

The physical property of epoxy/graphene nanoplatelets composites prepared by ball milling

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Abstract. Epoxy/graphene nanoplatelets(EP/GNs) composite was prepared by ball milling(BM), using diglycidyl ether of bisphenol A(DGEBA)as matrix, Diethyltoluene diamine(DETDA) as curing agent, GNs as thermal conductive filler. The mechanisms and influence of different BM time to exfoliate layered GNs and compound with Epoxy resin were investigated. The morphology, thermal conductivity of EP/GNs composite were investigated too. It showed that BM was an effective method to prepare EP/GNs conductive composite of low loading level by avoiding aggregation of GNs.

Introduction

Epoxy (EP) is a kind of thermosetting resin materials with characteristics of excellent physical chemical properties and moderate cost, widely used as adhesive, coating, encapsulating materials and so on. However, Its thermal conductivity is very low(about 0.2w/m.k), cannot be effective release the high quantity of heat, so the application in the field of electronic information is limited. The thermal conductive EP composite have attracted lots of attentions in recent years. Several thermal conductive fillers such as graphite[1],carbon black(CB)[2-3],carbon nanotube(CNT)[4-7], polyaniline (PANI) [8-9], graphene nanoplatelet(GNs)s have been reported for the thermal conductive EP. GNs, is also called as Graphite nanosheets, has advantages in forming thermal conducting networks in polymer matrices for the high aspect ratio. However, viscosity of EP's raw materials is very large, GNs is easy to aggregate and can't complete disperse while stirring. Ball milling (BM) which is a technique in powder industry, can be used for exfoliate and disperse GNs efficiently in suitable solvent[10-12]. Fig.1. shows the schematic illustration of the process for in situ synthesis EP/GNs composite by BM: 1, GNs is exfoliated and dispersed in EP's raw materials by shear forces from rotating balls; 2, GNs is equably dispersed in EP matrix.

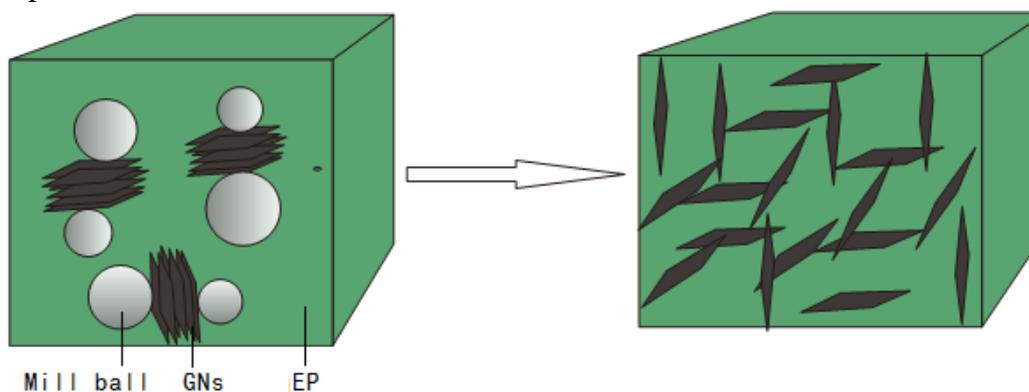


Fig. 1. Schematic illustration of the process for synthesis EP/GNs composite by BM

In this paper, EP/GNs thermal conductive composite was prepared by BM using GNs as thermal conductive filler, diglycidyl ether of bisphenol A(DGEBA)as matrix and Diethyltoluene diamine(DETDA) as curing agent and acetone (ACE) as solvent.

Experimental

Materials

GNs(k-180) with the thickness of 30~80nm, diameter of 5~20 μ m, were provided by Xiamen KNANO Graphene Technology Corporation Limited (China). DGEBA (6002, The epoxy value =0.48eq/100g) and DETDA were provided by Shanghai Resin Factory Corporation Limited (China). ACE were provided by Aladdin Chemistry Corporation Limited (China).

Preparation of EP/GNs thermal conductive composite

The EP/GNs thermal conductive composite was prepared by BM. The formula was devised as

$$W=(M/Hn)\times Ev=178.3/4\times 0.48g=21.4g$$

W is the quality of DETDA for Every 100 g DGEBA

M is the molecular weight of DETDA

Hn is the number of active hydrogen atoms on DETDA molecules

Ev is the epoxy value of DGEBA

First, the premixture with GNs, 10g DGEBA and 15g ACE was placed in a 100 ml grinding bowl with 200g zirconia milling beads, BM for some hours such as 2h, 6h, 10h, 12h, 16h, 20, 22h and 24h in a planetary ball mill with 300 rpm rotational speed at room temperature. Then the EP premixture was dried in vacuum oven(60 $^{\circ}$ C) for 24hr till the weight no decreased, mixed with 2.14g DETDA in the condition of 1500 rpm for about 5min using stirrer, poured into a silicon rubber mold to react at 135 $^{\circ}$ C for 1.5hr, then 170 $^{\circ}$ C for 2.5hr. Lastly, the resulted composite slices were directly removed from the mold before the subsequent measurement. The EP/AlN composite was prepared in the same process as contrast. The process of fabrication EP/GNs thermal conductive composite by BM is shown in Fig.2.

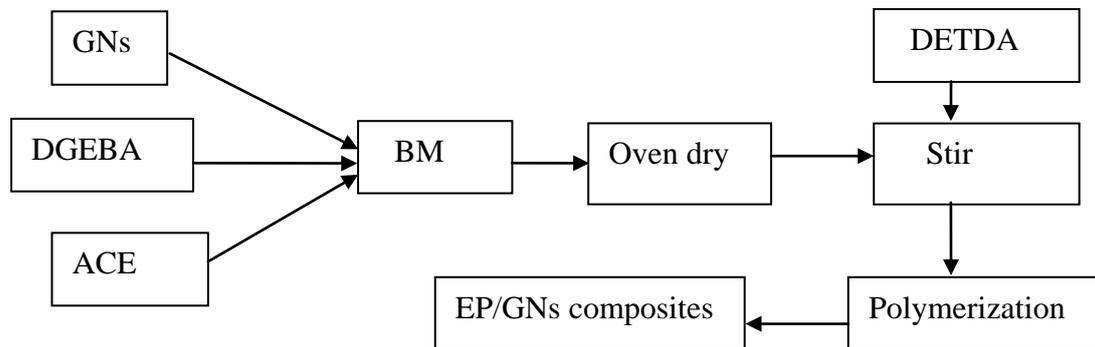


Fig. 2 Process of fabrication of EP/GNs thermal conductive composite by BM

Measurement of Sample

HITACHI S-4800 field-emitting scanning electron microscope at an operating voltage of 5 KV was used to perform Scanning electron microscopy (SEM), the sample's surfaces were vacuum coated with a thin gold layer before testing. D8-Advance instrument using Cu-K α radiation generated at a voltage of 40 kV with a current of 40 mA to scan the sample surface from 2 $^{\circ}$ to 40 $^{\circ}$ at a rate of 2 $^{\circ}$ per minute was used to record X-ray diffraction (XRD) patterns. The thermal conductivity(k,W/m.K) of the samples (diameter: 12.7 mm, thickness: about 2 mm) was calculated by the product of thermal diffusivity (δ , mm 2 /s), specific heat (C, J/g.K), and bulk density (ρ , g/cm 3): $k=\delta\times C\times\rho$ (1) where δ and C were measured using an LFA447 light flash system (NETZSCH, Germany). Before testing, we also sprayed the Graphite coating on the sample's surface following the LFA447 light flash system's request.

Results

Morphological analysis

The morphology of the EP/ GNs composites with 10wt% GNs prepared by BM 0h and 12h is shown in Fig.3. we can see that GNs can be exfoliated efficiently in EP while elongating the BM time. The diameter of GNs without BM is about 10 μ m, the diameter of GNs while BM 12h is about 5 μ m.

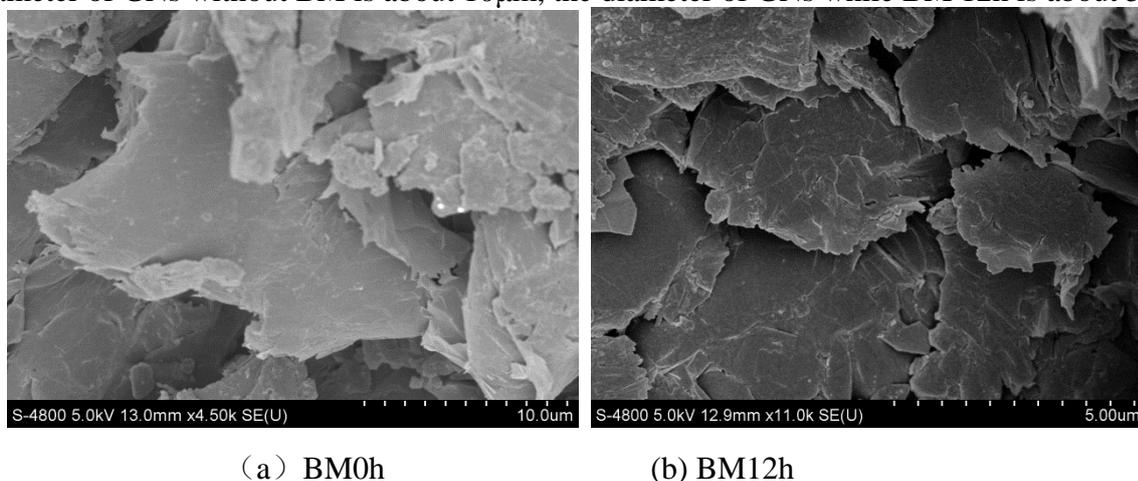


Fig. 3 SEM micrographs of EP/ GNs composites prepared by BM for different hours

XRD analysis

The X-ray diffraction patterns of EP/ GNs composite with 5wt% GNs by BM 0~12h is shown in Fig.4. In the case of EP/GNs composite, there is the characteristic strong diffraction peak (about 18 $^{\circ}$) of EP's hard segment crystallizing, and another characteristic weak diffraction peak (about 6 $^{\circ}$) of EP's soft hard segment crystallizing. There is the characteristic 002 sharp diffraction peak (about 26 $^{\circ}$) of graphite, while EP/ GNs composites with 5wt% GNs by BM 6h&12h shows a characteristic 002 weak diffraction peak of graphite (the peak's intensity is obviously lower than that by BM 0h), which indicates that GNs' multi-layered structure was reduced significantly by BM.

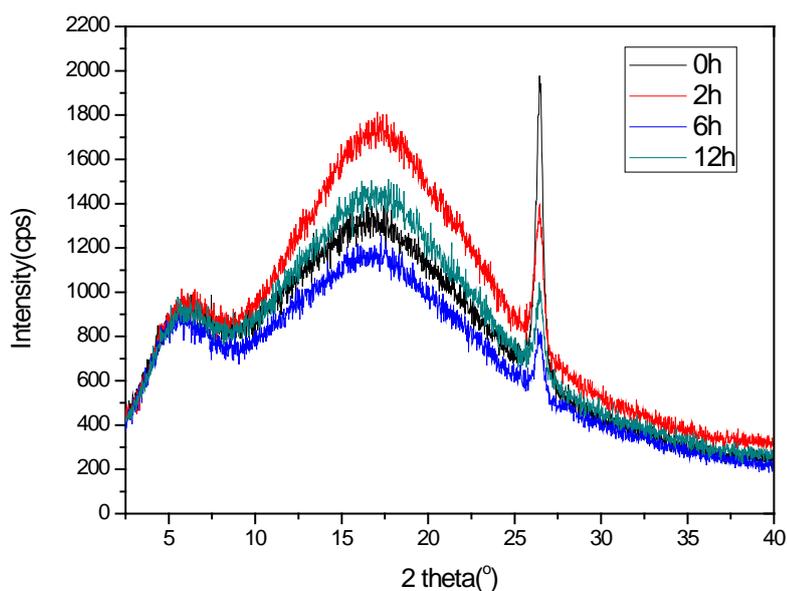


Fig.4 XRD patterns of GNs, EP, EP/ GNs composite

Thermal conductive properties

The thermal conductivity of the EP/GNs composite as a function of the GNs weight content is shown in Fig.5. The addition of conducting fillers and temperature significantly increase the thermal conductivity of composite. While the raw material of the composite can't be mixed uniform if the filler's content is more than 25%, so we have not gone beyond the particular value. The above results is attributed to the much high aspect ratio of GNs, sheet-like filler will result in forming thermal conducting networks in polymer matrices.

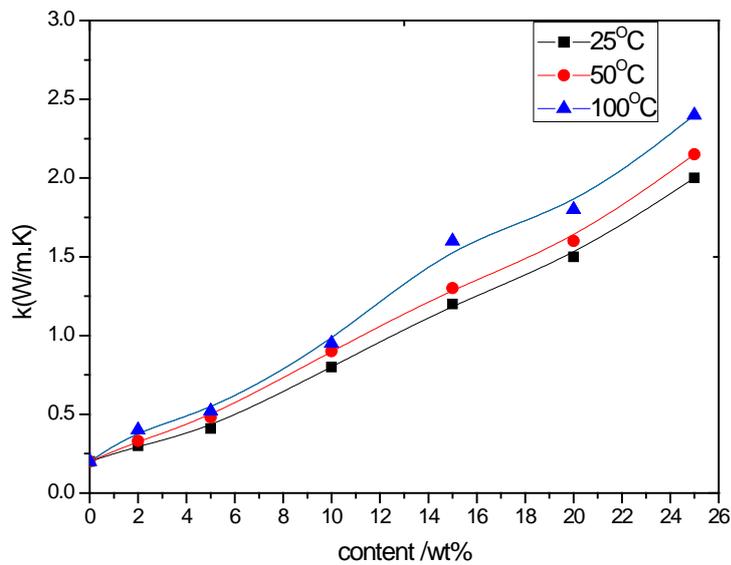


Fig.5 Thermal conductivity of composite as a function of the filler's content

The effect of BM time on thermal conductivity of EP/ GNs composite with 5wt% GNs is shown in Fig.6. The thermal conductivity increased sharply with the increasing BM time to 12h, then attained a steady state till 22h, then dropped after 22 hrs. The main reason is that GNs can be exfoliated and dispersed in EP matrices while increasing the BM time from 0h to 10h, keep a steady state from 12h to 22h, thermal conductivity will drop after 22 hrs because ball milling too long also may destroy the structure.

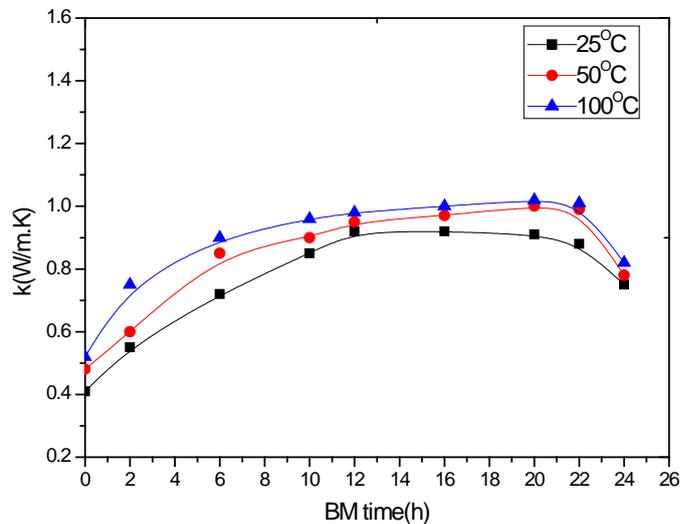


Fig.6 The effect of BM time on thermal conductivity of composite

Conclusion

EP/GNs thermal conductive composite was prepared by BM, using GNs as thermal conductive filler, diglycidyl ether of bisphenol A(DGEBA) as matrix and Diethyltoluene diamine(DETDA) as curing agent and acetone (ACE) as solvent. GNs can be exfoliated and dispersed efficiently by BM 12h and equably located in the EP phase. Due to the moderate cost and simply operating(BM at room temperature) and good thermal conductive property, this kind of EP/GNs thermal conductive composite can be extensive used in encapsulating materials and so on.

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