

Properties of AlN-MWCNTs/epoxy Nanocomposites

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Abstract. Synergistic effect of AlN in combination with MWCNTs in AlN-MWCNTs/epoxy nanocomposites was found. Thermal conductivity of AlN-MWCNTs/epoxy nanocomposites increased obviously with the increase of AlN content. The added AlN can be filled in the networks of MWCNTs to form a more dense three-dimensional thermal conductivity network and provide more thermal conductivity channels. In addition to that, mechanical and flame-retardant properties of the nanocomposites were improved also. AlN-MWCNTs/epoxy nanocomposites presented optimum mechanical properties with the addition of 5~7.5%wt AlN powder. With the addition of AlN powder in AlN-MWCNTs/epoxy nanocomposites, its LOI value is increased from 30.8% to 43.4% and UL 94 test achieves V-0 ranking.

1. Introduction

In electronic devices, thermally conductive polymer composites have been widely applied [1]. To improve the thermal conductivity of polymers, an effective way is to incorporate the thermally conductive fillers [2,3]. Carbon nanotubes (CNTs) possess excellent properties in thermal conductivity and have been used as the fillers to fabricate polymeric composites materials. [4]. The conductivity of a single multiwalled carbon nanotubes (MWCNTs) is about 3000W/mK, for a single-walled carbon nanotubes (SWCNTs) is about 2000W/mK [5,6].

In order to improve the thermal conductivity of CNTs-nanocomposites, various filler combinations have been investigated, such as boron nitride/CNTs, hydrotalcite clay/ CNTs and graphite nanoplatelets/CNTs, etc [7~9]. In this work, aluminium nitride (AlN) and MWCNTs were incorporated into the epoxy resin to prepare AlN-MWCNTs/epoxy nanocomposites. Thermal conductivity, mechanical and flame-retardant properties of the above nanocomposites were investigated. The synergetic effects of AlN and MWCNTs were also discussed.

2. Experimental

2.1. Materials

A EP828 epoxy resin (Diglycidyl ether of bisphenol-A, Epoxy equivalent weight (EEW) of 185~195 g/mol) was obtained from Momentive Specialty Chemicals Inc., Columbus, USA. 4,4'-diaminodipheny ethane was purchased from Aladdin Reagents (Shanghai) Co., Ltd. The carbon nanotubes used were multi-walled carbon nanotubes (MWNTs, Shenzhen Nanotech Port Co., Ltd.) and their properties are listed in Table I. The particle size of AlN powder (Shanghai Chaowei Nano Technology Co. Ltd.) is about 50 nm with purity over 99.9%.



Table 1. Properties of MWNTs

Diameter	Length	Purity	Ash	Amorphous carbon	Special surface area
10~30nm	5~15 μ m	\geq 95%	\leq 0.2%	< 3%	40~300 m ² /g

2.2. Preparation of AlN-MWCNTs/Epoxy nanocomposites

In order to minimize the effects of moisture, MWNTs and AlN powder were dried at 120°C in vacuum for 24 hours at first. With the aid of solvent of acetone, the epoxy resin, MWCNTs and AlN powder were added in a vessel and put in ultrasonic bath sonicator for 2 hours at 60°C to achieve good distribution of MCNTS and AlN powder in epoxy resin. Then, the acetone in the mixture was removed under vacuum condition. After that, DDM was added to the mixture by stoichiometry and it was stirred further for 5 minutes at 90°C. The above mixture was degassed in a vacuum oven. To prepare AlN-MWCNTs/epoxy nanocomposites samples, the mixture was cast into the a mould and cured for 3 hours at 95°C, for 2 hours at 115°C, and for 2 hour at 145°C, then heated for 2 hours at 175°C. After that, to avoid stress cracking, the samples were cooled to the ambient temperature. The ratios of AlN:MCNTs:epoxy resin for AlN-MWCNTs/epoxy nanocomposites are 2.5:3:94.5, 5:3:92, 7.5:3:89.5, 10:3:87 and 12.5:3:84.5, respectively.

2.3. Characterization

Thermal conductivity of AlN-MWCNTs/epoxy nanocomposites was measured by a thermal constants analyzer (Hot Disk TPS2200, Sweden). According to the ASTM D2863-1997 standard, limiting oxygen index (LOI) measurement was conducted on an oxygen index instrument manufactured by Fire Testing Technology Co.Ltd., UK. The dimension of the sheets is 150 \times 6.5 \times 3.2 mm³. According to ANSL UL 94-1985, a UL 94 flammability meter (Fire Testing Technology Co.Ltd., UK) has been used to carry out vertical burning tests, the dimension of the sheets is 130 \times 13 \times 3.2 mm³. According to ASTM standards D 790-07e and D 638-08, a universal testing machine (Z010, Zwick/Roell Company, Germany) has been used to measure flexural and tensile properties. Six specimens for each set were tested with a 5 mm/min crosshead speed and the average value was calculated.

3. Results and discussion

3.1. Thermal conductivity of AlN-MWCNTs/epoxy nanocomposites

Fig.1 shows the thermal conductivity of AlN-MWCNTs/epoxy nanocomposites.

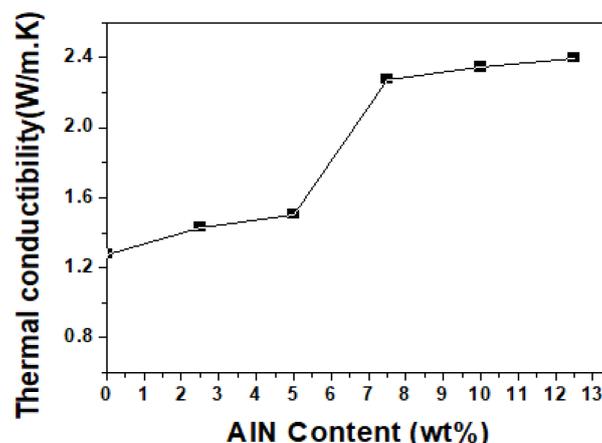


Figure 1. Thermal conductivity of AlN-MWCNTs/epoxy nanocomposites

According to Fig.1, it can be found that the thermal conductivity of AlN-MWCNTs/epoxy nanocomposites increased obviously with the increase of AlN content. When AlN content exceeds 7.5wt%, thermal conductivity of the nanocomposites is over 1.75 w/m.k.

Fig.2 shows the structural models of the nanocomposites.

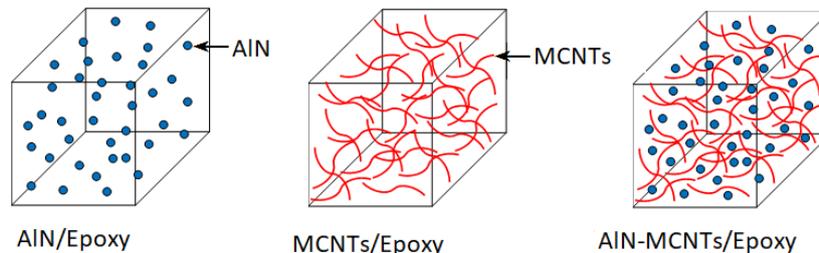


Figure 2. Structural models of AlN/epoxy, MWCNTs/epoxy and AlN-MWCNTs/epoxy nanocomposites

It is well known that the thermal conductivity of polymer composites with conductive fillers has been dominated by thermal conductivity channels and networks formed with fillers in the matrices [10]. As showed in Fig.2, the contact and overlap of dispersed MWCNTs can form thermal conductivity channels and networks. The AlN added can be filled in the networks of MWCNTs, thus to form a more dense three-dimensional thermal conductivity network and provide more thermal conductivity channels, which improved the thermal conductivity of AlN-MWCNTs/epoxy nanocomposites significantly.

3.2. Mechanical properties of AlN-MWCNTs/epoxy nanocomposites

Carbon nanotubes present the excellent mechanical properties, for example, high tensile strength and elastic modulus etc., which make them the most ideal and promising reinforce material in enhancing the mechanical properties of carbon nanotubes/polymer composites [11]. Table 2 presents the measurements of tensile strength and flexural strength of AlN-MWCNTs/epoxy nanocomposites.

Table 2. Mechanical properties of AlN-MWCNTs/epoxy nanocomposites

AlN:MCNTs:epoxy(wt)	Tensile strength(Mpa)	Flexural strength(Mpa)
0:0:100	58.9±2.1	122.3±1.5
0:3:97	76.7±1.9	171.3±3.0
2.5:3:94.5	78.2±1.7	176.5±2.7
5:3:92	81.9±2.3	182.1±2.9
7.5:3:89.5	80.3±2.7	185.2±1.8
10:3:87	73.6±2.6	176.7±2.6
12.5:3:84.5	67.3±3.1	142.8±2.9

According to Table 2, the addition of 3%wt MWCNTs results in a significant improvement of epoxy resin. The measurements in Table 1 also revealed that a synergetic effect with the incorporation of AlN in MWCNTs/epoxy resin. AlN-MWCNTs/epoxy nanocomposites presented optimum mechanical properties with the addition of 5~7.5%wt AlN powder. At the same time, the content of MWCNTs in nanocomposites is reduced. It can be inferred that the addition of a certain amount of AlN can reduce the agglomeration and winding of MWCNTs in AlN-MWCNTs/epoxy nanocomposites and improve the dispersion of MWCNTs, thus enabling the AlN-MWCNTs/epoxy nanocomposites to exhibit better tensile strength and flexural strength.

3.3. Flame-retardant properties of AlN-MWCNTs/epoxy nanocomposites

To characterize the flame-retardant properties of AlN-MWCNTs/epoxy nanocomposites, UL-94 and LOI tests were performed. The results are listed in Table 3.

Table 3. Flame-retardant properties of AlN-MWCNTs/epoxy nanocomposites

AlN:MCNTs:epoxy(wt)	LOI(%)	Total burning time (s)	Drop	Classification
0:0:100	22.4	67	No	UL94 V-2
0:3:97	30.8	50	No	UL94 V-1
2.5:3:94.5	32.1	46	No	UL94 V-0
5:3:92	35.9	39	No	UL94 V-0
7.5:3:89.5	38.3	31	No	UL94 V-0
10:3:87	40.6	23	No	UL94 V-0
12.5:3:84.5	43.4	22	No	UL94 V-0

It can be found that the LOI value of epoxy composites increased from 22.4% to 30.8% with the addition of 3wt% MWCNTs. Three-dimensional network structure in epoxy matrix can be formed by adding a certain amount of MWCNTs. During the combustion of MWCNTs/epoxy nanocomposites, a protective char network layer covering the sample surface is formed that acts as insulative barrier and resulting in a significant increase in the flame retardant properties.

In addition to that, combination of AlN and MWCNTs in epoxy nanocomposites shows a positive effect on both LOI and UL94 test: LOI value is increased from 30.8% to 43.4% and UL 94 test achieves V-0 ranking with the further addition of AlN powder. Compared with individual MWNTs component filled sample, the coexistence of MWNTs and AlN can reduce the flammability of the nanocomposites more efficiently, which indicated that the coexistence of AlN and MWNTs in the composites can form a more effective network structure, which is responsible for the improved flame retardancy for AlN-MWCNTs/epoxy nanocomposites. Similar synergetic effect has also been found in ABS/clay/MWCNTs nanocomposite [12].

4. Conclusion

The introduction of AlN and MWCNTs to the epoxy resin matrix is an effective methods for improving thermal conductivity, mechanical and flame-retardant properties of AlN-MWCNTs/epoxy nanocomposites. Synergistic effect on improving the related properties was found between AlN and MWNTs. The thermal conductivity of AlN-MWCNTs/epoxy nanocomposites increased obviously with the increase of AlN content. The AlN added can be filled in the networks of MWCNTs, thus to form a more dense three-dimensional thermal conductivity network and provide more thermal conductivity channels, which improved the thermal conductivity of AlN-MWCNTs/epoxy nanocomposites significantly. At the same time, mechanical and flame-retardant properties of the nanocomposites were improved also. AlN-MWCNTs/epoxy nanocomposites presented optimum mechanical properties with the addition of 5~7.5%wt AlN powder. With the addition of AlN powder in AlN-MWCNTs/epoxy nanocomposites, its LOI value is increased from 30.8% to 43.4% and UL 94 test achieves V-0 ranking.

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