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Improving the Mechanical Properties of Polycarbonate Nanocomposites with Plasma-Modified Carbon Nanofibers

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The mechanical properties of polycarbonate film embedded with carbon nanofibers were studied based on plasma surface modification of carbon nanofibers by the use of polystyrene. The nanofiber surfaces were modified by various processing conditions including plasma polymerization power, nanofiber concentration, and ultrasonication time. The tensile strength and Young's modulus of the carbon nanofiber-polycarbonate composites were then measured. The mechanical behavior of the composite was found to be affected by dispersion of the nanofibers. Higher plasma power resulted in improved mechanical strength. A maximum strength (10% increase) was achieved at a low concentration (1 wt.%) of nanofibers. The optimization of ultrasonication time indicated that the maximum strength occurred at different times for the composites with different concentrations of the modified carbon nanofibers.

Keywords carbon nanofibers, polycarbonate, mechanical properties, plasma deposition, surface modification, ultrasonication

Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991,[1] extensive research has been carried out to use them to reinforce polymer matrices for enhancing their mechanical strength. Carbon nanotubes have exceptionally high axial strength and an axial Young's

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modulus of the order of one terra Pascal.[2,3] However, CNTs are subject to aggregation that limits their potential applications. Two main methods are used to disperse CNTs in a polymer: mechanical methods and chemical methods.[4–7] Recently, the plasma polymerization method has been effectively used to modify CNT surfaces leading to significantly improved dispersion in the polymer matrix.[8] Although ultrasonication has been used for dispersion of CNTs, the effect of ultrasonication time on dispersion is not very well understood. On the other hand, dispersion is also associated with different concentrations of CNTs in the polymer matrix, which, in turn, also affects the mechanical properties.

In this paper we describe a series of experiments conducted to determine the effects of plasma polymerization and ultrasonication time on the mechanical behavior of carbon nanofiber-polycarbonate composites. Carbon nanofibers (CNFs) are similar to multiwalled carbon nanotubes, but the CNFs are longer in diameter and much lower in cost, thus making them practical for more applications. The surface-modified carbon nanofibers were characterized by high resolution transmission electron microscopy (HRTEM) and secondary ion mass spectroscopy (SIMS).

Experimental Details

Carbon nanofibers (CNFs) (Pyrograft PR 24) were purchased from Applied Science Inc., Cedarville, Ohio. The average diameter of the CNFs ranged between 60–150 nm. Styrene of 99.5% purity, which was used to coat the CNF, was obtained from Alfa Aesar, Johnson Matthey Company, Ward Hill, MA. Polycarbonate resin was purchased from Fisher Scientific Inc., Chicago, IL with MW 64,000.

The plasma-coating facility is a specially designed system for small particle applications. The schematic diagram of the plasma reactor for thin film deposition of nanoparticles is shown in Fig. 1. It mainly consists of a radio frequency (RF) source, a glass vacuum chamber, and a pressure gauge. The vacuum chamber of the plasma reactor has a long Pyrex glass column about 80 cm in height and 6 cm in internal diameter. The CNF powder was vigorously stirred at the bottom of the tube and, thus, the surfaces of the particles were continuously renewed and exposed to the plasma for thin film deposition during the plasma polymerization processing. A magnetic bar was used to stir the powder. Before the plasma treatment, the pressure in the reactor was pumped down to under 375 Pa. Then the styrene monomer was introduced and the pressure was controlled at 2250 Pa. The operating pressure was adjusted by the gas/monomer mass flow rate.

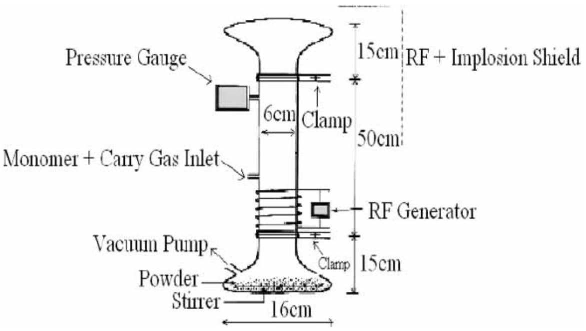

Figure 1. Schematic diagram of the low temperature plasma-coating system.

After the plasma treatment, the treated CNF was characterized using transmission electron microscopy (TEM). The high-resolution TEM (HRTEM) experiments were performed on a JEOL JEM 4000EX TEM. The fracture morphologies of nanotube composites were studied using a Philips XL30 FEG scanning electron microscope (SEM). The coated CNFs were also characterized by secondary ion mass spectrometry (SIMS).

Dispersion of the uncoated and coated CNFs in polycarbonate polymer matrix was achieved by ultrasonication for different periods. Two grams of polycarbonate (polymer matrix) were weighed and placed in different beakers. At the same time, 1, 2, 3, and 5 wt.% uncoated and coated CNFs were also placed in other beakers, separately. Chloroform was added to each beaker. The beakers were then placed into an ultrasonication tank (L&R Solid Ultrasonic T-14B, Misawa Inc.) for mixing. After the polycarbonate was dissolved entirely, the solution containing CNFs was mixed with the solution containing polycarbonate. After ultrasonication for various periods (0.5 h, 1 h, 2 h, 4 h, 8 h, 12 h, and 24 h), each mixed solution was poured into an aluminum mold. After the chloroform evaporated, a CNF-polycarbonate (CNF-PC) composite was formed.

After the sample was completely dried, it was sectioned into 50 mm × 6 mm× 0.4 mm samples for tensile testing according to the ASTM D 822-97: "Standard Test Method for Tensile Properties of Thin Plastic Sheeting". An Instron mechanical testing machine, model 2525-818, with a 1 mm/min crosshead speed was used for the tensile test. Multiple measurements were performed in the tensile experiments. Five samples were tested and an average value was used for each datum point.

Results and Discussion

In the TEM experiments, it was found that an ultrathin amorphous film was deposited on the surfaces of the CNF (Fig. 2, 100 W plasma treatment) with thicknesses of

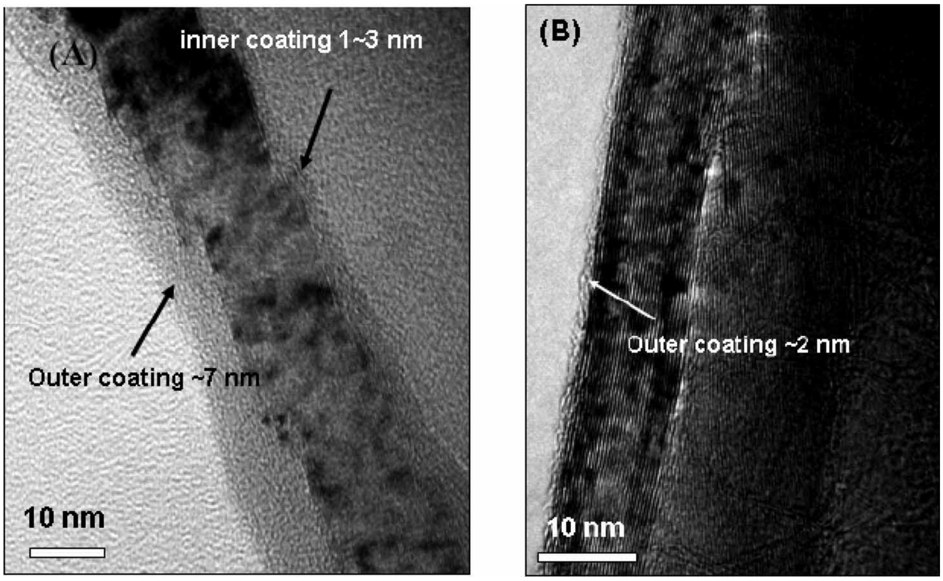

Figure 2. HRTEM images of coated CNF (100 W): (A) surface coating of polymers on both inner and outer walls of the nanofiber, and (B) carbon lattice.

approximately 2∼7 nm on the outer surface and 1∼3 nm on the inner surface. The lattice image of carbon can be clearly seen with an extremely thin layer of polymer film on the outer surface of the CNF (Fig. 2B). The main principle of the plasma polymerization technique is that the ionized/excited molecules and radicals, created by the electrical field, bombard and react with the surface of the substrate. As a result, the surface properties of CNF are modified. Due to the high surface energy of the nanofibers, condensation of the monomer vapor on the nanoparticles naturally lowers the surface energy by forming an extremely thin film. One of the critical issues addressed in this study is the deposition of thin films inside the nanofiber whose diameter is only about 20 nm. The length of these fibers is on the order of several microns. In order to obtain a uniform coating on the inner wall surfaces, the fluidization of the nanofibers and the plasma coating conditions must be critically controlled. The polymerization should take place relatively fast after the condensation on the nanofiber surfaces. This will ensure a uniform coating on the order of a few nanometers on both the inner and outer surfaces. As shown in Fig. 2A, there is an extremely thin (1∼3 nm) polymer film deposited on the inner wall surface while a relatively thicker film is deposited on the outer surface. This is an indication of the deposition rate difference within and outside the nanofiber. As observed previously,[1,8] nanofibers have open ends and can allow inflow of monomers. Therefore, the residuals could travel through the tube structure and deposit on the inner wall of the nanofibers. Because of the nanoscale diameter of the tube, for a given gas pressure, the collision frequency must be reduced inside the nanofiber resulting in a lower deposition rate.

To confirm the TEM observations shown in Fig. 2, SIMS was carried out to study the surface film of the CNF. Figures 3 and 4 show the positive SIMS spectra of uncoated and coated CNF. In Fig. 3, one can see that the spectra of the positive ions from the uncoated CNF have strong peaks of functional groups such as C_1, C_2, C_3, C_4, $C_7H_7^+$, and $C_{10}H_8^+$ indicating the CNF surface contains hydrocarbon. As the plasma coating of polystyrene only contains carbon and hydrogen, the hydrocarbon from the CNF surface may not be easily identified as being from the CNF surface coating. In order to solve this problem, C_6F_{14} was added to combine with the styrene monomer. In Fig. 4, one can see that the spectrum of the positive ion from coated CNF has strong peaks such as CF^+, C_2F^+, $C_4F_6^+$, $C_3F_7^+$, $C_4F_7^+$, and $C_5F_7^+$ indicating existence of fluorine in the coating film. The fluorine can only come from the monomer. This is a clear evidence that the thin film in the TEM image is indeed from the plasma polymerization.

In Fig. 5 and 6, one can see that both the tensile strength and Young's modulus of CNF-PC composites exhibited maximums for an early dispersion time near 2 hours. These include the composite with 1 wt.% CNF plasma-coated at 100 W (1c100 W), the same composite but coated at 10 w (1c10w), the composite with uncoated CNF (1un), and the pure polycarbonate (p). It has been reported[9] that hydrodynamic forces of repulsion and attraction are involved in an ultrasound field when two particles are separated by a distance of only a few particle diameters. The maximum tensile strength may be the balance state of the contracting force and the repelling force created in the ultrasound field. This may indicate that for the current systems, balances in contracting force and repelling force may be accessed in 2 hours, regardless of the other treatment conditions.

As can be seen in Fig. 5 and 6, except for the pure PC, all of samples experience minimums near 11 h; and thereafter, the mechanical strength increases again for a longer dispersion up to 24 hours. An interesting feature in the mechanical strength to be noted here is that both composites with coated CNF exhibit plateaus between 4 h and 8 h. However, the composite with uncoated CNF continues to slightly decrease after the

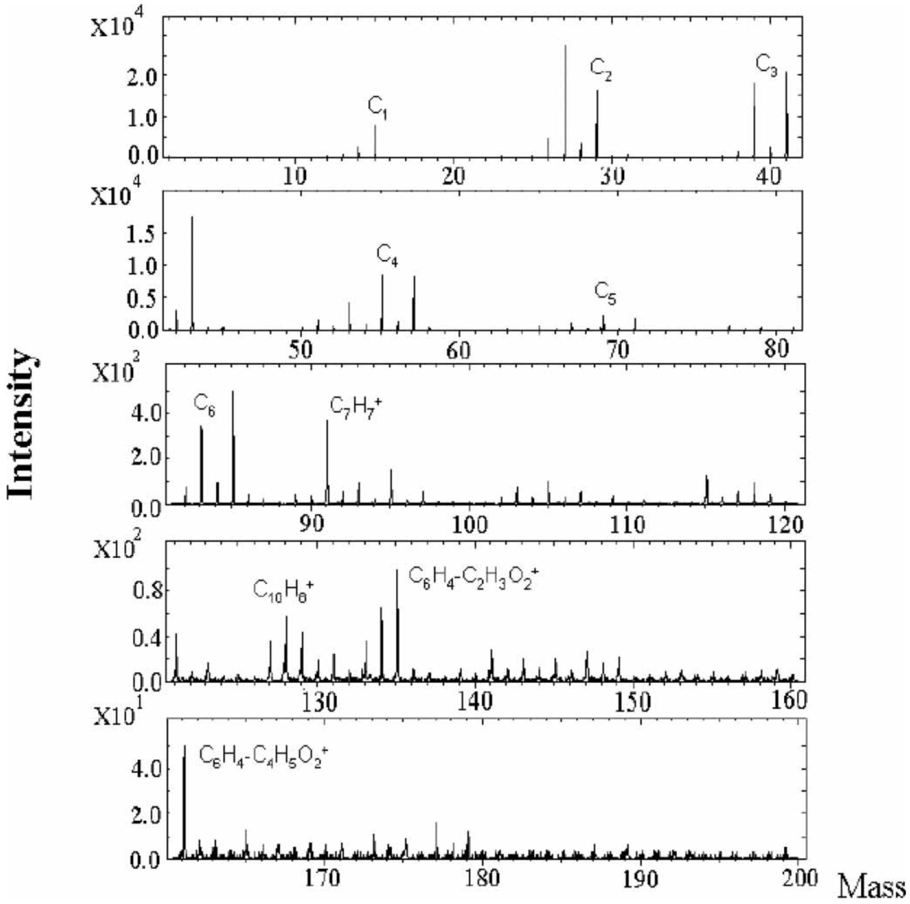

Figure 3. SIMS spectrum of uncoated CNF.

first maximum during this period. The modulus behavior of these composites shows similar trends as can be seen in Fig. 6. But the overall modulus values of composites with coated CNF are considerably larger than that of PC, except at their minimums. These experimental data suggest that the plasma surface treatment improves both mechanical strength and modulus. Based on these data, a 10% increase in mechanical strength and a 14% increase in modulus are achieved in the composites with coated CNF at 100 W.

The maximum strength varies with the CNF concentration. In Fig. 7 and 8, one can see that all composites exhibit a similar trend. The highest strength occurs at the beginning and then experiences a steady decrease. The composite with coated CNF under 100 W power has the highest strength within the entire dispersion period up to 24 h. The modulus values of all composites exhibit maximums at 3 wt.%, but the composite with coated CNF at 100 W has the highest value (Fig. 8). However, it was more difficult to reach optimum dispersion in the 5 wt.% composites compared to the low concentrations such as those in the 1 wt.% composites. The time required to reach these maximums varied for different CNF concentrations. It was found that the 1 wt.% CNF-PC composite needed only 2 hours to reach the maximum mechanical strength while the 2, 3, and 5 wt.% of CNF-doped composites needed 8 hours. The change of

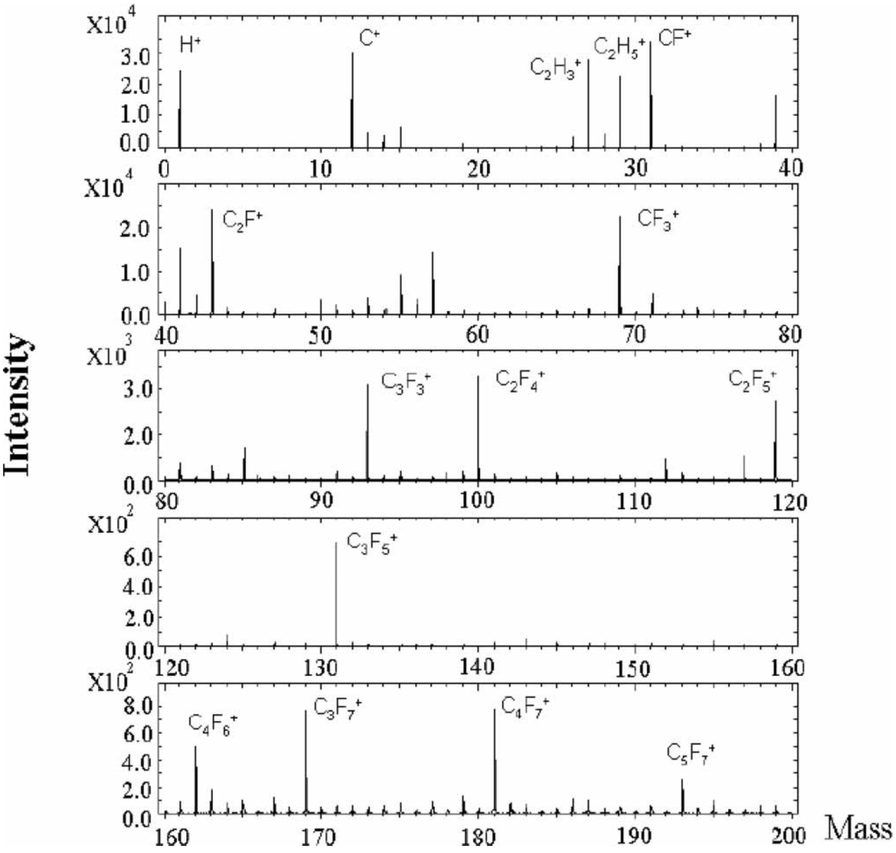

Figure 4. SIMS spectrum of coated CNF.

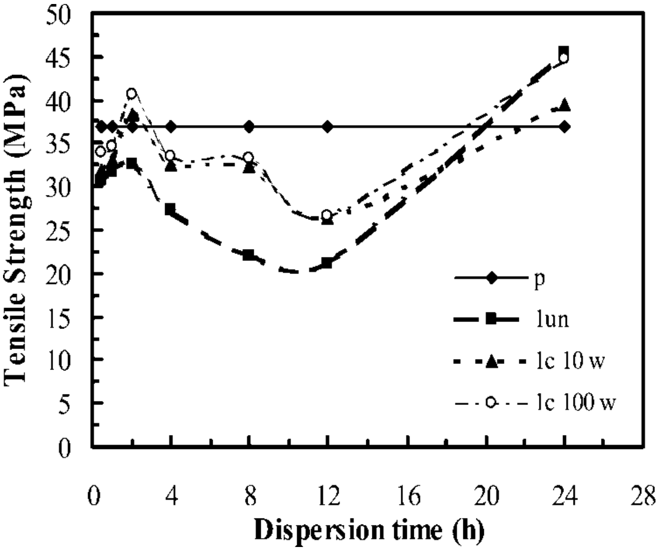

Figure 5. Tensile strength vs. ultrasonication time for samples indicated (p: pure PC; 1un: 1 wt.% uncoated CNF; 1c 10 W: 1 wt.% coated CNF at 10 W; 1c 100 W: 1 wt.% coated CNF at 100 W).

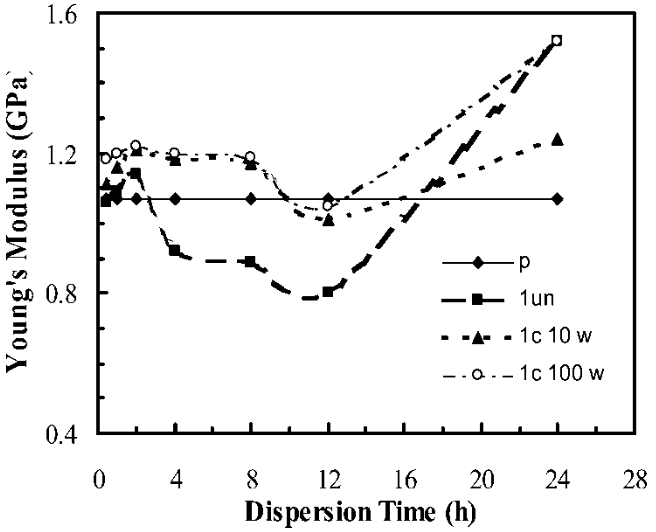

Figure 6. Young's modulus vs. ultrasonication time for samples indicated (p: pure PC; 1 un: 1 wt.% uncoated CNF; 1c10 W: 1 wt% coated CNF at 10 W; 1c 100 W: 1 wt % coated CNF at 100 W).

surface properties of the particles and a change in the structure of the dispersion also contributed to the increase of the mechanical properties at much longer ultrasonication times.

Generally, the maximum tensile strength decreases with the CNF concentration due to increasing inhomogeniety in the dispersion. But, the strength increases again at 5 wt.% CNF-doped PC where one might expect greater agglomeration and inhomogeniety. Composites with plasma-treated CNF exhibited higher tensile strength for all CNF

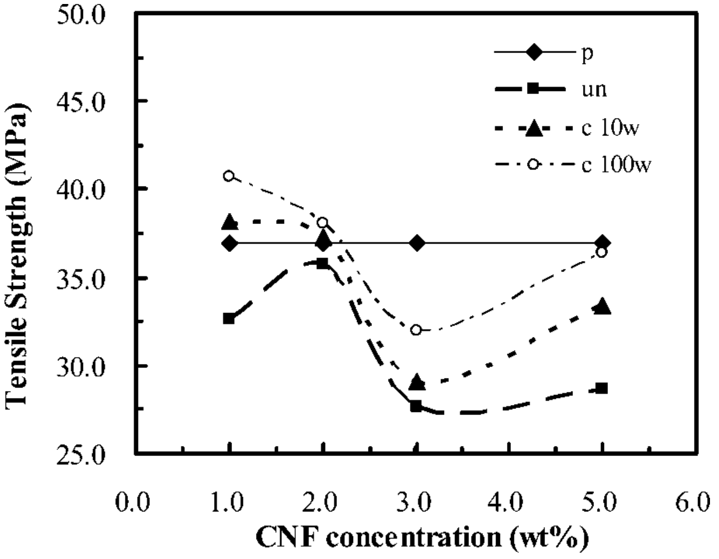

Figure 7. The maximum tensile strength vs. CNF concentration for samples indicated (p: pure PC, un: uncoated CNF, c 10 W: coated CNF at 10 W, c 100 W: coated CNF at 100 W).

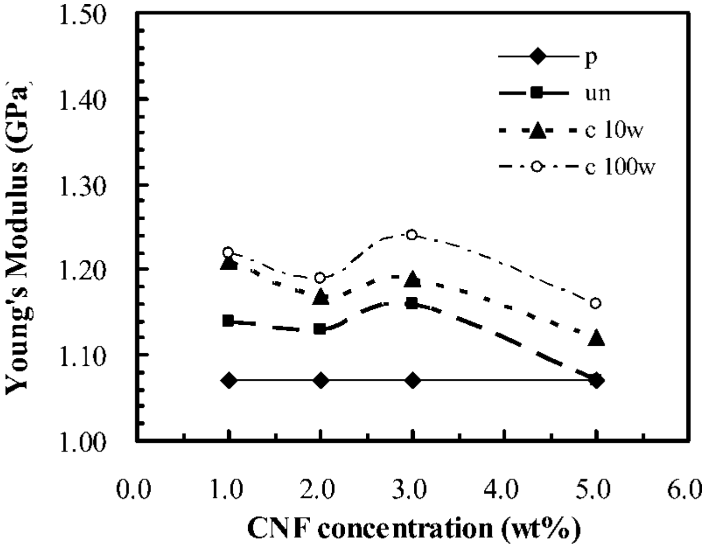

Figure 8. The maximum Young's modulus vs. CNF concentration for samples indicated (p: pure PC, un: uncoated CNF, c 10 W: coated CNF at 10 W, c 100 W: coated CNF at 100 W).

concentrations. However, the maximum Young's modulus does not take place at the same CNF concentrations. Furthermore, only at low concentrations (1 and 2 wt.%) does the strength of the composites exceed that of the pure PC. High CNF concentration does not improve mechanical properties. Lau and Hui[10] showed that the use of multiwalled nanotubes for advanced composite structures may not improve the mechanical strength of the structure because of the weak bond between the outer shell of the multiwalled carbon nanotube and the polymer matrix, and the nonuniform axial deformation inside the multiwalled nanotubes caused by rotation and sliding of the inner individual graphene shells. For the current CNF-PC composites, the mechanical strength was improved by the use of plasma surface–modified CNF. This improvement may result from the promotion of the weak bond between the outer shell of the carbon nanofiber and the polycarbonate matrix.

Conclusions

Based on the previous experimental results, we conclude that the mechanical properties of CNF-PC composites depend on the dispersion and surface properties of CNF in the PC matrix. The mechanical properties are apparently affected by the dispersion time. However, the quantitative measurement of dispersion needs new experimental approaches such as TEM, SEM, and small angle light scattering. On the other hand, the surface behavior of CNF and its interface with the PC matrix also plays a crucial role in the mechanical properties.

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