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Tribological performance of carbon nanotubes-alumina hybrid/epoxy composites

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An experimental investigation is conducted on hybrid nanofillers of multi-wall carbon nanotubes (MWCNTs) and alumina (Al_2O_3) on the tribological performance of pure epoxy nanocomposites for various weight fraction of 0.5, 1.0, 1.5, 2.0 and 2.5wt.% hybrid nanofillers. The hybrid ratio of MWCNTs-Al_2O_3 is maintained at 1:4. MWCNTs- Al_2O_3 hybrid reinforced pure epoxy matrix composites were prepared by sonication process. Wear and friction tests against steel disc show that, the introduction of 0.5, 1.0 and 1.5wt.% of MWCNTs-Al_2O_3 hybrid nanofillers will increases the specific wear resistance and decrease the friction coefficient. At an optimal hybrid nanofillers, i.e., 1.5wt.% addition of hybrid nanofillers in pure epoxy result in 85%, 82% and 81% improved wear resistance during low (30N), moderate (45N) and high (60N) loading conditions respectively than that of pure epoxy. Further addition of nanofillers content will lead to increase in specific wear rate and friction coefficient was observed. Microstructure studies demonstrated the homogeneous dispersion and aggregation of MWCNTs and alumina in the host matrix. Field emission scanning electron microscopy (FESEM) is used to study the worn surface morphology.

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1. Introduction

Epoxy resins have been used extensively in broad variety of industrial applications due to their excellent mechanical properties, good dimensional stability, improved chemical resistance and modification versatility make epoxy more attractive [1-3]. In recent years more attention devoted to improve the wear resistance of epoxy, because large quantity of epoxy used as matrices for composites to reduce the wear phenomena [4-8]. Nanotechnologies are new approaches of research and development involving precise control of molecules and atoms to develop novel material with unique deserving properties. The incorporation of nanoparticles in polymer matrix has been impressive as they predominantly improved the properties of polymer materials [9]. CNTs may become predominant reinforcing materials for innovating new class of nanostructured composites due to their light weight, attractive mechanical and excellent thermal properties [10-12]. However, the main challenge is to transmit the significant properties of CNTs can only be realized in composites by combining the appropriate processing method and optimal quantity of materials [13-14]. Alumina (Al_2O_3) is cost effective ceramics and widely used materials in the group of engineering ceramics. It posses high hardness, excellent mechanical property and superior high stiffness and thermal properties [15]. Tian et al. reported that homogenious distribution of MWCNTs/alumina hybrid in a High density polyethylene matrix achieved improved young's modulus and tensile strength [16]. Zakaria et al. studied the tensile and thermal properties of CNTs-Al_2O_3hybrid epoxy composites. Their results showed that the tensile modulus, strength, thermal conductivity and glass transition temperature value were improved compared to neat epoxy [17]. Khashaba in conventional and ultrasonically dispersion of alumina nanoparticles into epoxy matrix, he reported that in the conventional processing method structural properties were improved [18]. Li et al. reported that CNTs were synthesized and dispersed with the help of the alumina 'vehicle' in mg matrix and improvement in the mechanical properties were achieved [19]. Yue et al. concluded that better dispersion of hybrid filler in the epoxy matrix will improve the mechanical and electrical properties [20]. Wear in polymer materials is closely attributed to the mechanical and thermal properties of polymer. Recently alumina-CNTs has been used as a hybrid component of the polymer matrix to develop high performance multifunctional advanced composites materials. Shen et al observed that the tribology performance of carbon nanotube – graphane oxide hybrid epoxy composites will increase the friction coefficient and it will lead reduction in the specific wear rate [21]. Similarly, Fu et al. reported that the natural rubber nanocomposites containing hyper branched polyster modified Al_2O_3 and carbon blacks gave the best abrasion resistance and thermal stability.

In this study, we fabricated epoxy matrix composites reinforced by a nano scale hybrid (MWCNTs/Al_2O_3) in which the MWCNTs are evenly dispersed and strongly bonded with Al_2O_3 particles. Combining MWCNTs with

Al_2O_3 the following advantages have been recognized during these investigations. First, both MWCNTs and Al_2O_3 nanoparticles combination in a composites exhibits improved mechanical properties. Second, Al_2O_3 may be helpful with homogeneous dispersion of MWCNTs in neat epoxy. In which the ceramic act as 'vehicles' for MWCNTs to easier dispersion during ultrasonication. The foremost problem addressed by the researchers in the CNTs dispersion (or) form large aggregate in the matrix may be overcome by means of using surface pretreated MWCNTs. Tian and He reported that Functionalized MWCNTs surface form a mechanical interlock with Al_2O_3 to improve matrix properties.

Many investigations are paying attention on further improving polymer materials using nanofillers, and in particular hybrid composites to enhance the tribological properties as well as obtaining multi – functional materials. The last few year's publications elaborately discussed on improvement in the mechanical and thermal properties of MWCNTs-Al_2O_3 hybrid into the polymer matrix and limited investigation reported on the prediction of tribological performance and optimum weight of hybrid composites. Therefore the potential advantage of the MWCNTs – Al_2O_3 hybrid particles is employed to improve the tribological properties of the pure epoxy and the optimum weight of MWCNTs- Al_2O_3 hybrid composites also discussed.

2. Materials and methods

2.1 Materials

The epoxy resin Diglycidyl Ether of Bisphenol A used in this work was commercially available. The multiwall carbon nanotubes synthesize by the chemical vapour deposition (CVD) method and functionalized with COOH for to enhance the wall surface. The MWCNTs had an average outer diameter of 20-30 nm, length 15µm, number of walls 7-8, and specific surface area of 180-200 m^2g^{-1}. The alumina nano filler used in this study was commercially available alumina oxide nano powder. The physical features of this nano powder are as follows: < 100 nm particle size, gamma phase, specific surface area of 350- 420 m^2 g^{-1} and melting point 2100ºC (materials supplied by Bottomup Technologies, India).

2.2 Preparation of MWCNTs-Al_2O_3 hybrid powder

The quantify amounts of MWCNTs were dispersed in sodium dodecyl sulphate containing acetone solution through sonication process. The process continues for 1.5 hour with the power of 450- 500 W and the frequency range between 10-15 KHz. The alumina nano powder was added and the sonication continued for another 30 min. The liquid suspension was transferred to ball milling machine and milled for 12 hours at 200 rpm. The milled suspension mixture was dried at 100^oc for 8 hours in an oven and then transferred to a vacuum chamber at 75^oc for 48 hours for complete removal of dispersion. The dried mixture was spread in a vacuum chamber plate and drying process continued at the same temperature for another 24 hours for complete removal of the solvent. The MWCNTs-Al_2O_3 mixed in a weight ratio of 1:4.

2.3 Preparation of MWCNTs-Al_2O_3 epoxy nanocomposites

MWCNTs-Al_2O_3 hybrid powder were dispersed in the epoxy resin with the various weight percentage of 0.5, 1.0, 1.5, 2 and 2.5wt.% using an ultrasonic mixture at the frequency range of 25 KHz for 30 min. The mixture temperature was maintained between 50^oc to 60^oc during the sonication process. The obtained mixture was kept in the vacuum chamber for 30 min to remove the micro air bubbles. The curing agent Araldite HY951 was added in the volume ratio of 10:1. The mixed suspension was poured into the acrylic plastic mould of 100 mm length and 6 mm diameter for wear test. The mould was kept in the oven at 100^oc for 6 hours for curing. This process continued for all the samples.

2.4 Wear test

Wear test were carried out by a TR20 pin on disc machine using the following conditions. A sliding load of 30N (low), 45N (moderate) and 60N (high), sliding speed of 200 rpm, experiment running time 30 min at room temperature under dry sliding condition. The size of the wear pin was 30 mm length and 6mm in diameter. A disc of 100Cr6 steel was served at the counterpart. The pins contact surface was polished with fine emery to ensure uniform contact with the rotating counterpart. The machine was connected with software and hardware unit to initialize and set the parameter of disc speed, load and time. The pure epoxy and epoxy/hybrid nanocomposites pin sample was initially weighed to an accuracy of 0.1mg in an electronic balance. The wear rate and the friction coefficient were recorded throughout the experiment. The difference between the initial and final weight is the measure of sliding wear loss. The surface of the sample and steel counterpart were cleaned with a soft paper which is socked in acetone and dried thoroughly before and after test. The worn surface of pure epoxy and epoxy-hybrid nanocomposites pin samples was examined by field emission scanning electron microscopy (FESEM) after being coated with a thin gold layer.

3. Results and discussion

The variations of specific wear rate of the pure epoxy and epoxy/hybrid nanocomposites are plotted as a function of the sliding distance as show in Fig. 1(a-c). The results plotted as the average values recoded in the steady state during the wear process. The reduction in specific wear rate was achieved by adding considerable amount of MWCNTs-Al_2O_3 hybrid nanofillers. The specific wear resistance of the pure epoxy improved drastically after the incorporation of only 0.5wt.% and 1.0wt.% of MWCNTs-

Al_2O_3 hybrid nano filler into the epoxy matrix. Then the specific wear resistance was further improved by about 85%, 82% and 81% during low, moderate and high load once 1.5wt.% of MWCNTs-Al_2O_3 hybrid nano filler is added. Similarly, the coefficient of friction of the composites is decreased once the hybrid nano fillers added. The significant reduction in the friction coefficient was achieved in the 1.5wt.% hybrid nanocomposites. This can be due to the formation of thin transfer film on the sample worn surface and counterpart. However, MWCNTs posses self lubricant properties and act as load bearing element in composites. Similarly, alumina form a tribo layer on the counter face to protect the composites worn surface from the hard asperity. These perceptions have been used to developed multifunctional wear resistance materials. From the experimental investigation it is clear that MWCNTs self lubricating properties and alumina tribo layer formation is responsible for lower wear rate. Further increase of hybrid nano filler into 2.0wt. % exhibited improved wear resistance as that of pure epoxy and poor performer than 1.5wt.% hybrid nanocomposites. Further increasing hybrid nano filler 2.5wt.% in to matrix will lead increasing wear loss due to fracture occurred on the worn surface. This is stated that excessive addition of MWCNTs-Al_2O_3 hybrid nano filler form a localized bundle and fillers failed to act as a load bearing element. The morphology of worn surface of the flatted pin surface was analyzed by field emission scanning electron microscopy and possible wear mechanism was discussed.

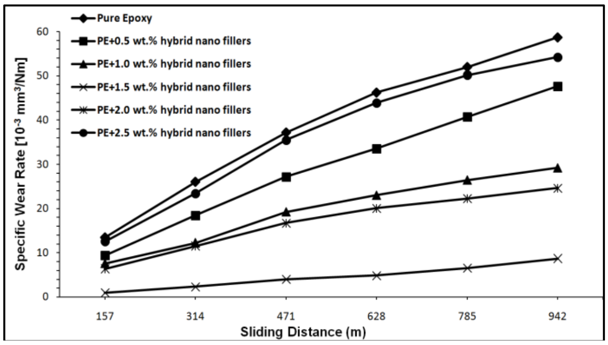

Fig. 1(a). Specific wear rate of pure epoxy and epoxy-hybrid nano filler nanocomposites. Pin on disc machine. speed: 200rpm; load 30N; time 30min.

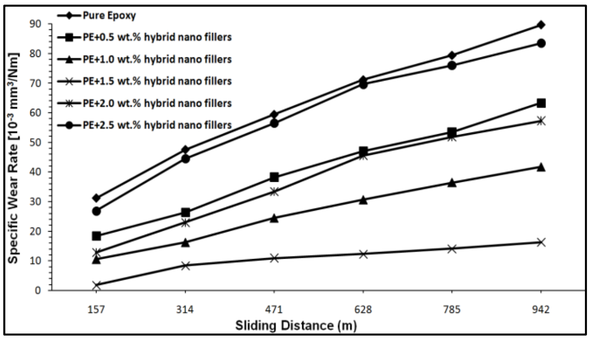

Fig. 1(b). Specific wear rate of pure epoxy and epoxy-hybrid nano filler nanocomposites. Pin on disc machine. speed: 200rpm; load 45N; time 30min.

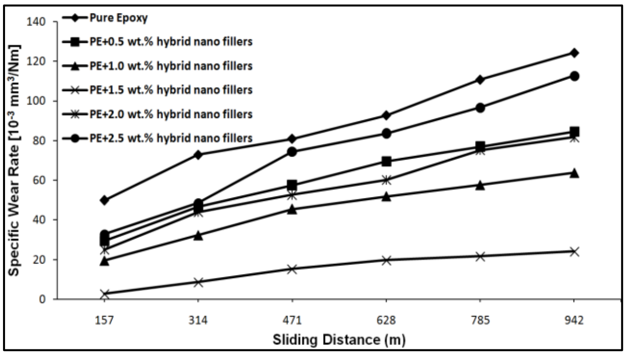

Fig. 1(c). Specific wear rate of pure epoxy and epoxy-hybrid nano filler nanocomposites. Pin on disc machine. speed: 200rpm; load 60N; time 30min.

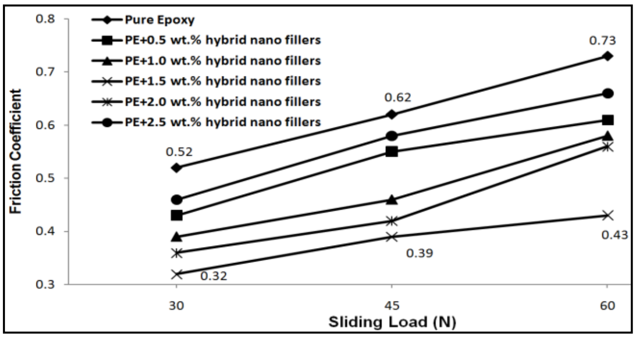

Fig. 2. Friction coefficient of pure epoxy and epoxy-hybrid nano filler nanocomposites.

4. Discussion

4.1 Direct contribution of MWCNTs-Al_2O_3 hybrid nano filler on tribology behavior

The significant goal of this experimental investigation is to exhibit the wear behavior of pure epoxy and epoxy/MWCNTs-Al_2O_3 hybrid nanocomposites. In the MWCNTs-Al_2O_3 hybrid composites prediction of wear characteristics is more complicated, because some physical interactions and chemical reaction may occur during the tribology process and significantly affect the wear performance of the hybrid nanocomposites. Under low load (30N) the pure epoxy and MWCNTs-Al_2O_3 hybrid nanocomposites worn surface are shown in Fig. 3 (a-f). It can be seen on the worn surface of the pure epoxy and epoxy contains different weight fraction hybrid nano fillers. Fewer micro crakes and pedals on the worn surface exhibits the interfacial adhesion between hybrid nano fillers and epoxy matrix seems to be reasonably good. This is beneficial to the stress transfer between epoxy matrix and hybrid nano fillers. As a result, the specific wear resistance of the hybrid composites significantly improved by introduction of MWCNTs-Al_2O_3 hybrid nanofillers. Similarly, moderate load (45N) the pure epoxy and MWCNTs-Al_2O_3 hybrid nanocomposites worn surface morphology was studied as shown in Fig. 3 (a-f). The pure epoxy displayed fractured step on the worn surface, it revealed that the material removal was brittle in nature. However, 0.5 and 1.0 wt.% of MWCNTs-Al_2O_3 hybrid nanocomposites worn surface exhibit few micro cracks and grooves.

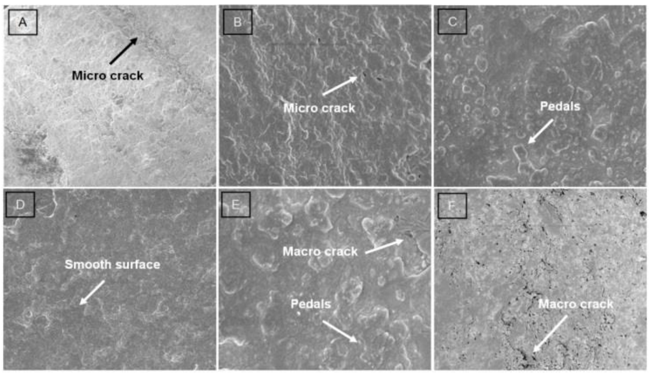

Fig. 3. Worn surface of (a) pure epoxy, (b) 0.5wt.% (c) 1wt.% (d) 1.5wt.% (e) 2wt.% and (f) 2.5wt.% of MWCNTs / alumina hybrid nanocomposites at load of 30N.

Similarly 1.5wt.% hybrid nanocomposites display smooth surface on worn surface. This can be due to the sharpen edges of alumina and wavy surface of the MWCNTs, which would harden the surface of the hybrid nanocomposites. On other hand 2.0 and 2.5wt.% loading nanofillers composites displayed deep grove, crack and cutting on worn surface. This can be due to the increasing in sliding load, the material removal mechanism changing from mild to severe. Furthermore during high load (60N) the pure epoxy exhibit large crack and material plugging and 0.5 and 1.0wt.% loading composites showed groove, peel off and micro crack on the worn surface. Large smooth surface and few micro cracks displayed in the 1.5wt.% MWCNTs-Al_2O_3 hybrid nanocomposites worn surface. However 2.0 and 2.5wt.% nanofillers composites worn surface morphology shown wave like crack, deep cutting and plugging shown in Fig. 5 (a-f). There are two reason for this improved wear resistance employed in 0.5, 1.0 and 1.5wt.% MWCNTs-Al_2O_3 hybrid nanocomposites. On the one hand, the MWCNTs posses self lubricating properties and the homogeneous dispersion of MWCNTs is greatly improved the wear resistance pure epoxy. The alumina formed mechanical interlocks with matrix to improve the nanofillers interface properties. On other hand the ceramics as vehicles to carry the MWCNTs into uniform dispersion of matrix and both alumina and MWCNTs nanofillers have excellent thermal stability, and their significant combination may improve the tribological properties of the matrix. This outcome is consistent with the literature. However, unlike the 2.0 and 2.5wt.% addition of nanofillers in the epoxy hybrid nanocomposites the specific wear rate is drastically increased equal to the pure epoxy. This may be attributed to the following reason: aggregation of MWCNTs and alumina in host matrix at high contents as shown in Fig. 6 (a), results in high stress concentration at nanofillers leading to an increase in specific wear rate.

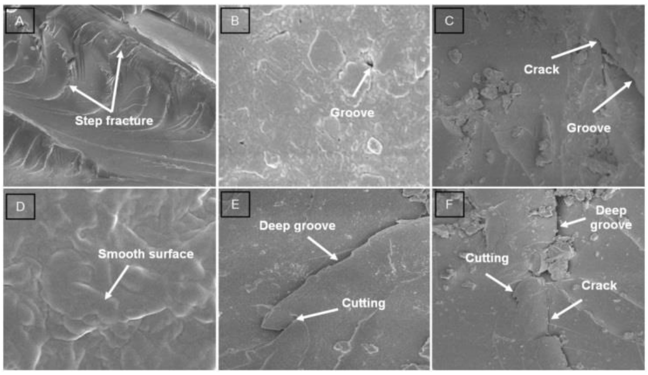

Fig. 4. Worn surface of (a) pure epoxy, (b) 0.5wt.% (c) 1wt.% (d) 1.5wt.% (e) 2wt.% and (f) 2.5wt.% of MWCNTs / alumina hybrid nanocomposites at load of 45N.

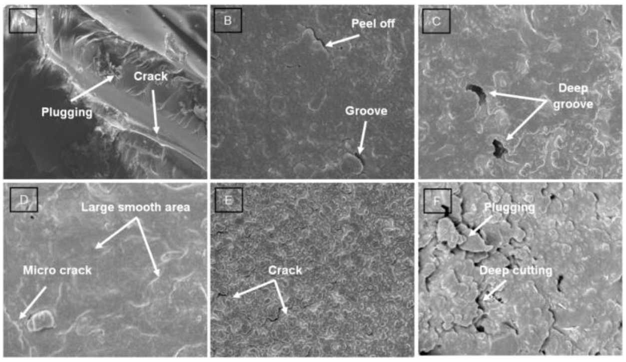

Fig. 5. Worn surface of (a) pure epoxy, (b) 0.5wt.% (c) 1wt.% (d) 1.5wt.% (e) 2wt.% and (f) 2.5wt.% of MWCNTs / alumina hybrid nanocomposites at load of 60N.

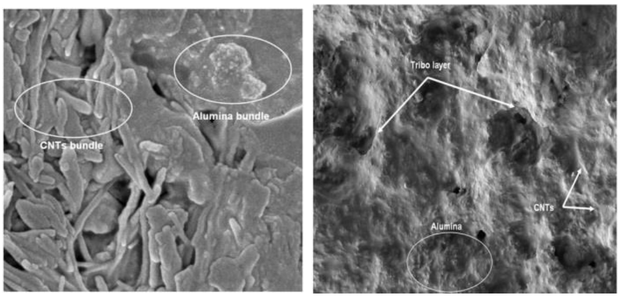

Fig. 6. SEM image of (a) localized bundle of undispersed CNT and alumina (b) thin tribo layer.

The optimum weight percentage (wt.%) nanofillers embedded in to the host matrix will improved the specific wear resistance, is given in this study. At higher contents of nanofillers (>1.5wt.%) form aggregates in the matrix. This means that the dispersion of MWCNTs-Al_2O_3 nanofillers will become worse at higher content. As a result lead higher specific wear rate due to weak interfaces between matrix and nanofillers. In the morphology analysis can be studied with respect to various loading conditions, from this cracking and fractured was observed in pure epoxy and micro cracks and peel off observed in the 0.5 and 1.0wt.% hybrid nanocomposites. The large smooth surface signs can be seen on 1.5wt.% hybrid nanocomposites. Similarly, formation of thin layer on the worn surface also observed as shown in Fig. 6(b). However, when hybrid addition will increased to 2.0 and 2.5wt.% large crack, deep groove and plugging signs can be observed in the hybrid nanocomposites worn surface. All these observation are consistent with the wear results.

5. Conclusion

In summary, incorporation of MWCNTs-Al_2O_3 hybrid at a low content has leads to a significantly enhanced the tribological performance of pure epoxy matrix. The addition of 1.5wt.% MWCNTs-Al_2O_3 hybrid nanofillers leads to 85%, 82% and 81% improved wear resistance than that of pure epoxy during low (30N), moderate (45N) and high (60N) loading conditions. This is based on two reasons. Firstly, the dispersion of MWNCTs- Al_2O_3 hybrid fillers in the matrix was greatly achieved. Secondly, alumina formed mechanical interlock to enhance the epoxy-hybrid nanofillers interface properties. High content of hybrid nanofillers form an aggregation in the matrix which leads to increase the specific wear rate. Further research can be carried to optimize the optimum content of nanofillers between 1.0 to 1.5wt.% to discover the multifunctional novel materials engineering applications.

Reference

[1] Laura M. McGrath, Richard S. Parnas, Saskia H. King, John L. Schroeder, Daniel A. Fischer, Joseph L. Lenhart, Polymer **49**, 999 (2008).

[2] I. Neitzel, V. Mochalin, J. A. Bares, R. W. Carpick, A. Erdemir, Y. Gogotsi, Tribol Lett. **47**, 195 (2012).

[3] C. Chen, A. B. Morgan, Polymer, **50**(26), 6265 (2009).

[4] L. C. Zhang, I. Zarudi, K. Q. Xiao, Wear, **261**, 806 (2000).

[5] B. Wetzel, F. Haupert, M. Q. Zhang. Compos. Sci. Technol., **63**, 2055 (2003).

[6] A. Dasari, Z. Z Yu, Y. W. Mai, Mater.Sci. Eng., R., **63**, 31 (2009).

[7] A. Dasari, Z. Z. Yu, Y. W. Mai, Mater. Sci. Eng., R., **63**, 31 (2009).

[8] L. Guadagno, L. Vertuccio, A. Sorrentino, M. Raimondo, C. Naddeo, V. Vittoria, G. Iannuzzo, E. Calvi, S. Russo Carbon, **47**, 2419 (2009).

[9] V. Puchy, P. Hvizdos, J. Dusza, F. Kovac, F. Inam, M. J. Reece, Ceramics International **39**, 5821 (2013).

[10] X. Zhang, Q. Li, T. G. Holesinger, P. N. Arendt, J. Huang, P. D. Kirven, Advanced Materials **19**(23), 4198 (2007).

[11] A. H. Barber, R. Andrews, L. S. Schadler, H. D. Wagner, Applied Physics Letters **87**(20), 203106 (2005).

[12] S. Berber, Y. K. Kwon, D. Tománek, Physical Review Letters **84**(20), 4613 (2000).

[13] A. L. Martinez-Hernandez, C. Velasco-Santos, V. M. Castano, Curr. Nanosci., **6**, 12 (2010).

[14] W. J. Chen, Y. L. Li, C. L. Chiang, C. F. Kuan, H. C. Kuan, T. T. Lin, M. C. Yip, J. Phys. Chem. Solids., **71**, 431 (2010).

[15] I. M. Ahmad, H. Unwin, H. Cao, H. Chen, A. Zhao, Y. Q. Kennedy, Composites Science and Technology **70**, 1199 (2010).

[16] F. Tian, C. N. He, Materials Research Bulletin **46**, 1143 (2011).

[17] Muhammad Razlan Zakaria, Hazizan Md. Akil, Muhammad Helmi Abdul Kudus, Siti Shuhadah Md. Saleh, Composites: Part A **66**, 109 (2014).

[18] U. A. Khashaba, Composite Structures **116**, 523 (2014).

[19] Weikang Li, Anthony Dichiara, Junwei Zha, Zhongqing Su, Jinbo Bai, Composites Science and Technology **103**, 36 (2014).

[20] Liang Yue, Gholamreza Pircheraghi, Seyed Ali Monemian, Ica Manas-Zloczower, CARBON **78**, 268 (2014).

[21] Xiao-Jun Shen, Xian-Qiang Pei, Yu Liu, Shao-Yun Fu, Materials Science and Engineering A **528**, 906 (2011).

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