Nanoscale Resin Flow and Permeability of Preformed Single-Walled Nanotube (SWNT) Networks

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SUMMARY: Unlike current techniques of directly mixing carbon nanotube with polymer resin, we fabricate SWNT nanocomposites by using a novel three-step process: SWNT networks are first preformed; a resin solution is then infiltrated through the preformed SWNT networks to realize tube/resin impregnation; and then the impregnated SWNT networks are hot pressed to produce the final nanocomposites. Using this method, uniform nanostructures, tube alignment and high nanotube loading can be achieved in the resultant nanocomposites. In the preformed SWNT networks, individual tubes form ropes or bundles approximately 30~60 nm in diameter and the open distance between ropes in the pore structures are about 50~200 nm. Therefore, resin flow and infusion will occur at nanoscale. In this study, the through thickness permeability (K_{zz}) of the random SWNT preforms were measured. The influences of molecular interactions on resin flow within preformed SWNT networks were examined using molecular dynamics simulation.

Keywords: Nanocomposites, SWNT, Resin flow, Permeability

INTRODUCTION

The single-walled carbon nanotube (SWNT) has received considerable notice because of its unique and exceptional material properties. SWNTs are considered by many researchers the most promising reinforcement for the next generation high performance composites [1,2]. Unlike conventional fibrous reinforcements, SWNTs interact intensively with resin matrix due to their nanoscale dimension (0.4~18 nm in diameter and up to 1 several μm in length), extra-large surface area (as high as 1500m^2/g) and strong van der Waals forces caused by the sp^2 electronic structure. For example, by adding only 1 or 2% by weight SWNTs to resin, the viscosity of the resin/SWNT mixture could dramatically increase.

Sometimes the mixture becomes a thick paste and loses its flow ability, which will lead to poor tube dispersion in nanocomposites.

The authors developed a new approach to prepare SWNT-reinforced nanocomposites that avoids the drawbacks of directly mixing tubes/resin matrix during nanocomposite processing [3,4]. This new method employs preformed tube networks or nanotube mats called buckypapers and a special resin infiltration method. In this process, SWNTs were first dispersed into water with the aid of the selected surfactant and sonication to form a well-dispersed, stable suspension. The SWNTs suspension was filtrated to form buckypapers, which are composed of uniformly preformed SWNT rope networks. Buckypapers are a macroscale dimension and can be handled as conventional fiber mats to attain controllable reinforcement distribution and volume content. In the preformed SWNT networks, individual tubes form ropes or bundles approximately 30~60 nm in diameter, with openings between the tube ropes in the pore structures about 50~200 nm. Therefore, resin flow and infusion will occur at nanoscale. In this study, the through thickness permeability (K_{zz}) of the random SWNT preforms was measured. The influences of molecular interactions on resin flow within preformed SWNT networks were investigated using molecular dynamics (MD) simulation.

NANOSTRUCTURE OF THE PREFORMED SWNT NETWORK

Fig. 1 shows the produced buckypapers for the study. The buckypapers demonstrate good strength and flexibility to allow for handling similar to traditional glass fiber mats. The nanostructure of the buckypaper can be seen in Fig. 2. The buckypaper images show that the tube networks were composed of continuous SWNT ropes, which was the result of the self-assembly of the nanotubes by van der Waals force during buckypaper filtration [5]. The rope size and porous structure of the buckypapers were uniform, indicating very good tubes dispersion in the suspension. The ropes' diameters were in the range of 30~60 nm. The buckypaper nanoscale structures had pores with openings ranging from 50-200 nm, which are much smaller than those in traditional glass fiber and carbon fiber fabrics or mats.

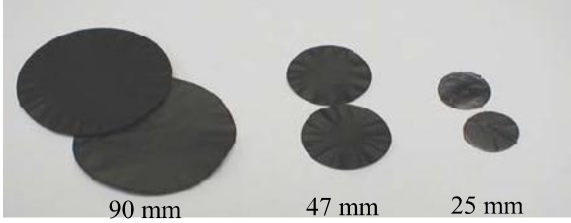
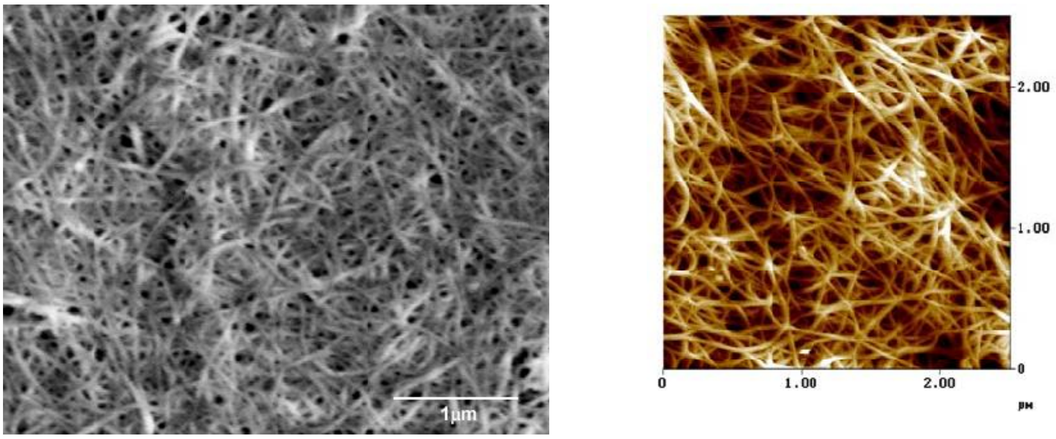


Fig. 1. Single-walled carbon nanotube buckypapers



AFM image SEM image

Figure 2. Nanostructures of the preformed SWNT network in the buckypapers

COMPARISON OF PORE SIZE AND DIMENSION OF RESIN MOLECULES

Since the buckypaper porous structures were at nanoscale, confirming the comparability between the buckypaper pore size and the dimension of the resin/curing agent molecules in necessary. Under minimum energy conditions, MD simulation revealed that the resin system used in this study, Epon 862 epoxy resin and curing agent molecules (DETDA), have the approximate dimensions of 23 Å × 9 Å × 6 Å and 6.7 Å × 6.5 Å × 1.8 Å, respectively. This is a low viscosity resin system, which is widely used for RTM process. The simulation results indicate that both resin and curing agent molecules could penetrate through the nanostructure and form a 3D cross-link network of resin matrix [6].

PERMEABILITY MEASUREMENT OF SWNT BUCKYPAPER

The through thickness (z-direction) permeability (K_{zz}) of the produced buckypapers was measured for the study. Deioned water was used as the working fluid in the permeability test. The buckypapers acted as filter membranes in the test filter setup. The buckypapers were placed inside a filter and sealed. Under a full vacuum, deioned water was drawn through the buckypaper along the thickness direction. The water flow rate, buckypaper thickness, buckypaper surface area and vacuum pressure were recorded to calculate the K_{zz} of buckypapers with 10-50mm thickness and nanoscale pore structures. The z-direction permeability K_{zz} (saturated permeability) was calculated by the following Darcy's Law [7, 8].

The results of the z-direction permeability tests on the buckypapers are shown in Table 1. The average value of buckypapers' K_{zz} was about $2 \times 10^{-19} m^2$. Compared to conventional glass fiber reinforcement fabrics or mats (V_f=60%), the buckypaper permeability was 8-10 times lower. Therefore, infusing the resin through buckypapers in the in-plane direction, as with conventional RTM and VARTM process of fiber reinforced composites, is almost impossible due to nanoscale pore structure and extremely high flow resistance. The buckypapers had to be infused with resin and impregnated along their thickness direction.

Under this condition, the z-direction permeability is a key parameter for the buckypaper/resin infusion process.

Table 1: K_{zz} of the buckypapers

Buckypaper Thickness (μm)	25.4	31.2	35.7
K_{zz} (m^2)	3.358×10^{-19}	1.105×10^{-19}	1.442×10^{-19}
Average K_{zz} (m^2)	1.968×10^{-19}		

NANOSCALE RESIN FLOW MODELING

Since intensive molecular interactions between nanotubes and resin molecules are expected during nanocomposite processing, MD simulation was used to explore the phenomena of nanoscale resin flow [6]. Assuming the nanotubes were individually dispersed in the buckypaper and the nanotubes' diameters were about 1 nm, a molecular model for illustrating the nanoscale resin flow was developed. The model indicated that the Epon 862 epoxy resin and EPI CURE curing agent molecules are at the same length scale as the pore structure of the (10,10) SWNT networks. In this model, a square nano-pore was constructed with four (10,10) SWNTs 97 Å long. The resulting pore dimensions were 6 nm x 6 nm and the thickness of the model was 3 nm. When processing nanocomposites, the EPON 862 epoxy resin was infused into the buckypaper after mixing with the curing agent. The liquid resin matrix consisted of Shell EPON 862 epoxy resin and EPI-CURE W curing agent (DETDA) with a weight ratio of 100:26.4. The ratio of the resin molecule number to the curing agent molecule number was about 2:1. Finally, 7145 atoms were included in the simulation model. Snapshots of the MD simulations are shown in Fig. 3 and 4. Initially, the epoxy resin and curing agent molecules were placed near the pore opening (some slightly inside the pore, some well outside the pore). During the initial 10 ps of the simulation, the resin molecules were changing their orientations and moving towards the nanotubes. After an equilibration period of 80 ps, the resin molecules close to the nanotube moved closer and wetted the nanotube. However, the resin molecules in the middle of the pore remained in place due to the resin molecules' weak interactions with the nanotubes. This suggests that at nanoscale, strong molecular interactions between SWNTs and resin molecules affect resin flow behavior, possibly because the majority of resin and curing agent molecules interacting with the SWNTs due to their nanoscale dimension and extra-large surface area.

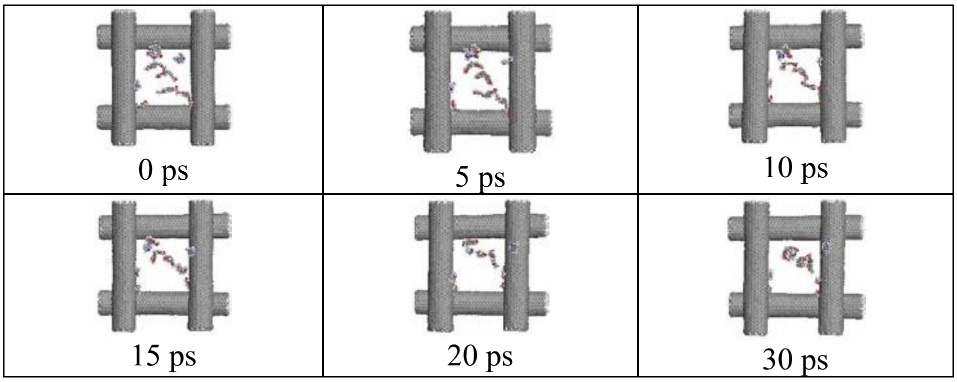


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Fig. 3. Top view of the MD simulation results

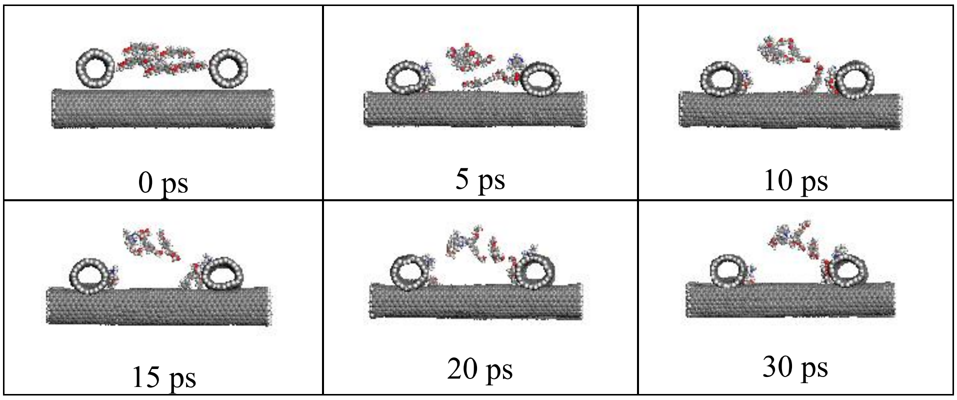

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Fig. 4. Side view of the MD simulation results

This simplified MD simulation clearly indicates the molecular interactions on nanoscale resin flow behavior. The effect of molecular interactions is usually ignored in conventional resin flow models, such as Darcy's Law and Kozeny-Carman (K-C) Equation, used for liquid composite molding processes. For nanocomposite processing, molecular interactions must be considered. New nanoscale resin flow and permeability models require further development.

CONCLUSIONS

In this study, permeability of preformed SWNT networks and nanoscale resin flow behaviors were investigated. Unlike conventional fiber preforms, the pore structure of the preformed SWNT network is at nanoscale and the z-directional permeability of the buckypapers was as low as $2x10^{-19}m^2$. Compared to normal glass fiber reinforcement fabrics or mats (V_f=60%), the buckypapers' permeability is 8-10 times lower. The influences of molecular interactions on the resin flow within the SWNTs' nanoscale pore structure were investigated.

Preliminary MD simulation results show that during nanocomposite processing, strong molecular interactions between SWNTs and resin molecules exist and as a result, resin molecules will likely be attracted to the SWNT surface because of the van der Vaals interactions and extra-large SWNT surface area. The effects of molecular interactions should be considered and new nanoscale resin flow and permeability models require further development for nanocomposite processing.

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