Preparation and Mechanical Properties of Short Carbon Fiber Networks Reinforced Anionic Polymerized Nylon 6 Composites

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Abstract. Short carbon fiber three-dimensional network reinforcement (SCFNR) was prepared by bonding two different lengths of short carbon fibers (SCF) with phenolic resin powder (PF), and then carbonized at 800 °C. Two kinds of SCFNR/anionic polyamide 6 (APA6) composites were fabricated via vacuum assisted impregnation process (VAI). The microstructures and mechanical properties of the composites were characterized by scanning electron microscopy and universal testing machine. The thermal stability of the composites was evaluated by thermogravimetric. The results show that the carbonized phenolic resin can effectively bond SCF to form a rigid three-dimensional network reinforcement, both types of SCFNR can significantly improve the mechanical properties of the composites. The maximum thermal decomposition temperature of SCFNR/APA6 composite prepared with the carbon fiber length of 1 mm is 150°C higher than that of APA6.

1. Introduction
Carbon fiber reinforced polymer composites (CFRP) have excellent properties: good chemical resistance, excellent mechanical properties at low density, designable strength characteristics, material cost and manufacturing cost reduction, and so on, which promotes the wide application of composite materials in many fields [1], such as the aerospace industry, automotive, sports equipment and wind energy applications [2-5]. Thermosetting resin (vinyl ester, epoxy resin and polyester) possesses good mechanical, thermal and chemical properties [6-8]. However, reusable thermoplastic resins have become a research hotspot with the improvement of environmental awareness; APA6 has the advantages of short forming cycle, simple process and excellent mechanical properties [9-11]. CF/APA6 composites can not only maximize the performance advantages of carbon fibers, but also have the advantages of easy processing and moulding. At present, the main research objects of CF/APA6 composites are continuous carbon fiber/APA6 composites, braided carbon fiber/APA6 composites and SCF/APA6 composites. Continuous carbon fiber/APA6 composites have good mechanical properties and good forming properties, however, their in-plane shear and interlaminar shear strengths are low. Although the braided carbon fiber/APA6 composite has excellent mechanical properties (including shear properties and bending properties), the manufacturing process is too complex and the production cost is high. The mechanical properties of SCF/APA6 composites are not...
very good, but if SCF can be effectively bonded together, the mechanical properties can be significantly improved and the cost is also acceptable.

There are many reports about bonded short-cut carbon fiber reinforced composites including thermal insulation materials, adsorption and separation materials [12-14], for example, Liu [15] have studied the thermal insulation application of carbon bonded short carbon fiber composites produced by a simple pressure filtration technique. However, there are few reports on the mechanical properties of bonded short-cut carbon fiber reinforced composites [16-17]. In this work, we reported an approach to fabricate the rigid three-dimensional network reinforcement SCFNR with SCF and PF, and SCFNR/APA6 composite was prepared by VAI, and its mechanical and thermal properties were further studied.

2. Experimental procedure

2.1. Material

SCF (the lengths of 1 mm and 10 mm) was used in this work, phenolic resin powder (PF, Artificial Resin Factory Co., Ltd., Changchu) was used as binder. Caprolactam (CL, Branch of China Petrochemical Co., Ltd., Baling), toluene diisocyanate (TDI, Xiya Chemical Industry Co., Ltd., Shangdong) and sodium hydroxide (NaOH, Jinfeng Chemical Co., Ltd., Tianjin) were used in anionic polymerization as monomer, catalyst and initiator, respectively.

2.2. Preparation of SCFNR

PF powder is dispersed in water under intensely stirring, and then poured into a self-made mold with the SCFs evenly arranged to fully infiltrate into the surfaces of carbon fibers. After that the mixtures were ultrasonicated for 30 minutes so that the PF powder can uniformly distribute on the surfaces of carbon fibers. After the water was filtered out, the formed precursor was placed in an air dry oven at 80 °C for 10 h. The precursor was cured in the mold at 165 °C for 2 h. Finally, SCFNR was obtained after the precursor was carbonized at 800 °C for 30 min in a tubular furnace under nitrogen atmosphere.

2.3. Preparation of SCFNR/APA6 composites

The CL was put into a 500 mL three-neck round bottom flask and heated to 120 °C. The melt was stirred with a magnetic stirring and refluxed under vacuum about 30 min to eliminate moisture, and then NaOH (CL: NaOH=500: 1) was added with stirring intensely. Subsequently, the melt was refluxed under vacuum for 30 min to remove water, and TDI (CL: TDI=50: 1) was added. After being quickly mixed up, the mixture was cast into a mold, which was preheated sufficiently at 160 °C with SCFNR and degassed thoroughly. The polymerization reaction lasted for 30 min and SCFNR/APA6 composites were molded. The neat APA6 was prepared at the same conditions except SCFNR. SCFNR/APA6 composites were fabricated according to the varying conditions of SCFNR, and were designated as SCFNR-x/APA6, where “x” indicated the carbon fiber length (mm) in the SCFNR.

2.4. Characterization

Tensile testing and bending testing were tested by universal testing machine (Instron3369, USA). Tensile properties and bending properties are tested according to GB/T 1040-2006 and GB/T9341-2008, respectively. Impact strength is tested by impact testing machine (UB-5, Wuzhong, China) according to ISO/79-1: 2010 (E). Five samples were tested for each SCFNR/APA6 composite, and the average value was taken. The SCFNR and impact profile of SCFNR/APA6 composites were observed by SEM. The thermal properties of composites were performed on a thermal analyzer (TG/DTA7300, SEIKO, Japan) from 40 °C to 600 °C at a heating rate of 10°C/min under nitrogen flow.
3. Results and discussion

3.1. Reinforcement Mechanism of SCFNR

As shown in Fig. 1, the three-dimensional structure of SCFNR differed at the lengths of carbon fibers. When the fiber length is 1 mm, the carbon fibers are disorderly dispersed, and the fibers are bonded each other by the carbonized PF bonding points. However, when the fiber length is 10 mm, most of carbon fibers are arranged in parallel, and adjacent fibers are bonded into bundles through the carbonized PF bonding point. A small number of irregularly dispersed carbon fibers serve as a bridge between these bundles and carbon fibers, forming a three-dimensional reinforcement body. The reinforcement mechanisms of SCFNR/APA6 composites are different with two kinds of three-dimensional SCFNR. The reinforcement effect of SCFNR on APA6 matrix is mainly realized by transferring stress through rigid three-dimensional network skeleton structure and preventing matrix crack propagation via the destruction of the three-dimensional network structure. With the increase of carbon fiber length, the regularity of carbon fiber arrangement increases, the more efficiency of stress transfer increases and the more carbon fibers pull out when the SCFNR/APA6 composite is damaged under the action of external forces. Therefore, SCFNR has remarkable reinforcement effect on SCFNR/APA6 composites compared with short-cut carbon fiber.

![Fig. 1 Schematic diagram of reinforcement mechanism.](image)

3.2. Microstructure of SCFNR and SCFNR/APA6 composite

![Fig. 2 SEM images of (a) SCF-1 and (b) SCF-10.](image)
Fig. 2 shows that SCF-1 and SCF-10 are successfully bonded each other by the carbonized PF bonding points, but the bonding ways are distinctly different. When the length of SCF is 1mm, the carbon fibers have a higher degree of disorder and the carbon fibers are mainly connected in the form of lap joints (Fig. 2a). As the fiber length increases to 10 mm, the parallel arrangement of carbon fibers increased significantly and the connection between carbon fibers is mainly surface joints and a small number of lap joints.

![Fig. 2 SEM images of impact section of SCFNR/APA6 composites at different SCF length: (a, b) SCF-1, (c, d) SCF-10.](image)

**Fig. 3** presents the SEM images of impact fracture surfaces of SCFNR-1/APA6 and SCFNR-10/APA6 composites. As shown in Fig. 3a, the surface of SCFNR-1/APA6 composite is uneven and some holes and circular grooves leave after the fibers are pulled out. The pulled-out CF is short, which is mainly due to the damage of three-dimensional network structure and the fracture of short carbon fiber. A layer of matrix can be seen on the surface of SCF in Fig. 3b, it indicates that the interfacial bonding strength of fibers and matrix resin is excellent and SCFNR/APA6 composites can effectively absorb more energy during the impact process. The impact fracture surface of SCFNR-10/APA6 composite is more uneven and more fiber breakage points (Fig. 3c). Due to the increase of fiber length, the failure of SCFNR-10/APA6 composites is mainly caused by the fracture of carbon fiber which forms the three-dimensional network structure. As shown in Fig. 3d, the surface roughness of carbon fiber increased significantly because of the bonding and carbonization of phenolic resins, and the interface bonding between carbon fibers and APA6 is significantly improved due to mechanical bonding.

3.3. Mechanical properties

As shown in Fig. 4a, the maximum tensile strength of SCFNR-1/APA6 composite reaches 71.7 MPa when the volume fraction of SCF is 12.5 vol%, which is close to that of APA6. Fig. 4b presents the
tensile strength of SCFNR-10/APA6 composite at different volume fraction of SCF, the tensile strength increases with the increase of volume fraction. The maximum value of the tensile strength is 112.7 MPa, which is 1.6 times higher than that of APA6. With the increase of SCF length, the arrangement of SCF in the SCFNR is more regular. When the external forces load on the SCFNR/APA6 composite, the material failure of the shorter SCF in SCFNR-1/APA6 composite is mainly caused by the failure of the lap joints, while the longer SCF in SCFNR-10/APA6 composite is mainly caused by the fracture of carbon fibers. Therefore, the tensile strength of SCFNR-10/APA6 composite is significantly higher than that of SCFNR-1/APA6 composite.

As shown in Fig. 4, the tensile strengths of SCFNR/APA6 at different volume fraction of SCF: (a) SCFNR-1/APA6, (b) SCFNR-10/APA6.

As shown in Fig. 5a, the flexural strength of SCFNR-1/APA6 composite reaches 169.0 MPa when the volume fraction of SCF is 10.0 vol%. The flexural strength of SCFNR-10/APA6 composite can increase into 273.6 MPa, which is 4.3 times higher than that of APA6 (Fig. 5b). With the increasing of SCFNR loadings, SCFNR-10/APA6 composite has higher flexural strength, which is due to the different reinforcement mechanism of the two kinds of three-dimensional network reinforcement materials.

As shown in Fig. 6, the impact strength of two kinds of SCFNR/APA6 composites increases first and then decreases with the increase of volume fraction of SCF. Maximum impact strength of
SCFNR-1/APA6 reaches 92.5 KJ/m² when the volume fraction of SCF is 7.5 vol% in Fig. 6a. As shown in Fig. 6b, the maximum value of SCFNR-10/APA6 is 39.5 KJ/m² when the volume fraction of SCF is 15.0 vol%. It is obvious that the impact strength of SCFNR-1/APA6 composite is greater than that of SCFNR-10/APA6 composite. This is because the joints of shorter SCFs in SCFNR can deform, slip and destroy when the composite bears the impact force, resulting in a significantly improved toughness of SCFNR-10/APA6 composite.

Fig. 6 The impact strength of SCFNR/APA6 composites at different volume fraction of SCF: (a) SCFNR-1/APA6, (b) SCFNR-10/APA6.

3.4. Thermal properties

The TGA results of two kinds of SCFNR/APA6 composites with the same volume fraction (15.0 vol%) of SCF are shown in Fig. 7, the SCFNR/APA6 is thermally stable from 40 to 230 ºC, the weight loss of APA6 (4.2 %) between 40 and 230 ºC is due to desorption of adsorbed water molecules and volatilization of monomer and low molecular substances. The lower the water absorption of SCFNR-1/APA6 composite is, the better the dimensional stability of the composite will be. The maximum decomposition temperature of SCFNR-1/APA6 is 150 ºC higher than that of APA6, which indicates the heat resistance of composites is obviously enhanced. The maximum decomposition temperature of
SCF-10/APA6 composites is close to that of APA6. We assume the short SCF (1 mm) acts as a heterogeneous nucleation agent to APA6, which improves the crystallinity of APA6 and the thermal stability of the SCFNR-1/APA6. However, SCF cannot be used as an effective heterogeneous nucleating agent for APA6 when the length of carbon fiber increases into 10 mm.

4. Conclusion

Three-dimensional network SCFNR was prepared via PF bonding SCF and carbonization, which ensures that the carbon fibers bond each other through the carbonized PF bonding points. SCFNR/APA6 composites were successfully fabricated by anionic polymerization via VAI process. The connection mode of SCF in SCFNR varies from lap joint to surface joint with the increasing of carbon fiber length, which leads to the difference of reinforcement mechanisms. The mechanical properties of two kinds of SCFNR/APA6 composites are obviously improved, the maximum of tensile strength, flexural strength and impact strength are 2.0, 4.3 and 6.4 times higher than that of APA6, respectively. The short SCF can act as a heterogeneous nucleating agent for APA6, which improves the crystallinity and the thermal stability of the composites.

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