g/m²) produced by Shenzhen Hexing Textile Co. Ltd. china.

2.2 Preparation of multi-walled carbon nanotube-ramie fiber/epoxy resin composite

2.2.1 Experimental procedures

(1) The proportion of epoxy resin (E-51), methyl tetrahydrophthalic anhydride (MeTHPA) (curing agent) and 2,4,6-tri(dimethylamiomethyl) phenol (DMP-30) (accelerant) weighed was 100:85:2. The mass fraction of MWCNT used in the experiments was separately 0%, 0.05%, 0.1%, 0.3% and 0.6%. The number of ramie fiber layers was 8 (thickness of single layer was 0.44mm). And, the mass fraction of ramie fiber was 40%.

(2) The MWCNT filled epoxy resin was mixed with the epoxy resin (E-51) mechanically in a 250ml 3-mouth flask at 40°C, and then the mixture was placed in a numerical controlled ultrasonic cleaner to let it subjected to ultrasonic dispersion for 30min until the MWCNT was uniformly dispersed in the epoxy resin.

(3) The methyl tetrahydrophthalic anhydride (MeTHPA) (curing agent) and 2,4,6-tri(dimethylamiomethyl) phenol (DMP-30) (accelerant) were added into the 3-mouth flask in turn, stirred with the mixture at 40°C and ultrasonically dispersed for 30min at a power of 200W until all these were mixed evenly.

(4) The solution mixed well was placed at 80°C in vacuum drying oven and vacuumed until there was no bubble in the solution.

(5) Solution in the 3-mouth flask was transferred into a beaker, poured into a vacuum fiber preform by vacuum infusion process and then cured in a vacuum drying oven under normal pressure at a curing temperature of 80°C 4h+120°C 2h+150°C 2h.

2.2.2 Vacuum infusion

The bagging pattern of the composite laminate prepared by vacuum assisted resin infusion molding is as shown in Fig. 1(a). The aluminum sheet was applied with release agent, 8 layers of 150mm×150mm×3.5mm plain weave ramie fiber cloth preform (reinforced fabric) were laid along 0° direction layer by layer. Then, the fabric cloth was covered by a layer of release cloth and a layer of flow medium. Two sides of the fiber cloth were secured with a spiral pipe with sealed tube externally. Finally, the specimen was encapsulated with sealing tape and vacuum bag membrane.

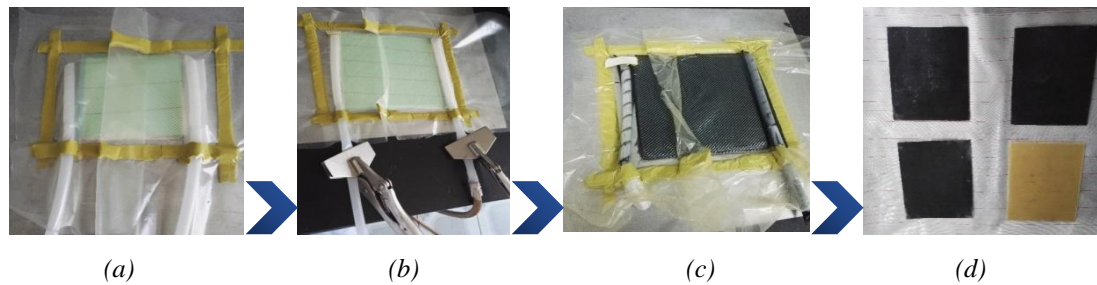


Fig. 1 Vacuum assisted resin infusion molding

(a) Bagging pattern of vacuum assisted resin infusion molding (b) The molding of after vacuum (c) The molding after curing and composite sheet (d) MWCNT-ramie fiber/epoxy resin composite

After the fiber layer was bagged, we firstly checked air tightness of the vacuum bag. Then, we pre-compact the fiber preform by repeated vacuum supplying (vacuum degree ≥ 98 kPa). And, the sealed tubes were clamped with a vise grip plier respectively in order to maintain the vacuum, as shown in Fig. 1(b).

In the process of resin infusion, the mold and fiber were preheated to set temperature and the resin was infused into the preform at 40°C under vacuum pressure. After infusion, the package was placed into the oven (which has been heated to 80°C) while the vacuum pressure (vacuum degree ≥ 98 kPa) in the vacuum bag was kept unchanged to heat it for curing at 80°C for 4h, then heat it at 120°C for 2h and finally heat it at 150°C for 2h. After curing, the mold was placed to the work bench to cool it down to the room temperature, as shown in Fig. 1(c). Finally, the MWCNT-ramie fiber/epoxy resin composite was released from mold and weighed, and the composite laminate was obtained, as shown in Fig. 1(d).

2.3 Characterization of MWCNT-ramie fiber/epoxy resin composites

2.3.1 Differential scanning calorimetry (DSC)

The glass-transition temperature (T_g) and curing reaction of epoxy resin was tested with the Diamond DSC produced by PE Corporation (in the United States). After curing, the epoxy resin was heated from room temperature to 200°C at a heating rate of 5°C/min, cooled down to room temperature and then heated to 200°C again at a heating rate of 10°C/min under nitrogen atmosphere. The uncured liquid epoxy resin was heated to 200°C at a heating rate of 10°C/min for 3h, cooled down to room temperature and then heated to 200°C again at a heating rate of 5°C/min under nitrogen atmosphere.

2.3.2 Thermal gravimetric analysis (TGA)

The thermo gravimetric analyzer (SDT Q600) produced by TA Corporation (in the United States) was used to determine thermal stability of MWCNT-ramie fiber/epoxy resin composites in which the content of MWCNT is 0%, 0.05%, 0.1%, 0.3% and 0.6% respectively when the composites were heated to 1,200°C from room temperature at a heating rate of 10°C/min under air atmosphere.

2.3.3 Vicat softening point analysis

Heat resisting properties of MWCNT-ramie fiber/epoxy resin composites were evaluated by analyzing vicat softening point of the 3mm thick specimen (5mm×15mm). The temperature recorded when the specimen was heated from 50°C at a rate of 2°C/min, pressure was 50N and needles (sectional area is 1mm²) were pressed 1mm into the specimen. The vicat softening points of MWCNT-ramie fiber/epoxy resin composites in which the content of MWCNT is 0wt%, 0.05wt%, 0.1wt%, 0.3wt% and 0.6wt% respectively were measured separately. In each group, two specimens were tested and an average was taken. The value was deemed as an effective one when the temperature deviation was less than 2°C.

2.3.4 Bending performance test

The bending strength is a very important indicator for measuring of mechanical properties of materials. The bending strength refers to the bending stress at breaking load or the maximum load when the material is subjected to bending failure, in MPa. The calculation formula is as follows:

$$\sigma_f = \frac{3P \cdot l}{2b \cdot h^2}$$

Wherein: σ_f is bending strength, in MPa; P is breaking load, in N; l is span, in mm; h is thickness of the specimen, in mm; and, b is width of the specimen, in mm.

The breaking bending stress is another indicator to measure bending properties of materials and refers to the stress at bending breaking point when the material is subjected to bending failure.

In order to eliminate internal stress of the specimen, the test stripes were placed in an environment with specified temperature and humidity for 24h. Then, bending test of the stripes was carried out on the microcomputer control electronic universal testing machine to obtain the bending strength and breaking bending stress. In the test, the GB/1449-2005 standard was referred to, no restrained brace was used, the specimen was bent from three points, test speed was 3mm/min and attenuation rate was 70%. Dimensions of the specimen were 60mm×15mm×3mm. And, the test temperature was 23°C.

2.3.5 Impact resistance test

The impact strength is used to measure toughness of material at high-speed impact or evaluate impact resistance of material. Therefore, the impact strength is an important indicator to measure brittleness and toughness of materials. The impact strength is defined as the energy that is absorbed by unit cross-sectional area of the specimen in the process of impact breakage. The calculation formula is as follows:

$$\alpha_t = 1000 \times \frac{A}{b \times d}$$

Wherein, α_t is impact strength, in KJ/m^2 ; A is the amount of work expended when the specimen is broken under impact, in J; b and d is separately width and thickness of the specimen, in mm. In the test, the GB/T 1451-2005 standard was referred to, the test strips (70mm×10mm×3mm) prepared were placed in an environment of specified temperature and humidity for 24h to eliminate their internal stress, and then were used to carry out the impact test on the ZBC-4 type Charpy impact tester produced by Shenzhen SANS Testing Machine Co., Ltd., in order to determine impact strength (kJ/m^2) of test materials at a test temperature of 23°C.

2.3.6 Impact breakage section morphology observation

One end of the tested impact test stripe where the breakage section was relatively smooth was sawed off, so as that the length of the stripe was less than 10mm. Surface morphology of broken test stripe and dispersion state of the filler were observed with the Nova NanoSEM 450 produced by FEI Corporation. The section was handled by spraying metal first, in order to prevent the electrons from aggregating at the surface. Then, the test stripe with broken section was pasted to a bronze pan with the electronic conductive adhesive, in order to observe surface morphology of the test stripe broken by impact under the scanning electron microscope.

3. Results and discussions

3.1 Epoxy resin curing behavior analysis

In the thermosetting epoxy resin system, curing behavior determines cross-linked structure of epoxy resin. Therefore, the curing behavior also determines properties of thermosetting resin. For this, curing behavior of epoxy resin shall be studied first before vacuum infusion of composites. In the experiment, glass transition temperature (T_g) of epoxy resin and curing behavior of epoxy resin system were analyzed by DSC measurements. The curing process used in the experiment is as follows: bisphenol-A epoxy resin (E-51) + methyl tetrahydrophthalic anhydride (MeTHPA) + 2,4,6-tri (dimethylamiomethyl) phenol (DMP-30) (80°C 4h+120°C 2h+150°C 2h).

The DSC curve of cured epoxy resin was as shown in Fig. 2. There was a relatively obvious exothermic peak in the figure and this was just the glass transition peak of epoxy resin (the glass transition temperature was 127.6°C).

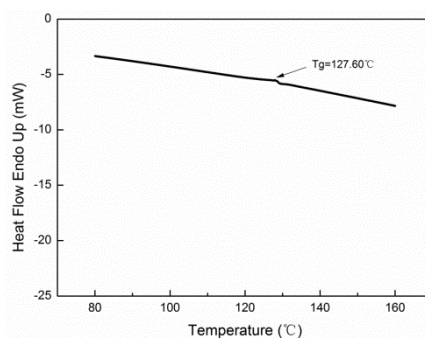


Fig. 2 DSC curve of cured epoxy resin

The DSC curve of liquid epoxy resin curing system was as shown in Fig. 3. It can be seen from the figure that there was an obvious exothermic peak at 144.5°C and no other obvious exothermic peak appeared with rising of temperature. This showed that fast curing temperature of epoxy resin system was 144.5°C. Therefore, the 80°C 4h+120°C 2h+150°C 2h heating curing mode used in the experiment is reasonable.

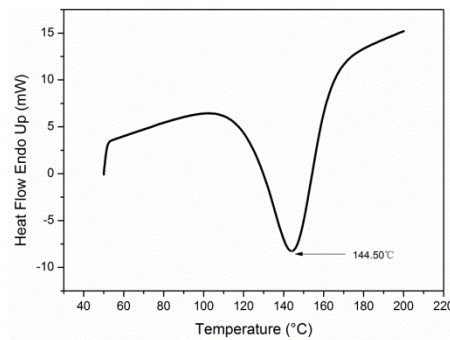


Fig. 3 DSC curing curve of liquid epoxy resin system

3.2 Thermo gravimetric analysis (TGA)

In order to determine thermal stability of MWCNT-ramie fiber/epoxy resin composite, thermo gravimetric analysis was carried on the specimens in the experiment. The thermo-gravimetric curve of composite was as shown in Fig. 4(a) and the thermo-gravimetric differential curve was as shown in Fig. 4(b). The specimens showed obvious loss in weight when the temperature was 250°C-600°C and the maximum weight loss rate was observed when the temperature was 350°C-360°C. The similar degradation process of each specimen showed that their thermo-gravimetric mechanism was the same. As shown in Fig. 4(a), thermal decomposition temperature of the composite added with MWCNT was obviously higher than that of pure ramie fiber/epoxy resin composite. As shown in Table 1, when the content of MWCNT was 0.6%, $T_{10\%}$ and $T_{50\%}$ of the composite was 177.9°C and 379.0°C respectively, increased 28.0°C and 12.5°C than the composite which was not added with MWCNT. This is because that good thermal stability of MWCNT delays thermal decomposition process of composite.

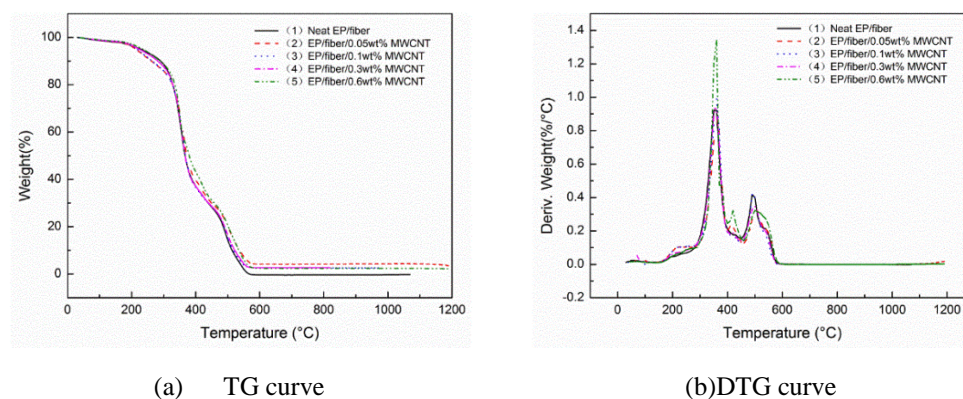


Fig. 4 TGA and DTG curve of the epoxy composites

Table 1 Thermal stability of the epoxy composites

Specimen	T _{10%} (°C)	T _{50%} (°C)	T _{max}
0wt% MWCNT	149.9	366.5	355.1
0.05wt% MWCNT	158.6	366.7	361.5
0.1wt% MWCNT	167.9	367.9	360.2
0.3wt% MWCNT	170.9	372.1	357.8
0.6wt% MWCNT	177.9	379.0	356.8

3.3 Vicat softening point analysis

The relation curve that the vicat softening point of epoxy resin-based composite varies with content of MWCNT was as shown in Fig. 5. It can be seen from the figure that vicat softening point of the composite gone up simultaneously with increasing of MWCNT content. When the load is 50N, the vicat softening temperature of the composite without MWCNT was 116.3°C. and the vicat softening temperature of the composites in which the mass fraction of added MWCNT is 0.05%, 0.1%, 0.3% and 0.6% was respectively 119.0°C, 123.7°C, 133.5°C and 159.6°C, increased up to 37.2% (see Table.2).

This showed that adding of the rigid MWCNT hardened the composite. And, the excellent thermal and impact resistance of MWCNT improved thermal properties and increased vicat softening point of the composite.

Table 2 Vicat softening point improvement of the epoxy composites

MWCNT content	0%	0.05%	0.1%	0.3%	0.6%
Improvement percent	---	2.3%	6.4%	14.8%	37.2%

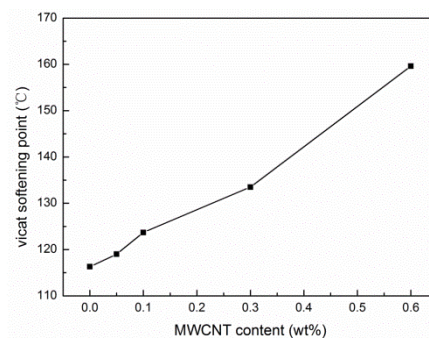


Fig. 5. Vicat softening point of the epoxy composites as a function of CNT content

3.4 Mechanical properties

3.4.1 Bending property

The bending property is an indicator that shall be usually considered during actual applications of composite. In order to explore improvement of epoxy resin-based ramie fiber

composite realized by adding MWCNT, bending property of the composite was tested. And, the obtained bending strength and breaking bending stress were as shown in Fig. 6 and Fig. 7 respectively. The relation between content of MWCNT and bending strength and breaking bending stress improvement percent of the composite was as shown in Table 3. This showed that bending strength and breaking bending stress of the composite increased with increasing of MWCNT content. This is because that, in most cases, mechanical properties of the fiber reinforced epoxy resin-based composite depends on the phase-to-phase interface structure. Adding of MWCNT enhanced the interface between epoxy resin and ramie fiber and made epoxy resin infiltrated into the fiber better. In addition, the MWCNT can be dispersed in the composite more evenly. With increasing of MWCNT content, the interface bonding strength was increased significantly, the reinforcement effect was strengthened further and mechanical properties of the composite laminate were improved accordingly.

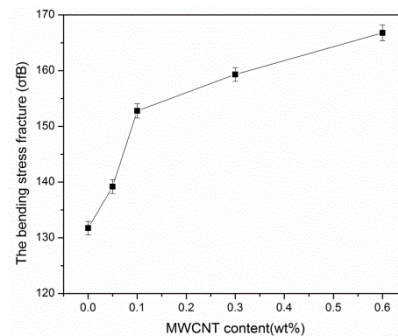


Fig. 6 Bending strength of the epoxy composites with different MWCNT content

Table 3 Bending performance improvement of the epoxy composites

MWCNT content	0%	0.05%	0.1%	0.3%	0.6%
Bending strength improvement percent	---	5.8%	13.1%	16.0%	21.7%
The breaking bending stress improvement percent	---	5.6%	17.8%	20.9%	26.6%

3.4.2 Impact property

The impact strength of the ramie fiber reinforced epoxy resin-base composites added with different MWCNT contents was as shown in Fig. 7. This showed that impact resistance of the composite was improved significantly with increasing of MWCNT content. The impact strength was the highest when mass fraction of MWCNT was 0.6%, 7.1% higher than the impact strength of the composite without MWCNT (see Table 4).

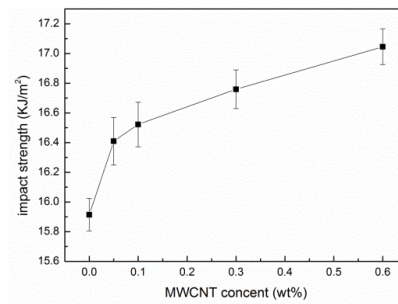


Fig. 7 Impact strength of the epoxy composites with different MWCNT content

Table 4 Impact strength improvement of the epoxy composites

CNT content	0%	0.05%	0.1%	0.3%	0.6%
Impact strength improvement percent	---	3.1%	3.8%	5.3%	7.1%

3.4.3 Broken section morphology observation

In order to analyze morphology of MWCNT-ramie fiber/epoxy resin composite impact section and distribution of ramie fiber in epoxy resin matrix, broken section of the composite laminate was tested with the scanning electron microscopy (SEM) in the experiment. The macroscopic SEM diagram of the composites in which content of MWCNT was 0wt%, 0.05wt% and 0.6wt% was as shown in Fig. 8(a), (b) and (c), respectively. The section of impacted test stripe showed that the ramie fiber distributed in the composite evenly. As shown in (a), in the composite without MWCNT, bonding between epoxy resin matrix and ramie fiber was relatively loose and the section was comparatively smooth. As shown in (b) and (c), the sections observed were rough and uneven. When content of MWCNT was 0.05wt%, many holes left by the fiber in the matrix were observed. However, the holes in (c) were less. This showed that most of the fibers in (c) broken directly and were not pulled out from the matrix. Therefore, with increasing of MWCNT content, the ramie fiber combined with matrix of the composite more closely.

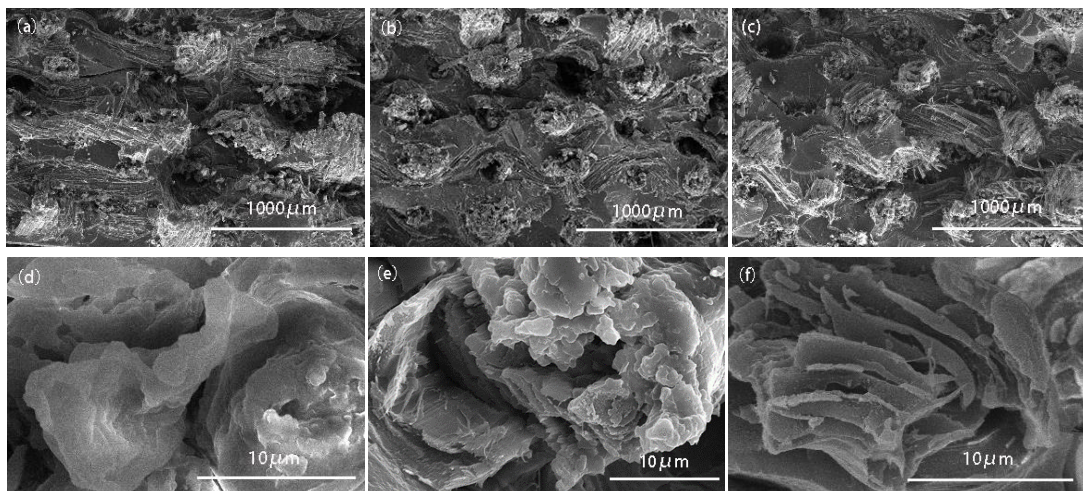


Fig. 8. Macroscopic SEM observation of broken morphology of epoxy composites: (a) pure epoxy resin composite, (b) EP/0.05wt% MWCNT composite, (c) EP/0.6wt% MWCNT composite SEM observation of epoxy composites surface: (d) pure epoxy resin composite, (e) EP/0.05wt% MWCNT composite, (f) EP/0.6wt% MWCNT composite

The SEM broken section observations of the composites in which the mass fraction of MWCNT was 0%, 0.05% and 0.6% respectively were as shown in Fig. 8(d), (e) and (f). With increasing of mass fraction of MWCNT, broken section of fibers was rougher. This showed that strength of the composite increased and less likely to be broken.

4. Conclusions

In this paper, a small quantity of MWCNT was evenly dispersed in epoxy resin system by ultrasonic dispersion and the MWCNT-epoxy resin was infused into the fiber preform by vacuum infusion to obtain the MWCNT-ramie fiber/epoxy resin-based composite. The used mass fraction of MWCNT was 0%, 0.05%, 0.1%, 0.3% and 0.6% respectively. In the paper, thermal resistance, mechanical properties, hydrophobic property and micro morphology change, etc. of the composite was researched by DSC, TGA, vicat softening point analysis, bending property, impact property and SEM test, etc. of the composite. And, the following conclusions were obtained:

1. When carrying out DSC test on the cured epoxy resin, the determined glass transition temperature was 127.6°C and fast curing temperature of epoxy resin system was determined at 144.5°C. Therefore, the 80°C 4h+120°C 2h+150°C 2h heating curing mode used in the experiment was reasonable.
2. The TG and DTG curve showed that thermal stability vicat softening point of the MWCNT reinforced composite were improved greatly. Compared with the composite without MWCNT, the vicat softening point was increased 2.3%, 6.4%, 14.8% and 37.2% when the content of MWCNT was 0.05wt%, 0.1wt%, 0.3wt% and 0.6wt% respectively.
3. Compared with the composite without MWCNT, the bending strength and impact resistance were increased by 5.8% and 3.1% when the content of MWCNT was 0.05wt%, when the content of MWCNT increased to 0.6wt%, the properties above mentioned increased by 21.7% and 7.1%. Mechanical properties of ramie fiber reinforced composite were improved effectively by adding of MWCNT.

Acknowledgments

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