Influence of activated carbon fibres with different specific surface areas on the thermal conductive and electrical insulating properties of polyamide-imide composites

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Abstract: In this study, the authors reported an influence of activated carbon fibres (ACFs) with different specific surface areas on the thermal conductive and electrical insulating properties of polymeric composites. Here, the polyamide-imide composites were obtained via solution blending and cured method. The composites exhibited thermal conductivity (TC) up to 0.62 W·m⁻¹·K⁻¹. In addition, the composites were still insulating, having an electrical resistance of 0.7 MΩ. The experimental results suggested that the mechanical and electrical insulating properties decreased with the increasing of the specific surface area of the ACFs. Meanwhile, it was found that the introduction of boron nitride was conducive to the TC and electrical insulating properties of the polymeric materials.

1 Introduction

Polymer composites based on various carbon fillers offer affected performance and opportunities for commercial applications since carbon materials act as fillers in composite to affect the mechanical, electrical and thermal properties [1–4]. High temperature thermoplastic materials have attracted great attention in recent years since, in addition to the classical advantages of thermoplastic polymers (recyclability, resistance to chemicals, solvents and radiation, ability to be re-melt and reprocessed etc.), they generally offer enhanced mechanical properties (high level of toughness, strength, stiffness and resistance to fatigue) [5]. Moreover, they keep their physical properties at high temperatures and exhibit thermal stability even in the longer run.

Carbon fibres (CF) have been harnessed in optical, electronic and catalytic devices because of their well properties. The main studies were performed on CF filled poly(phenylene sulphide) [6], polyetheretherketone [7], polyimide [8] matrices. Activated CF (ACF) [9] is some kind of CF (such as phenolic fibre, polyacrylonitrile fibre, asphalt base fibre etc.) through high temperature activation, make it surface to produce nanoscale pore size, increase the specific surface area, thereby changing its physical and chemical properties. ACF has a number of significant advantages over the traditional CF. These include high specific surface area and adsorption capacity, as well as very high rates of adsorption from the gas or liquid phase. ACFs are currently available commercially in the form of felts, fibre tows and fabrics.

The insulating property is critically important because they pay a role of electrical insulator [10, 11]. Graphene were proved to be a good choice as thermal conductive fillers for thermal transfer due to their superb thermal conductivity (TC), but it also has high electrical conductivity. Ma et al. [12] reported that the introduction of graphene could improve the thermally stability obviously, but the electrical conductivity was also increased to 2.1 × 10⁶ S/m. Chen et al. [13] reported that the nanocomposites exhibit TC enhancement of about 1400% at a low boron nitride (BN) loading, and the epoxy nanocomposites were still highly insulating.

In this work, we reported the effect of ACF with different specific surface areas on the mechanical and electrical insulating properties of polyamide-imide (PAI) composites. Furthermore, we found that the properties were the best when the specific surface area of the ACF was the lowest. Then a reinforced effect of BN coating on the surface of the ACF with the lowest specific surface area on the enhancement of the TC and electrical insulating properties of composites was studied and described.

2 Experiment section

2.1 Materials and equipment

ACF was provided by Jiangsu Sutong Carbon Fiber Co., Ltd (Jiangsu, China), the fibre diameter of ACF is in the range of 5–20 μm and the average size of the ACF is in the range of 1.0–4.0 nm. h-BN powder (1 μm) was purchased from Qingdao Jinrilai Co., Ltd. (Qingdao, China). PAI was provided by Shanghai Huayi Group Technology Research Institute (Shanghai, China). Dimethylformamide (DMF, 99%) was purchased from Sigma-Aldrich Co. LLC. All the reagents and solvents were used without further purification. The tip-type sonication machine (Bilon-1000Y) was manufactured by Shanghai Bilon Instrument Manufacturing Co., Ltd. (Shanghai, China). Ultrasonic bath SK5210LHC was from Shanghai Kudos Ultrasonic Instrument Co., Ltd. (Shanghai, China). Centrifugal machine (TGL-10C) was from Anting Scientific Instrument Factory (Shanghai, China). Vacuum oven (DZF-6050) was from Shanghai Jinghong Experimental Equipment Co., Ltd. (Shanghai, China).

2.2 Preparation of PAI/ACF

The ACFs were dried at 100°C before using. The polymeric composites were prepared by solution blending and cured method [14]. In a typical procedure, PAI solution was prepared by dissolving 1.5 g PAI in 10 mL DMF solution. Then, ACFs were mixed in PAI solution and vacuum in a vacuum oven, and then the blending was cured in an oven at 80°C for 48 h. The as-prepared samples were designated as PAI/ACF.

2.3 Preparation of BN nanosheets (BNNSs)

BNNSs were prepared through exfoliation of h-BN powder with a typical sonication process [15]. BN powder (1 g) in DMF (40 mL) was tip-type sonicated to disperse the powder for 10 h. The solution was then centrifuged at 8000 rpm in order to remove residual large-size BNNSs particles. The liquid supernatant was collected subsequently and around 2 mg BNNSs could be routinely from 1 g BN powder as a precursor.
2.4 Preparation of PAI/ACF/BNNSs

BNNSs/DMF was used as the precursor in the preparation of the ACF/BNNSs. The ACFs were immersed into the BNNSs/DMF solution to be ultrasonically treated for 10 min, and then stand for 30 min at room temperature. At the end, dried at 100°C in the atmosphere of air for 1 h. These solution dipping and ultrasonic treatment was repeated for three times to increase the contain of BNNSs. The polymeric composites were prepared by solution blending and cured method.

2.5 Characterisation

The specific surface areas were measured on a Quantachrome instrument (Autosorb IQ2-2MP-C). The Brunauer–Emmett–Teller (BET) specific surface area ($S_{BET}$) was calculated by BET theory. Prior to each measurement, the samples were degassed at 300°C under N$_2$ atmosphere for 3 h. The morphology and microstructure of ACFs were investigated by scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan), transmission electron microscopy (TEM, 220CX, JEOL, Japan), Fourier-transform infrared (FTIR, AVATAR370, Nicolet, USA), Raman spectra (INVIA, Renishaw PLC, UK). The TC, electrical resistance and mechanical properties of the composites were performed on a Netzsch STA409PC simultaneous thermal analyser, four-probe resistivity tester and INSTRON 5569A Materials Testing System, respectively.

3 Results and discussion

3.1 Structural characterisation

$S_{BET}$ of the ACFs is obtained and the results are shown in Fig. 1. The specific surface areas of ACF-1, ACF-2, ACF-3 and ACF-4 were 1052.4, 1427.0, 1441.1 and 1547.1 m$^2$/g, respectively. Results showed that ACFs have high specific surface area.

The morphologies of the samples were observed by SEM. The pristine ACFs were shown in Figs. 2a–5a, which showed smoothly fibrillar in shape. From the SEM images, we could see that the diameter of ACF-1 was the lowest, about 6 μm and the diameter was increased with the increasing of the specific surface area of the ACF. The corresponding fracture surface of the PAI/ACF was also investigated. It can be observed that there were some notable differences in the fracture surfaces between the addition of different specific surface area ACFs. In the case of the PAI/ACF-1, the PAI remain generally well bonded to the fibres indicated that the ACF and PAI closely joined together and formed a complete whole with the PAI (Fig. 2b). However, in the case of PAI/ACF-2 and PAI/ACF-4, the gaps between ACF and PAI were obviously (Figs. 3b and 5b). As for PAI/ACF-3 (Fig. 4b), although there are no obvious gap between ACF and PAI, the ACF was destroyed seriously because of the introduce of PAI and the same phenomenon was also found in the PAI/ACF-4.

The distribution of the functional groups upon the ACF was studied by FTIR analysis (Fig. 6a). The ACF with different specific areas showed that an intense and broad at 3434 cm$^{-1}$ corresponds to –OH stretching vibrations in the adsorbed H$_2$O by ACFs. Intense bands at 1643 cm$^{-1}$ are observed for the two samples, which are associated with –C = O in a six-membered ring or aromatic ring [16, 17]. The broad bands present in the two spectra at 988 cm$^{-1}$ are due to the stretching C–O vibrations [18, 19].
Fig. 6 shows the Raman spectra of the ACFs studied in this work. In all cases, the spectra exhibited the same appearance, i.e. two well-resolved bands, namely D (\(\sim 1330 \text{ cm}^{-1}\)) and G (1580 cm\(^{-1}\)). All these bands have been previously identified in CF and other carbon materials [20–22].

The Raman peak of BNNS at 1369 cm\(^{-1}\) blue shift to 1373 cm\(^{-1}\) (Fig. 6c), which was caused by a hardening of the corresponding
E2g phonon mode in layers, which indicated that the BNNSs were exfoliated into few layers [23, 24].

3.2 PAI/ACF composites

As mention above, high filler loading may result in the loss of the mechanical integrity of the polymer materials. In this work, we found the specific surface area of ACF have an effect on the mechanical properties of the composites. Fig. 7 displayed tensile-stress-strain curve, Young's modulus and tensile strength of composites. The results (Figs. 7c and d) showed that Young's modulus and tensile strength of pure PAI were 2588.78 and 53.77 MPa, respectively. The values significantly decreased with the increasing of the specific surface area of ACFs. It was obvious that from PAI/ACF-1 to PAI/ACF-4, Young's modulus decreased from 1513.83 to 111.14 MPa, and tensile strength decreased from 53.77 to 1.02 MPa.

On the one hand, this trend was because the introduction of ACFs generates pores which reduce the fibre strength. On the other hand, the higher specific surface area was more likely increased the crack between the filler and polymer, which finally made the decreased of the composites with different specific surface area ACFs. It should be noted that the mechanical properties of composites were the largest when the specific surface area of the ACF was 1052.4 m²/g.

For electrical insulation applications, a high enough electrical resistance of the composites is important. Fig. 8 presents the electrical resistance of the composites. The experimental results demonstrated that the values significantly decrease with the increasing of the specific surface area of ACFs. It was obviously that from PAI/ACF-1 to PAI/ACF-4, the electrical resistance decreased from 495.15 to 1.31 kΩ, and the electrical resistance of PAI/ACF-1 was ~0.5 MΩ, indicating that it was highly insulating. The results showed that the electrical insulation properties of composites were the highest when the specific surface area of the ACF was 1052.4 m²/g.

3.3 PAI/ACF/BNNSs composites

BN was proved to be a good choice as thermal conductive and electrical insulate fillers due to their super TC and electrical insulating properties [25–27]. Here, we chose ACF-1 as the filler and introduce BNNSs coating on the surface of ACF-1 through solution dipping and ultrasonic treatment. Fig. 6c shows the morphologies of BNNSs. BNNSs were smooth hexagonal. The Raman peak of BNNSs at 1369 cm⁻¹ blue shifted to 1373 cm⁻¹ which was caused by a hardening of the corresponding E2g phonon mode in layers, indicating that the BNNSs were few layered [23, 24] (Fig. 6d). The morphologies of the fracture surface of the PAI/ACF/BNNSs composite were observed by SEM (Fig. 9a). It can be observed that some notable BNNSs fine particles in almost uniform size were found on the surface of PAI and ACF. It indicated that the BNNSs, ACF and PAI closely joined together and formed a complete whole. Fig. 9b gives the TC of the
composites by transient laser flash technique. The TC of the pure PAI was only about 0.13 W·m⁻¹·K⁻¹. With the introduction of ACF-1, TC of the PAI/ACF increased consistently. The TC of PAI/ACF reached 0.49 W·m⁻¹·K⁻¹. After further compounded 0.4 wt% BNNSs, we can see that the PAI/ACF/BNNSs results in a dramatic enhancement of TC of the composites reached 0.62 W·m⁻¹·K⁻¹ in comparison with the pure PAI. The results showed that BN had an effect with ACF for improving the TC of the composites and indicating that the introduced BNNSs contribute to the enhancement of thermally conductive pathways in the composites.

Fig. 9c gives the electrical resistance of the composites. One can see that the addition of BNNSs results in a dramatic enhancement of electrical resistance of the composites reached 0.7 MΩ in comparison with the pure PAI and PAI/ACF. The results showed that BN had an effect with ACF for improving the electrical insulating of the composites and indicating that the introduced BNNSs prevent the formation of conductive pathways in the composites.

4 Conclusion

In this work, we achieved an influence of ACF with different specific surface areas on the thermal conductive and electrical insulating properties of polymeric composites. The introduce of ACF could effect the mechanical and electrical properties of the composites and we found that the ACF with the lowest specific surface area had the best performance. Young's modulus of PAI/ACF-1 was 1513.83 MPa and the electrical resistance was 495.15 kΩ. We further introduce low BN loading coating on the surface of the ACF and make high TC up to 0.62 W·m⁻¹·K⁻¹ and the composites were still insulating, having an electrical resistance of 0.7 MΩ. The obtained polymeric materials have potential applications in thermal management application.

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6 References

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