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A comparative study of nanoscale glass filler reinforced epoxy composites: Electrospun nanofiber vs nanoparticle

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ABSTRACT

Electrospun glass nanofibers (EGNFs) are emerging fillers to improve mechanical properties of polymer matrix composite materials. However, questions concerning their reinforcing effectiveness in comparison with other nanoscale fillers such as glass/silica nanoparticles (GNPs) are still to be answered because reinforcing mechanisms for conventional fiber reinforced polymer composites might not be applicable at distinctive nanometer scale. Herein a comparative study on reinforcing effect of EGNFs and their conventional counterpart GNPs was carried out for the first time. Four types of glass nanofillers, including pristine EGNFs and GNPs as well as amino surface-functionalized EGNFs and GNPs were investigated to make epoxy matrix nanocomposites at ultra-low loading level ($\leq$0.5 wt%). Mechanical properties of these glass nanofiller reinforced epoxy composites were investigated and corresponding reinforcing and toughening mechanisms at nanometer scale were discussed. Due to shape factor (aspect ratio), EGNFs demonstrated much more pronounced reinforcing and toughening effectiveness and completely outperformed GNPs in all cases despite much lower specific surface area. This research provided meaningful data to fully understand the merit of EGNFs as reinforcing filler in polymer nanocomposites and paved the road for designing and modeling next-generation polymer matrix composite materials.

1. Introduction

Nano-scaled fillers have attracted growing attention in the field of polymer matrix composite (PMC) on account of their remarkable potential for improvement of mechanical properties [1–3]. Recently electrospun nanofibers have been explored as a new promising reinforcing filler in PMCs [4]. Compared to traditional engineering fibers such as Kevlar, glass, and carbon fibers for fiber reinforced polymer (FRP) composites, benefits of electrospun nanofibers come from their significantly higher specific surface area and concurrent enormous interfacial area. This may lead to substantially stronger interfacial bonding between electrospun nanofiber filler and polymer matrix and consequently significant mechanical property improvement in resultant composite materials. As a result, there is increasing research effort that is devoted to electrospun nanofiber reinforced composite materials in the past few years. Among all electrospun nanofibers that are currently involved in reinforcing polymer composites, polymer based nanofibers so far have received the most of attention because they were firstly developed and relatively matured for applications.

Non-polymer nanofibers such as glass (SiO_2), ceramic or carbon nanofibers have been successfully developed in recent years through electrospinning with primary goal to explore their electronic, energy, and/or catalytic applications [5]. A noteworthy fact is that these inorganic nanofibers may also possess outstanding mechanical properties like their bulk counterpart and thus can be employed as reinforcing fillers to make high performance FRP composites [6]. Up to date, however, very limited research endeavors have been devoted to electrospun glass nanofibers (EGNFs) for reinforcement purpose in polymer composites. Fong et al. used EGNFs as reinforcing filler in Bis-GMA/TEGDMA dental composites for the first time [7]. Their results indicated that 7.5 wt% substitution of conventional glass powder filler with short EGNFs brought about considerable improvement in flexural strength, modulus, and work of fracture of the dental composite by 44%, 29%, and 66%, respectively. Short EGNFs (ca. 400 nm diameter) were applied to SC-15A epoxy resin later and remarkably outperformed

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conventional glass microfibers (ca. 10 μm diameter) in both tensile and impact tests, yielding simultaneous enhancement in strength, stiffness, and toughness of the epoxy based nanocomposites [8]. Although EGNFs have demonstrated great potential in reinforcing epoxy based composites, corresponding reinforcing mechanisms still require further clarification. Conventional reinforcing mechanisms for FRP composites may be discounted in polymer nanocomposite due to distinctive “size effect” at nano-scale. For example, GNPs have been substantially demonstrated to enhance mechanical properties of polymer nanocomposites including simultaneous strengthening and toughening effect, but there are still large discrepancies in reported results [1,9].

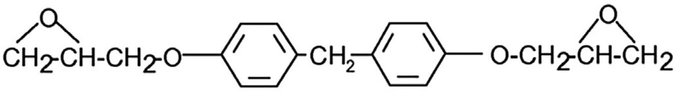
There is no side-by-side direct comparison of EGNFs with other nano-scale glass fillers such as GNPs on reinforcing effectiveness in polymer nanocomposite thus far. In order to fully understand the merit of EGNF as reinforcing filler in PMCs, a comparative study on reinforcing effect of EGNFs and its popular counterpart GNPs in epoxy nanocomposite was carried out herein. Since EGNFs and GNPs share the same chemical structure and “size effect”, “shape factor” (aspect ratio) might play a dominating role in corresponding polymer nanocomposites. This research was conducted in order to reveal role of “shape factor” at nano-scale in glass nanofiller reinforced epoxy nanocomposites especially at ultra-low filler loading (<0.5 wt%). Reinforcing effect of glass nanofillers at ultralow loading (<0.5 wt.%) in polymer nanocomposite remains to be fully understood [9,10]. In the meantime, ultra-low loading of nanofiller in composite material is appealing to industry if it can bring significant mechanical property improvement. Ultra-low nanofiller loading will reduce cost and avoid dramatic viscosity increase so as to improve processing and manufacturing of corresponding nanocomposite materials. Inspired by previous work [7,8,11,12], EGNFs were shortened in order to improve their distribution in epoxy matrix. Considering the fact that covalent bonding is far stronger than non-covalent bonding, silanization was performed to both EGNFs and GNPs before they were incorporated in epoxy resin to introduce covalent bond based strong interfacial interaction between nanofiller and surrounding epoxy matrix and ensure reinforcement in resultant composites.

2. Materials and methods

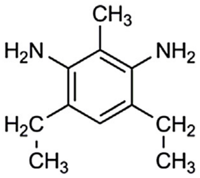
2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%) was purchased from Acros Organics. Polyvinylpyrrolidone (PVP, Mw = 1,300,000), *N*,*N*-dimethylformamide (DMF, 99%), dimethyl sulfoxide (DMSO, 98%), 3-aminopropyl triethoxysilane (APTES, silane coupling agent, 98%), glass nanoparticles (SiO_2, average diameter ~12 nm) were purchased from Sigma–Aldrich. Anhydrous acetone and ethanol were purchased from Fisher Scientific. The epoxy resin system, Epon 862 with EpiCure curing agent W, was purchased from Miller–Stephenson Chemical Company, Inc. The molecular structures of epoxy and curing agent W are listed below. All the chemicals were used as received.

Epon 862



Curing agent W



2.2. Preparation of short electrospun glass nanofibers

Detailed procedures and conditions for preparing electrospun glass nanofibers (EGNFs) were described in a previous publication [13]. The EGNFs used in this study were prepared using a spin dope consisting of 13 wt% TEOS and 13 wt% PVP in a DMF/DMSO (2:1, v/v) mixture solvent followed by pyrolysis at 800 °C. As-prepared EGNFs were continuous long fibers in form of a non-woven mat. Prior to silanization, such non-woven mat was first cut into small pieces with length and width of 1–2 mm. These small non-woven pieces were then immersed in distilled water at 1 wt% and the resultant suspension was subsequently subjected to vigorous ultrasonication with a 200 W ultrasonic probe (Sonics VCX500) for two 5-min time periods followed by centrifugation and drying under vacuum (~28 kPa) at 60 °C for 12 h.

2.3. Surface modification

APTES was adopted to modify EGNFs' surface in this research. APTES was first dissolved in an ethanol-water mixture (95:5 by wt.) at concentration of 2.5 wt%. The shortened EGNFs were next added to this silane solution at weight fraction of 1.5 wt%. The mixture was then stirred and kept at 60 °C for 2 h to fulfill the silanization reaction. Subsequently APTES modified EGNFs (APTES-EGNFs) were separated by centrifugation and washed thoroughly with ethanol to remove physically adsorbed silane molecules. The resultant APTES-EGNFs were dried in vacuum oven at 60 °C for 12 h before use. As-received commercial GNPs were also surface-silanized following the same procedure to get APTES modified GNPs (APTES-GNPs) for comparison.

2.4. Fabrication of nanocomposites

Herein, four types of nanofillers including EGNFs, APTES-EGNFs, GNPs, and APTES-GNPs were employed to make epoxy matrix nanocomposites at ultra-low loading: 0.125 wt%, 0.25 wt%, and 0.5 wt%, respectively. Each type of nanofiller was first mixed with acetone in a glass beaker and then ultra-sonicated for 5 min at 200 W to make a homogeneous mixture. The mixture was added into epoxy resin next at 40 °C under stirring along with sonication (100 W) for 10 min. Curing agent W was added into the system afterwards and the system was further stirred at 50 °C for another 2 h to remove solvent and get a uniform mixture. After being degassed, the mixture was poured into a 6 in. × 6 in. mold and cured initially at 82 °C for 4 h, then at 104 °C for 4 h, and finally at 121 °C for 4 h. Dog-bone-shaped specimens were cut from the