



Tailored interface resulting in improvement in mechanical properties of epoxy composites containing poly (ether ether ketone) grafted multiwall carbon nanotubes



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ABSTRACT

In this work, hydroxylated HPEEK [poly (ether ether ketone)], which is miscible with the pre-polymer (epoxy), was covalently grafted on to carboxyl functionalized multiwall carbon nanotubes (a-MWNTs) to tailor the interface between MWNTs and the host resin (epoxy). The grafted MWNTs were systematically characterized using spectroscopic techniques. The epoxy composites with a-MWNTs and HPEEK grafted multiwall carbon nanotubes (HPEEK-g-MWNTs) were prepared using mechanical stirring coupled with a bath sonicator to improve the quality of dispersion of the nanoparticles and were subsequently cured at 80 °C and 180 °C. With the addition of only a small amount (0.5 wt%) of HPEEK-g-MWNTs, an impressive 44% increase in the storage modulus, 22% increase in tensile strength, 26% increase in elongation to failure and 38% increase in fracture toughness was observed with respect to neat epoxy. In addition, the nanoindentation on the composites displayed significant enhancement in the hardness and diminution in the plasticity index. The resultant formulation also facilitated scratch filling ability and resulted in thermally stable coatings/formulations. Such simultaneous improvement in properties was attributed to the improved interface between HPEEK-MWNTs and epoxy matrix.

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1. Introduction

Epoxy is a widely used thermosetting polymer in composite materials due to its combined superior thermal and mechanical properties. The benefit of epoxy resins over other thermosets like phenol formaldehyde etc. is that during curing, it does not emit volatile products [1]. A lot of work has been done on improving different properties of epoxy resin by addition of carbon fiber, glass fiber etc. Alternatively, polymer blending is a technique to develop broad range of properties, sometimes synergistic too [2]. Recently, engineering thermoplastics and nanofillers like carbon nanotubes (CNTs) are being explored as modifiers for epoxy resins because of their exceptional properties such as chemical resistance, high strength, toughness, high modulus and better heat resistance [3]. CNTs are one dimensional, nanoscale carbon-based materials which possess very large aspect ratio (300–1000), low mass density (1.8 g/cm³), high flexibility and exceptional mechanical, electrical and thermal properties, which make them excellent

candidates for fabrication of multifunctional nanocomposites [4]. Their particularly high Young's modulus (up to 1.2 TPa) and tensile strength (50–200 GPa) makes them the strongest and stiffest materials, and, in principle, makes them potential candidates for reinforcement [5]. In context to CNT based composites, it has been observed that properties of composites depend greatly on the nanoparticle dispersion and CNT–polymer interactions. CNTs have a tendency to form agglomerates because of van der Waals' forces between them. Therefore, research has been carried out on functionalization of CNTs [3]. Various thermoplastics like polysulfone (PSF), polyethersulfone (PES), polyimides (PI), polyphenyl ether, poly (aryl ether ketone), poly(etherimide) (PEI) are also being used to improve fracture toughness, yet retaining high-temperature properties of epoxy resins [1]. Polysulphone and polyethersulphone have been used but, being amorphous in nature, their elastic moduli are relatively low and they are susceptible to solvent attack.

PEEK [poly(ether ether ketone)] is one such high performance engineering thermoplastic polymer with an excellent combination of properties like toughness, thermo oxidative stability, stiffness, chemical and solvent resistance, flame retardancy, extremely low

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smoke emission, high glass transition temperature and high melting temperature [5–7]. Due to this wide range of physical properties, PEEK is used in many high performance applications such as the aerospace and automotive industries [8].

Several studies on improvement of mechanical properties like tensile strength, fracture toughness, modulus of the composites have been reported either by grafting polymer chains on to multiwall carbon nanotubes (MWNTs) or by blending it with the host polymer matrix [9–11]. Improving the properties of composites at relatively low fraction of nanoparticles is most desired as it helps in retaining the physical properties (like ductility, flexibility) of the host matrix. However, most often, the enhancement in properties are only realized above a certain concentration (like percolation threshold etc.) as the nanoparticles often tend to agglomerate during processing of the composites (secondary agglomeration). Hence, retaining the dispersion quality is very essential to realize their exceptional properties. Towards this front several attempts have been made to arrest the 'primary' dispersion quality after the composites have been prepared although with only limited success till date. Several factors like curing, crystallization, phase separation etc. perturbs the 'primary' dispersion state and often results in properties which are far from expectations, especially the mechanical properties of the resulting composites. Hence, by adopting a strategy wherein the 'primary' state of dispersion could be retained, would result in improved dispersion and is also the focus of this study.

In the present work, the effect of combining the benefits of adding hydroxylated poly(ether ether ketone), HPEEK, which is miscible with the epoxy pre-polymer, and MWNTs into epoxy resins to improve the dispersion of MWNTs and hence, the mechanical properties of the composites, has been assessed systematically. An attempt has been made to improve the state of dispersion of MWNTs in the epoxy matrix and also to tailor the interfacial adhesion between epoxy and MWNTs by grafting PEEK on MWNTs to improve the mechanical properties of epoxy composites. Both mechanical and dynamic mechanical properties of the designed composites are evaluated and the state of dispersion is assessed using SEM. The hardness and the plasticity index of the composites are studied using nanoindentation. Further, the designed formulations are evaluated for their scratch healing ability.

2. Experimental

2.1. Materials and method

Epoxy resin (EPOLAM 2063, bisphenol A-epichlorohydrin, $M_n \leq 700$) and anhydride based hardener (1,2,3,6-tetrahydro-3-methyl methanophthalicanhydride) were provided by Axson technologies (France). Poly(ether ether ketone) (PEEK, 2000FP) was provided by Vestakeep, Germany. The pristine multi-walled carbon nanotubes (MWNTs, NC7000, average diameter and length of 9.5 nm and 1.5 μm respectively, with 90% purity) was obtained from Nanocyl, Belgium. Sodium borohydride (NaBH_4), Dimethyl sulphoxide (DMSO), *N,N*-dicyclohexyl carbodiimide (DCC), dimethylaminopyridine (DMAP) were procured from Sigma. Ethanol, Dimethyl formamide (DMF), nitric acid were procured from commercial source and were used without any pre-treatment.

2.2. Synthesis of HPEEK from PEEK

To synthesize hydroxylated PEEK (HPEEK), typically 12 g of PEEK was added to 3.6 g of NaBH_4 in 300 mL of DMSO and stirred vigorously [12]. This solution was then heated to 120 °C in oil bath for 20 h, as shown in Fig. 1. The solution was filtered after it was

cooled down to room temperature and washed with ethanol and water. Filtrate was then dried in oven under vacuum at 80 °C.

2.3. Synthesis of COOH functionalized MWNTs (*a*-MWNT) from pristine MWNTs

Typically, 500 mg of pristine MWNT was added to 10 mL of 60% HNO_3 aqueous solution. The solution was bath sonicated for 30 min followed by stirring for 24 h at 80 °C in oil bath [13]. The solution was filtered and washed with distilled water. The filtrate was dried in oven under vacuum for 12 h at 60 °C, as shown in Fig. 2.

2.4. Grafting of HPEEK on to *a*-MWNTs

The grafting of HPEEK on to *a*-MWNT was carried out by esterification reaction, as shown in Fig. 3. Typically, *a*-MWNTs (500 mg) were dispersed in DMF (125 mL) using bath sonication for 30 min. HPEEK (5.5 g) was suspended in DMF (125 mL) and maintained at 50 °C for 24 h under stirring with the help of a magnetic stirrer. This suspension was added to a mixture of DCC (23.1 g) and DMAP (1.7 g) in DMF (250 mL). Then, both suspension and *a*-MWNTs dispersions were mixed under sonication and maintained at 40 °C for 68 h in oil bath under stirring in presence of nitrogen. After completion, suspension was cooled to room temperature and anhydrous methanol was added to this suspension under vigorous stirring. The suspension was filtered, washed with methanol and dried at 50 °C under vacuum [6].

2.5. Preparation of epoxy composites

The epoxy composites were prepared by mechanical mixing using an overhead stirrer (Heidolph RZR 2102) equipped with a bath sonicator. This strategy ensures homogeneous dispersion of nanoparticles in the matrix. Epoxy composite containing 0.5 wt% of *a*-MWNTs or HPEEK-g-MWNTs were prepared. It is important to note that the effective concentration of MWNTs in the composites was fixed at 0.5 wt% in case of HPEEK-g-MWNTs. The grafting of HPEEK on MWNTs was analyzed by thermo gravimetric analysis and concentration of *a*-MWNTs was adjusted accordingly in the epoxy matrix. The *a*-MWNTs and HPEEK-g-MWNTs were dispersed in ethanol and sonicated for 30 min. The epoxy was added to this mixture and kept in vacuum oven at 60 °C to evaporate ethanol for 48 h. The resultant mixture was stirred and mixed mechanically at 400 rpm using an overhead stirrer equipped with a bath sonicator for 2 h at 60 °C and hardener was then added in 100:107 ratio followed by 15 min of mixing at 500 rpm. This mixture was poured in a teflon coated aluminum mould and cured at 80 °C for 6 h followed by post curing at 180 °C for 4 h. The rectangular samples for dynamic mechanical analysis and disc shaped samples were prepared for nanoindentation experiments. Samples for tensile testing and fracture toughness analysis were prepared according to the ASTM standards.

3. Characterization

Covalent functionalization of MWNTs and grafting of HPEEK on to MWNTs was confirmed by Fourier transform infrared (FTIR) spectroscopy using a Perkin-Elmer GX in the range of 4000–400 cm^{-1} using a resolution of 4 cm^{-1} . The grafting reaction further confirmed by X-ray photon scattering (XPS) spectra using a Kratos Analytical instrument with Al monochromatic source (1.486 keV). The percentage grafting of HPEEK on *a*-MWNTs was evaluated by thermo gravimetric analysis using Netzsch STA 409 PC analyzer (TGA). Modulated Differential Scanning Calorimetry measurements were conducted on DSC-Q2000 from TA

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