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EFFECT OF THE SINGLE WALLED CARBON NANOTUBE CONTENT ON RESIN FLOW

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SUMMARY: The integration of Carbon Nanotubes (CNTs) in polymeric resin systems demonstrated their potential as reinforcements and multifunctional additives in composite materials. Several composites mechanical properties such as stiffness, strength and toughness have been improved. However, due to their high aspect ratio, the viscosity of CNT-modified resins can significantly increase compared to the neat resin. As a result, the processing of these modified resins becomes problematic leading to poor composite performance. This paper investigates the processing aspect of CNT-epoxy composites at low and high CNT contents. The rheological properties of an epoxy resin at low CNT content (0.2% volume fraction) are presented. For the high CNT content nanocomposites, different techniques for the impregnation of CNT sheets (also known as buckypapers) with CNT volume fraction of 30% are investigated. The impregnation quality is verified by Scanning Electron Microscopy (SEM) and the mechanical performance is measured using a micro-scale testing fixture.

KEYWORDS: CNT-modified resin, rheological properties, CNT volume fraction, impregnation of CNT buckypaper, elastic properties

INTRODUCTION

Processing of nanocomposites is a challenging task due to the effects of nanotubes on the rheological behaviour of the polymer. Extensive research has been dedicated to better understand the nanotubes-polymer interaction and the consequential rheological behaviour of the composite system [1].

At low carbon nanotube content ($V_f < 1\%$), the viscosity sees orders of magnitude increase upon the addition of carbon nanotubes. A thorough understanding of the flow behaviour of low CNT content nanocomposites is required to enable their integration to the conventional composites manufacturing processes, such as Resin Transfer Moulding (RTM). The degree to which the viscosity is affected is highly dependent on the nanotubes aspect ratio and their dispersion state [2]. Kim et al. [3] found that when nanotubes were poorly dispersed, they exhibited lower complex viscosity than when they were well dispersed in an epoxy matrix. They also suggested that the strong interfacial bonding that occurred when the nanotubes were functionalized resulted in the epoxy composite having a higher viscosity compared to unfunctionalized nanotubes. For high CNT content ($V_f > 10\%$), CNT-sheets or buck papers (BP) are impregnated with resin. The porous carbon nanotube sheets are typically formed by vacuum infiltration of a suspended solution of carbon nanotubes. Buckypapers are used for a wide range of applications including electrodes [4], field emitters [5], actuators [6], and structural reinforcement [7-9]. In recent years, researchers have tried to manufacture composites using buckypaper and polymer [7-9]. Table 1 summarizes the mechanical properties of the nanocomposites obtained by various impregnation techniques.

This paper investigates the processing aspect of CNT-modified epoxy at low and high CNT content. At low CNT content, the rheological behaviour of nano-modified resins is studied and the effect of functionalization is discussed. At high CNT content, two impregnation techniques are presented, and the efficiency of the methods are investigated by SEM analyses and elastic property measurement.

Table 1 Elastic properties of dry and resin-impregnated buckypaper

Researcher		E_{BP}[†] (GPa)	Polymer	E_P[†] (GPa)	Impregnation method	Test method	E_C[†] (GPa)
Coleman *et al.*	[7]	2.3	PVA, PS, PVP	–	Intercalation	Tensile test (DMA)	6.9[*]
Song *et al.*	[8]	–	PEEK	2.7	Hot compress	Tensile test	8
Wang *et al.*	[9]	–	Epoxy	3.5	Resin infiltration	DMA	13.3

† BP, P, and C stand for buckypaper, polymer and composite, respectively.
* The improvement in Young's modulus was independent of the polymer types.

EXPERIMENTAL

Materials

The polymer used in this study was a standard aerospace grade epoxy, Araldite® MY0510 epoxy, supplied by Huntsman. This epoxy was used with 4, 4-Diaminodiphenyl Sulphone (DDS) hardener, also known by the commercial name of Aradur® HY976-2.

The nanotubes used in this work were Single Walled Carbon Nanotube (SWNT) supplied by the National Research Council Canada's Steacie Institute for Molecular Sciences (NRC-SIMS) located in Ottawa, Ontario, Canada. The nanotubes were prepared using a highly efficient laser-oven technique. The details of the production technique are given by Kingston et al. [10]. This production technique resulted in SWNT purity level of about 80 wt.% and metal catalyst contamination of under 6 wt.%. The remaining composition was made up of impurities such as amorphous and graphitic carbon particles. Some of the tubes were functionalized to the level of about 4 wt.% using alkoxy and carboxyl functionalized group to study the effect of functionalization. The functionalization is expected to improve the debundling and homogeneous dispersion of CNTs.

Sample Preparation

Low-CNT-Content Nanocomposites

The functionalized (alkoxy and carboxyl) and unfunctionalized SWNTs (0.2 wt.%) were mixed with MY0510 epoxy at NRC-SIMS. In order to facilitate the mixing of the nanotubes in the resin, the MY0510 was first dissolved in the organic solvent, Tetrahydrofuran (THF). The nanotubes were then dispersed using a highly efficient technique. The THF was removed by placing THF/SWNT/MY0510 under vacuum at 80°C for about 2.5 hours until all the solvent had evaporated. Once these were prepared, the neat MY0510, functionalized and unfunctionalized SWNT/MY0510 and the hardener were shipped separately. For the rheology experiments, the hardener was added to the resin system with hardener to resin ratio of 3:5, which reduced the nanotube content to 0.125 wt.%.

High-CNT-Content Nanocomposites

For high CNT content samples, two types of CNTs were used: unfunctionalized SWNT and carboxyl functionalized SWNT. The properties of the buckypaper sheets that are studied in this paper are summarized in Table 2.

Table 2 Buckypaper properties

Buckypaper properties		SWNT properties	
Thickness of the sheet	60-100 μm	**Diameter of SWNT**	~1.3 nm
Density	0.46-0.55 gr/cm^3	**Diameter of SWNT rope**	10-50 nm
Volume fraction	30-39 (%)	**Aspect ratio of SWNT rope**	>10000
Young's modulus	0.50±0.2*	**Impurities**	>10%

* average of all the tested buckypapers

Two buckypaper impregnation techniques were investigated: hot press moulding and vacuum bagging. For hot press moulding, a drop of resin was placed on top of the BP. Then, the BP was placed between two heated steel plates separated by a spacer. The assembly was then pressed under a 30 tons machine shop press. Similarly, for vacuum bagging, a drop of resin was placed on top of the BP. Then, a special bagging procedure was designed to infiltrate the resin into the buckypaper. Using vacuum bag and tape, the bag was sealed and placed in the oven for curing under vacuum. The assemblies were heated following a cure cycle that maintained the resin to its minimum viscosity for the longest possible time in order to maximize resin impregnation. The cure cycle was as follow: ramp up to 100°C, hold for 3 hours, ramp to 130°C, hold for 1 hour, ramp to 180°C, hold for 2 hours, and cooling to room temperature.

Low-CNT-Content Nanocomposite Characterization: Rheology Experimental Procedure

All the rheological experiments were conducted on a TAinstruments AR2000 rheometer with the Environmental Test Chamber (ETC) accessory. The measurement geometries used were 40 mm parallel aluminium plates cleaned with acetone. The resin thickness between the parallel plates was kept in the range of 500 to 1000 μm (volume of 0.628 to 1.257 ml) per sample. The rheological tests were conducted to verify the effect of time and temperature on the viscosity profile of the resin systems. These tests included both dynamic and isothermal runs.

Dynamic temperature tests (oscillatory temperature ramp) were performed to observe the variations in the viscosity profile of the resins with temperature. The experiment was heated from room temperature to 250 ºC at a ramp rate of 3ºC/min. The control variable of 12 % strain with the sampling rate of 1 point every 10 seconds was used. Several isothermal tests (oscillatory time sweep) were carried out at isothermal temperatures of 60 ºC, 100 ºC, 120 ºC and 140 ºC. These tests investigated the viscosity profile of the resin at these isotherms as a function of time. An oscillatory temperature ramp with the ramp rate of 20 ºC/min was used to bring the temperature up to the desired value. The sampling rate of 1 point every 10 seconds, the oscillation frequency of 1 Hz, and the control variable of 12 % strain were set. Once the desired temperature was reached, the oscillatory time sweep was engaged for 210 minutes.

High-CNT-Content Nanocomposite Characterization: Mechanical Testing

A commercial nano-indenter (Hysitron TriboIndenter) was utilized in an unconventional bending mode. From the bending behaviour of impregnated buckypapers in plate regime, the Young's modulus of the thin films was found. The detail of this technique can be found in [11]. This instrument is capable of applying loads ranging from 10 μN to 15000 μN, and can measure deflections with a resolution of 1 nm. To use the indenter in the bending mode, a fixture was designed to grip thin films of buckypapers, and to ensure clamped boundary conditions. Fig. **1** shows an exploded schematic and photograph of the fixture. From the constraints imposed by the TriboIndenter loading head, the minimum value for the film radius was 1.25 mm.

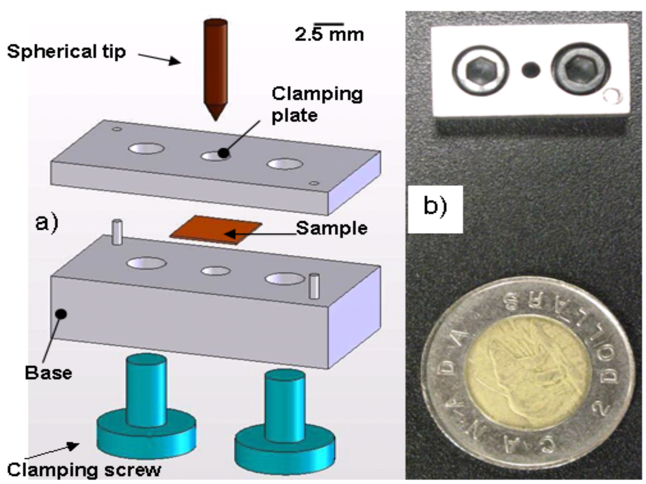

Fig. 1 a) Schematic of the film bending fixture; b) top view of the fixture.

RESULTS AND DISCUSSION

Low-CNT-Content Samples: Rheology Tests

Fig. 2 and 3 show the effect of SWNTs on the viscosity profile of MY0510/DDS during a temperature ramp and under isothermal condition. The figures show the effect of two different functional groups. It is clear that the nanotubes affect significantly the rheological behaviour of the resin. From Fig. 2, the initial viscosity (at room temperature) for alkoxy functionalized group was observed to be more than 7 times higher than that of the neat resin. However, unfunctionalized and carboxyl functionalized SWNT exhibited lower viscosity that was close to the neat resin resulting in higher processability at room temperature. Considering the gelation point as being the region at which the viscosity shows a sharp increase, it was also observed that for the alkoxy functionalized system, the gelation started at a temperature of about 30ºC lower and 10 minutes earlier compared to neat resin. The results of Fig. 2 can be used to verify the efficiency of the functionalization process, as an enhancer of the interfacial bonding between the CNTs and the polymer chains. The result indicated a higher efficiency of the carboxyl compared to alkoxy functional group. The isothermal results were also in agreement with the results of the temperature ramp. From the isothermal tests presented in Fig. 3, it can be seen that the gelation occurred significantly earlier in the presence of the alkoxy functionalized group. The lower gelation temperature could have been due to the advancement of the resin during the pre-processing with the nanotubes. The figures also depict the effect of functionalization at higher temperature.

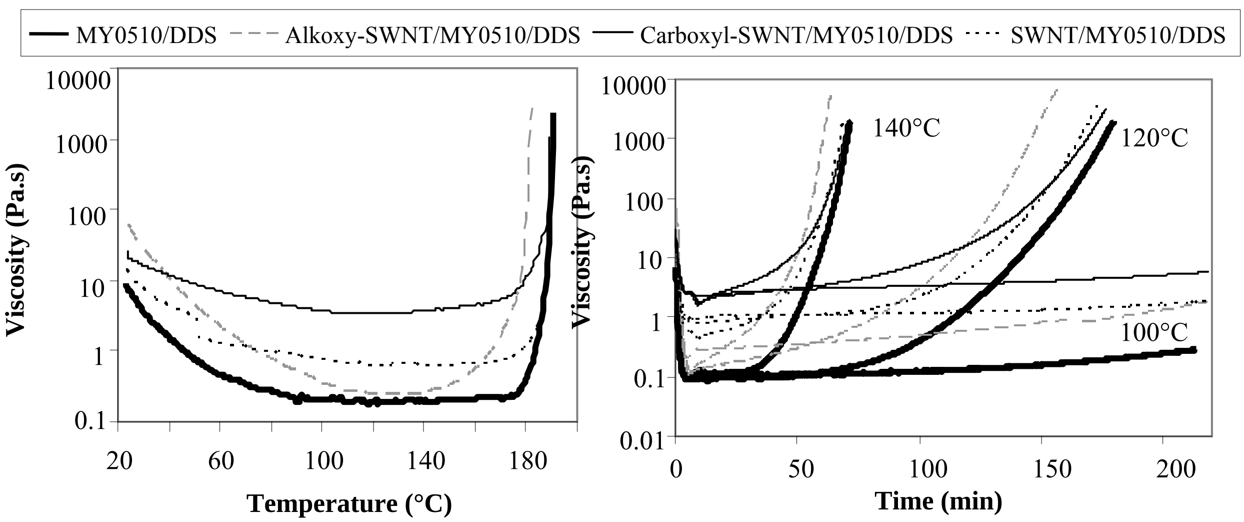

Fig. 2 Viscosity vs. temperature. Fig. 3 Viscosity vs. time.
Neat epoxy compared to alkoxy functionalized SWNT, carboxyl functionalized SWNT, and unfunctionalized SWNT epoxy.

The direct effect of alkoxy functionalized SWNT on the increase in the G' and G" values at the various isotherms is depicted in Fig. 4. The effect of these CNTs on the maximum value of the G' was much more pronounced at lower temperatures. Similar to the G' values, there was generally a decreasing trend with increasing isotherm temperatures for the loss modulus. The increase in storage modulus was much more significant compared to loss modulus at room temperature.

Another observation is that the isothermal temperatures affected the G' values more than the G" values (Fig. 4). This observation can be explained by the fact that the structure of polymer composites is more sensitively reflected on the G' values than on the G" as proposed by Pötschke et al. [12] as well as Sung et al. [2]. The 25°C results presented here showed similar trends to those of the above-mentioned authors' work with CNT-polycarbonate composites at low nanotubes loading. However, these similarities were not seen at higher isotherms as the thermal effects came into play as well.

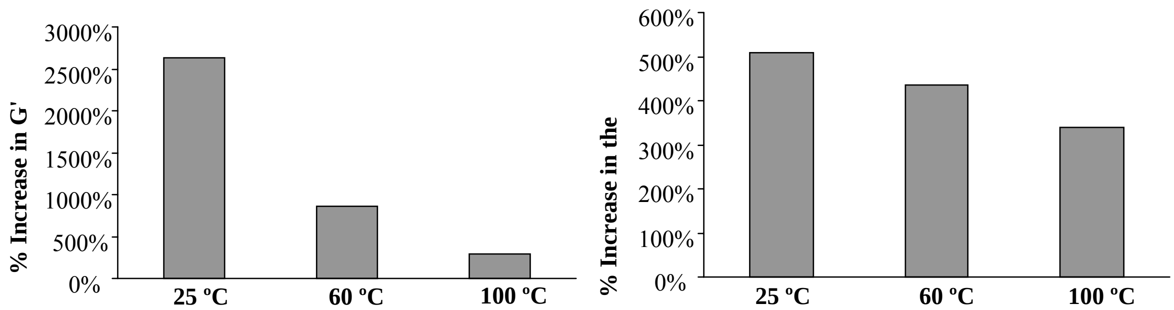

Fig. 4 Effect of 0.125wt.% alkoxy functionalized SWNT on the final G' and G” values measured at the angular frequency of 100 rad/s for each isotherm.

High-CNT-Content Samples: SEM and Mechanical Properties Characterization

SEM Analyses

In order to compare the efficiency of the impregnation techniques, Scanning Electron Microscopy (SEM) observation was used. A Hitachi S-4700 Field Emission SEM was utilized to characterize the pristine buckypaper. Field Emission SEMs provides high resolution at relatively high magnification. Fig. **5** shows images of pristine buckypaper taken at 25K and 100K magnifications. Based on these images, SWNT ropes have diameters ranging from 10 to 50 nm. This is consistent with the fact that buckypaper is made of ropes or arrays rather than individual SWNTs. These SEM images clearly show the presence of impurities inside the buckypaper.

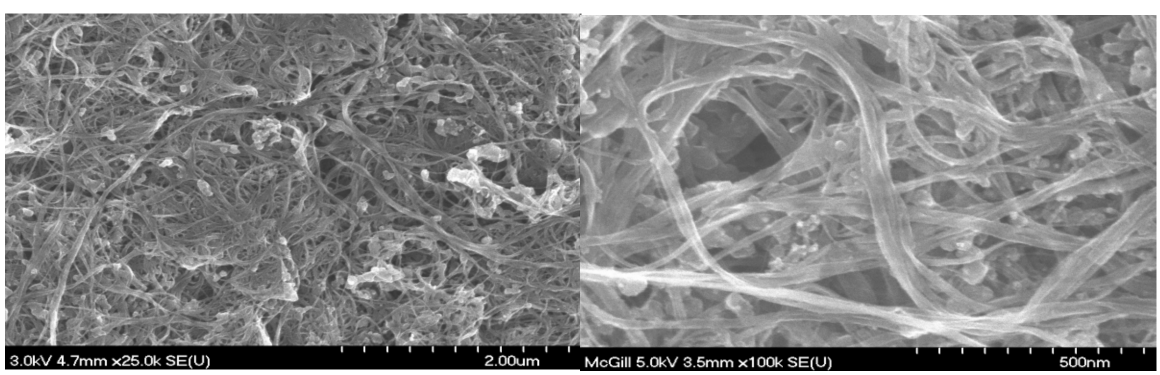

Fig. 5 SEM images of pure buckypaper with 25K and 100K magnifications.

Fig. 6 and 7 show SEM images of the buckypapers after impregnation with resin; i.e. hot-press and vacuum bagging impregnation technique, respectively. The images were taken from the cross-section of the impregnated samples. A comparison between pristine buckypaper and impregnated buckypaper clearly show a very different morphology confirming some resin infiltration of the buckypaper. However, the quality of the impregnation process was definitely different between the two techniques.

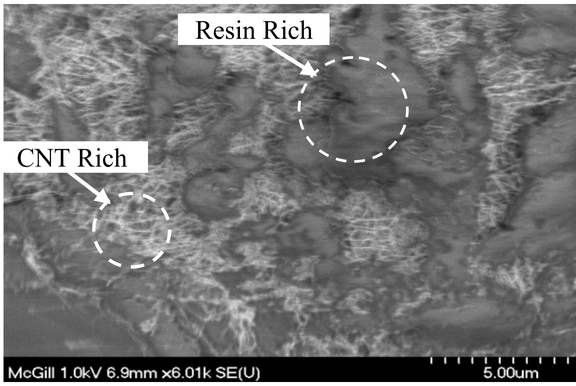

Fig. 6 SEM image from impregnated BP; hot press moulding.

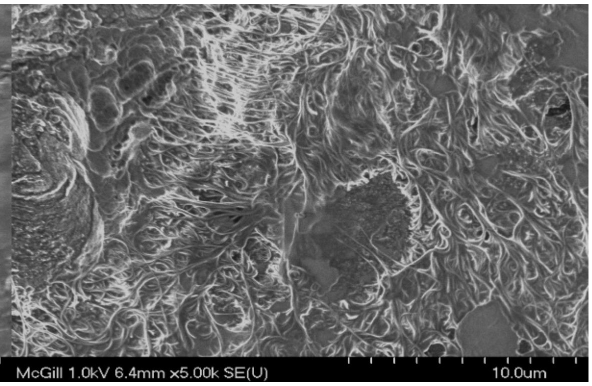

Fig. 7 SEM image from impregnated BP; vacuum bagging.

The main observation in Fig. 6 and 7 concerns the non-uniformity of the impregnation for the hot-press moulding technique. Two distinct regions can be observed in the hot-press samples (Fig. 6 at 6K magnification), i.e. resin rich region and CNT rich regions. The non-uniformity can be due to the applied pressure. As pressure enables the resin to flow into the buckypaper; the extremely low permeability of buckypaper causes the resin to displace the CNT ropes. This process created resin channels through the buckypaper resulting in resin rich regions. These channels had lateral dimensions of a few micrometers and prevented an efficient infiltration of the resin into the buckypaper. However for the vacuum technique, the buckypaper impregnation was more uniform (Fig. 7).

Elastic Properties Results

Fig. 8 shows the elastic properties of the pristine buckypaper, neat epoxy, and impregnated buckypaper samples. The Young's modulus of the neat epoxy MY0510 was measured with the thin film nano-indentation in bending mode. These results are the average of several tests on different impregnated samples; and also for each sample several pieces of the sample were tested. The experimental results are compared to the theoretical results based on the Mori-Tanaka method. The detail of the modelling is described in [13]. Fig. 8 shows that unfunctionalized buckypapers impregnated by vacuum bagging resulted in the maximum mechanical properties improvement with a 3 times increase in elastic properties compared to the neat polymer. For the hot-press impregnated buckypapers, there was no improvement of the elastic properties. Therefore, based on the SEM analyses and mechanical testing results, the hot press moulding technique is not an effective impregnation method. Carboxylic functionalized buckypapers were prepared to verify the effect of functionalization. The results of Fig. 8 clearly show the inefficiency of the functionalization process used in this work on the mechanical properties of impregnated buckypapers.

Another important observation in the results of impregnated buckypapers is the variability in the calculated Young's modulus. This shows that the impregnation procedure should be improved to produce a uniform material. Therefore, improving the impregnation quality is an important step for future investigation.

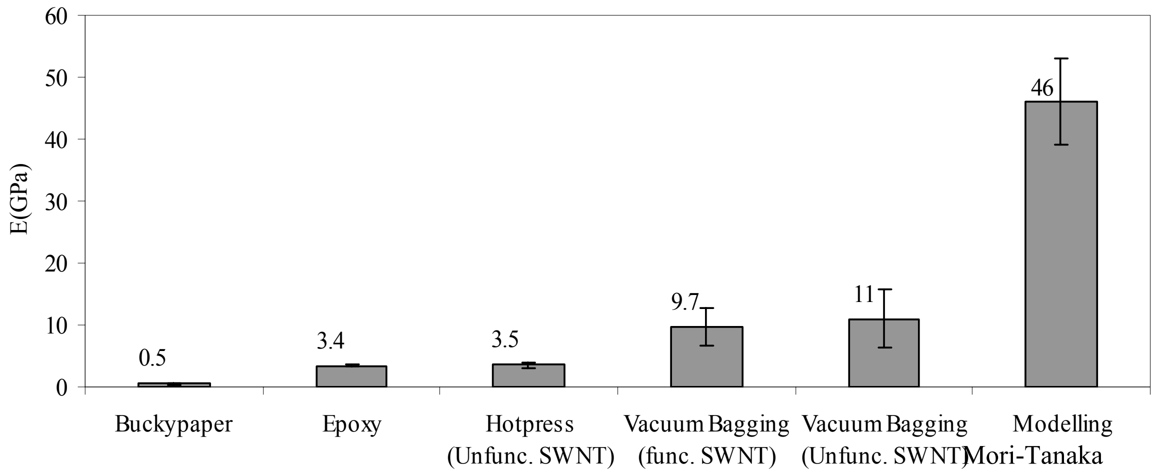

Fig. 8 Young's modulus of polymer-impregnated buckypaper.

CONCLUSIONS

At low CNT content, the viscosity profiles of the nano-modified resins can be used to verify the efficiency of different functionalization groups. The higher the viscosity, the better is the interaction of the functional groups with polymer chains. Also, the functional group which maintains the lowest viscosity at room temperature is more favourable from the processing point of view. Hence, the carboxylic functionalization is considered to be more effective than the alkoxy groups. The viscosity profiles can also be used to define the most effective temperature in terms of flow and processing properties of the resin. For example, 130°C is the optimum temperature for the alkoxy functional group. The role of the alkoxy as a mild hardener was supported by the rheology data as well, where the epoxy started gelling at a lower temperature in the presence of alkoxy functionalized nanotubes (Fig. 3).

For high CNT content samples, a maximum of 3 fold increase in the elastic properties was observed. However, the impregnation technique must still be improved to produce a more uniform material. In this regard, the interaction of the polymer chains with CNT bundles should be studied, as well as polymer flow in buckypaper as a porous media. This could help researchers design a more efficient impregnation technique to enhance the uniformity of the impregnation, and hence less variability of the mechanical properties. More investigation is also required to understand the effect of functionalization and its role on the mechanical properties of impregnated buckypapers.

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