Enhancing Mechanical Properties of Epoxy Resin While Reducing Viscosity Using "Liquid Nano-Reinforcement"

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ABSTRACT

Graphitic carbon nanofibers (GNFs) were first made into a "liquid nano-reinforcement" (LNR) that is composed of reactive nanofibers (r-GNFs) and an epoxy diluent through chemically reacting the functionalized GNFs with the diluents. Due to the uniform dispersion of r-GNFs in the diluent, simply mixing the LNR with epoxy led to a nano-modified epoxy with uniform dispersion of nanofibers, a so-called nano-epoxy. More importantly, the nanofibers were involved in the cross-linking structures of the epoxy through covalent bonding between the matrix and nanofibers. Results showed that the nano-epoxy possesses dramatically enhanced various performances by simply mixing two kinds of liquids: a very small amount of LNR, functioning as a "nector" and a base epoxy matrix. Compared with that of the pure epoxy resin, the enhancements in performances of the nano-epoxy with only 0.3wt% nanofibers include over 30% in flexural strength, 35% in flexural modulus, and 45% fracture toughness, as well as dramatically reduced viscosity (50% lower than pure epoxy), a significant factor in fiber composite manufacturing efficiency due to reduced power requirements for flow and part consolidation.

Key words: graphitic carbon nanofiber, epoxy, composite

1. Introduction

A resin matrix with good processability (e.g. low viscosity) and advanced comprehensive performance including high mechanical properties, thermal stabilities, good wetting and adhesion capability are highly desired for fiber reinforced polymer (FRP) composites. Through nanotechnology, properties of FRPs could be enhanced through developing high performance reinforcements and resin matrix materials, as well as increasing interfacial adhesion properties between the fiber and matrix (Fig. 1) [1].

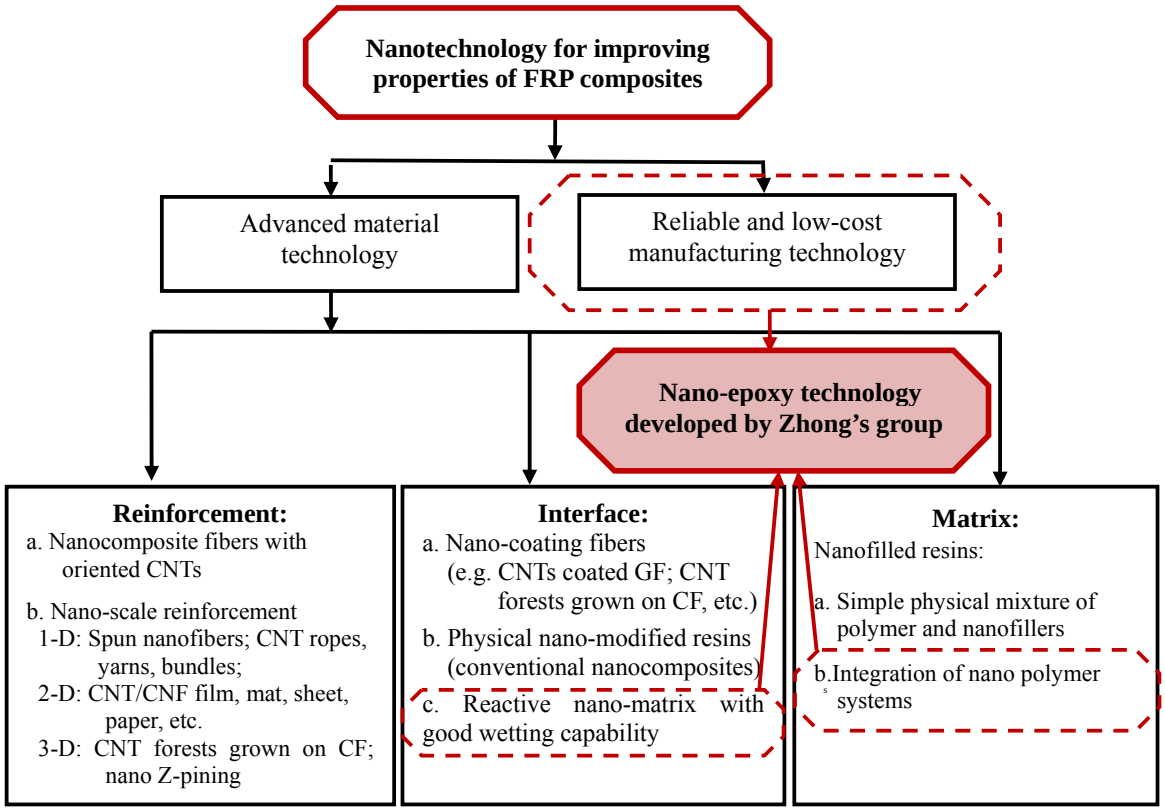

Fig. 1 Nanotechnology for FRP composite property enhancement [1]

Though the absolute properties of CNFs in the length direction, such as mechanical properties and electrical conductivity, are not as high as CNTs, there are several advantages available for CNFs. Firstly, because of the high

purity components of graphitic structures (extremely low contents of free carbon and non-carbon ingredients), there is little or no need to do any purification for commercial CNF products, which have much lower price and stable quality. Secondly, the stacked geometry of CNFs provide an abundance of reactive edges at the ends of the graphene sheets along the fiber direction, which can be used to enhance nanofiber chemical modification – edge sites are far more reactive than surface sites. Thus, CNFs can be surface-functionalized with reduced processing time. This can lead to great potential for applications in structural FRP composites with bulk volume needs.

2. Preparation of Liquid Nano-Reinforcement (LNR) from CNFs

Detailed procedures for preparing surface-functionalized herringbone CNFs with (3, 4'-oxydianilino)amidyl (ODA) linker molecules, 4', formed into CNF-ODA suitable for covalent incorporation into epoxy resins were provided in [2-4]. The subsequent treatment procedures that resulted in the "liquid nano-reinforcement", LNR, include cutting the as-received GNF-ODA nanofibers into shorter ones using appropriate ultra-sonication methods with controlled sonication conditions [5], and then these CNFs were further reacted with a "small epoxy", butyl glycidyl ether (BGE, a reactive diluent of epoxy) (Fig. 2) under special conditions [7]. This is because BGE has the epoxide group similar to the epoxy but being smaller molecules than typical epoxy molecules, thus it functioned as a reactant that can react with CNF-ODA. On the other hand, BGE was used as a dispersant for cutting GNF-ODA nanofibers through ultra sonication methods. After the reaction with the GNF-ODA to obtain the reactive nanofibers, r-GNFs, as shown in Fig. 2 [7], a controlled amount of BGE with uniform dispersion of r-GNFs will be kept. Because BGE is a reactive diluent the main function for conventional epoxy processing is to lower the viscosity of the epoxy. Through the series studies, an optimum ratio of r-GNFs to BGE in the solution was obtained. Through addition of a very small amount of this solution into the epoxy showed a dramatically improved multiple performances; in particular, the viscosity is decreased dramatically. Thus, the nanofibers were converted into a liquid form, the so-called "liquid nano-reinforcement", with a controlled ratio of the reactive nanofibers to BGE. This stable and uniform solution was then simply added to the epoxy resin. Because the nanofibers were evenly dispersed in the LNR, simply mixing two kinds of liquid: LNR and pure epoxy resulted in the nano-modified epoxy with good dispersion of the nanofibers. Thus, a nano-epoxy matrix with low concentration of nanofibers, such as 0.3 wt% r-GNFs, was obtained.

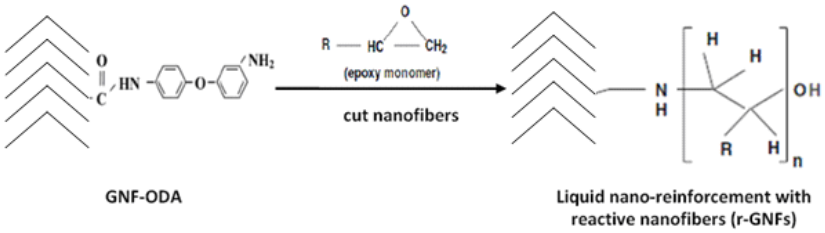

Fig. 2 Structure of GNF-ODA and formation of an r-GNF [7]

By developing a nano-epoxy based on the conversion from the dry nanofibers into the LNR, we have solved several key problems including: (1) strong interaction between graphitic nanofibers and epoxy resin through further treatment to achieve covalent bonding level; (2) uniform dispersion of the graphitic nanofibers in a polymer; (3) curing mechanisms for optimization of cure cycles [7-8]. Theoretically, strong interactions from covalent bonding between the nanofibers and polymer resins and good dispersibility have the capacity of enhanced properties for composite applications. Subsequent further work is underway to fully characterize the various properties and advantages of this nano-epoxy.

3. VISCOSITY AND WETTING OF NANO-EPOXY WITH LIQUID NANO-REINFORCEMENT (LNR)

Durability and reliability of a composite structure highly depends on the fiber/matrix interface, which can be a weak area of structural integrity and overall performance. Utilization of treatment methods can increase the surface energy of the reinforcements, which leads to improved wetting along the fiber/matrix interface. Our proposed approach (Fig. 3) is to fabricate a reactive matrix with low

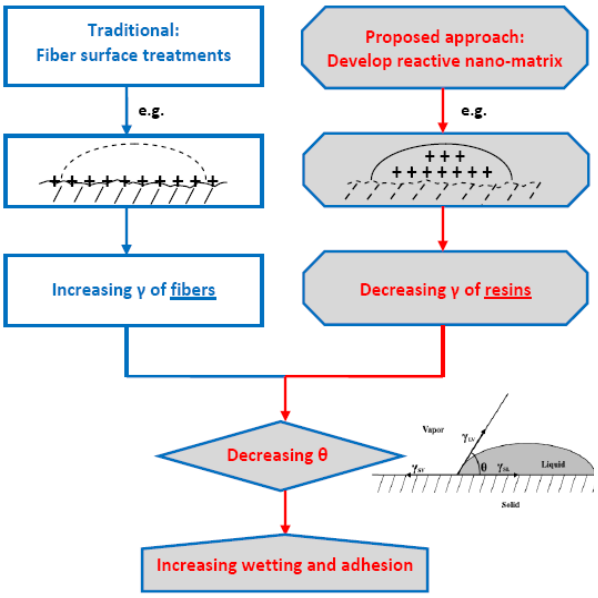

Fig. 3 Approaches for increasing wetting and adhesion

surface energy [8], which is a cost-effective way for manufacturing more durable composites. Thus far, there have been no reported studies on the improvement of fiber/matrix interface adhesion through fabricating reactive nano-matrix materials, besides the author's group's research.

Viscosity is one of the important factors that influence wetting of a liquid on a fiber surface. The more viscous or the higher the viscosity of a matrix, the longer the time it takes for the matrix to spread on the fiber surface. Since viscosity is temperature-dependent, even in the environmental temperature range of 23–27 ◦C, the viscosity fluctuates. However, in this case we found that compared to that of pure epoxy, the variation rates (decrease rates) of viscosity for various samples are fairly stable. The decrease rates of viscosity of five types of samples in comparison with pure epoxy were calculated and shown in Table 1 [8].

Table 1. Viscosity decreases: nano-epoxy vs. pure epoxy [8]

Samples	Concentration of Nanofibers, (wt%)		
	0.2	0.3	0.5
Nano-epoxy:	42	52	68
Epoxy + GNFs	30	12	-2
Epoxy + GNFs (non-cut)	20	8	N/A

*Note: Error is less than 2 %

Wetting the surface of reinforcing fibers with polymeric matrices is one of the critical aspects for obtaining good interfacial adhesion during the processing stage of fiber/polymeric composites. The term, wettability, is used to describe the extent to which a liquid spreads on a solid surface. The state of wetting between a resin matrix and a fiber can considerably affect the interfacial adhesion. It is evident that insufficient wetting generates interfacial defects and reduces the bonding strength. The wettability of a polymeric matrix on the surface of a fiber is characterized by the contact angle between the fiber and the polymer.

As comparison, wetting behavior of the nano-epoxy and pure epoxy samples on smooth surfaces were characterized using contact angle analysis method and are shown in Fig. 4 [9]. It can be seen that although variations in geometric shapes and contact angles between two matrix systems were observed on the smooth surfaces, it cannot fully reflect the differences in the practical application because in reality fewer solid surfaces are truly smooth.

Fig. 5 shows the wetting behaviors of nano-epoxy and pure epoxy on glass fabric surface [10]. It can be seen that the nano-epoxy matrix had significantly different wetting characteristics on the glass fabric surface from the pure epoxy. The nano-epoxy quickly spread and easily filled up the grooves on these rough fabric surfaces and hence showed a zigzag-like contact line on the rough fabric surfaces. However, the droplets of pure epoxy sat on the top of these rough fabric surfaces without filling up the grooves of the woven fibers so that air was enclosed between the droplet and the fabric substrate.

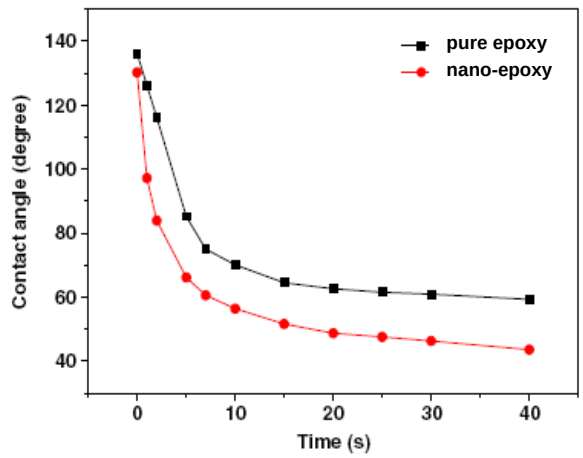

Fig. 4 Wetting behavior of pure epoxy and nano-epoxy[9]

This difference in wetting state of the two epoxy systems on the rough fabric surfaces reflected the influences of addition of the r-GNFs into epoxy resin.

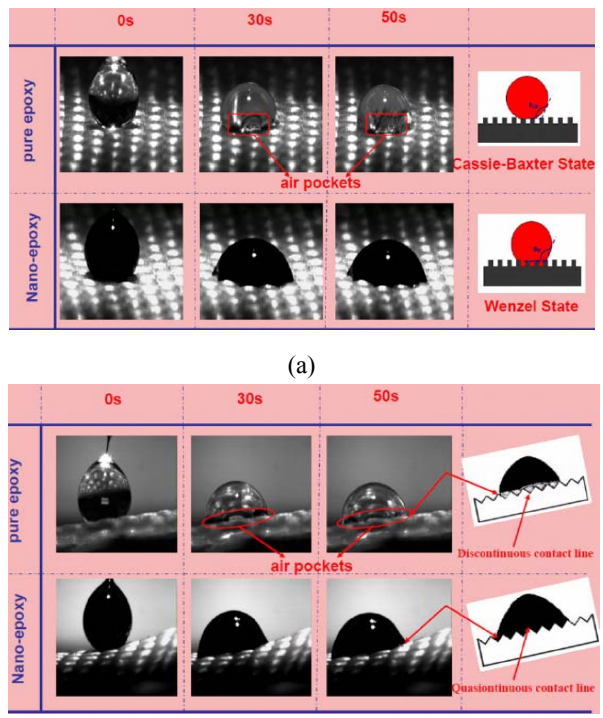

Fig. 5 Dynamic wetting phenomena of pure epoxy and nano-epoxy on the glass fiber fabric surfaces [9]: (a) horizontal surface; (b) on tilted surface

However, from this study it is seen that the conventional contact angle analysis approach and equipment cannot realize quantitative characterizations of wetting behavior of the nano-epoxy on rough or fabric surfaces as shown in Fig. 5. To investigate in-depth how the r-GNFs in the format of LNR affect the wetting behavior of the resulting epoxy system is our future research task, which is believed to be significant for the application of nanotechnology in manufacturing FRP composites.

4. PROPERTY SUMMARY OF NANO-EPOXY WITH REACTIVE NANOFIBERS

The previous research indicated that such nano-matrices, in which the covalent bond in nanofiber/epoxy resin and nanofibers are in the form of LNR, possessed greatly enhanced comprehensive performance with broad ranges of improvement [10-20]. The results showed that the nano-epoxy has very low nanofiber concentration (0.3 wt %) and interestingly, it showed lower viscosity compared with the pure epoxy [17]. Property enhancements for the developed nano-epoxy with 0.3 wt% r-GNFs vs. pure epoxy are summarized as follow [11-20]:

- Enhanced mechanical properties (three-point bending):
  - Strength (30%);
  - Modulus (>35%);
  - Toughness (45%)

- Increased thermal properties (DMA and TMA):
  - Higher Tg (14˚C higher);
  - Stable Coefficient of Thermal Expansion (CTE)

- Improved processability for manufacturing FRPs (contact angle, viscometer and rheometer):
  - Faster wetting rate on UHMWPE fiber surface (45%);
  - Lower viscosity (50%) and better resin infusion performance;
  - Improved overall rheological properties for commercial processing

- Improved interfacial adhesion property with UHMWPE fibers (by pullout tests):
  - Initial debonding force (35%);
  - Maximum pullout force (25%);
  - Energy to debonding (65%)

- Improved mechanical (tensile) properties of UHMWPE fiber composites:
  - Higher at RT: longitudinal stiffness and ultimate tensile strength
  - Hygrothermal effects: Lower diffusivity (60%) (60˚C, water, 30 days)
  - Hygrothermal + UV effects: Less effect (UV, 60˚C, water, 4 hours)

5. CONCLUSION REMARKS

This paper summarized the application of carbon nanofibers in modifying polymer resins used as matrices of structural fiber composites, and introduced the new nano-matrix technology that resulted in a nanofiber-reinforced epoxy matrix with greatly enhanced comprehensive properties. The developed nano-epoxy matrix has successfully tackled several daunting barriers for carbon nanofiber use. Through making carbon nanofibers into liquid nano-reinforcement (LNR), and then compounding with epoxy, the functionalized carbon nanofibers effectively translated their extraordinary performance to end products through covalent bonding between matrix and nanofibers. The liquid nano-reinforcement can easily be dispersed in the base epoxy matrix and proves highly effective for reinforcing and toughening the epoxy resin as well as contributing to dramatically reduced viscosity, which is significant to FRP composites manufacturing energy efficiency (reduced power requirements for flow and part consolidation).

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