Surface Modification of CNFs via Plasma Polymerization of Styrene Monomer and Its Effect on the Properties of PS/CNF Nanocomposites

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ABSTRACT: Carbon nanofibers (CNF) were modified via plasma assisted polymerization in a specially designed reactor. The effect of the plasma reactor conditions, such as power and time, on the extent of the CNFs modification was examined. Polystyrene (PS) coated nanofibers plus PS polymer were then processed in a Brabender torque rheometer mixing chamber to obtain PS/CNF nanocomposites, with 0.5, 1.0, 3.0, and 5.0 wt % of CNF. The effect of the plasma treatment on the dispersion of the nanofibers and on the compatibility between the nanofibers and the polymer matrix was also examined. Modification of the CNFs was assessed by measuring the contact angle of water in a ''bed'' of nanofibers and by examining its dispersion in several solvents. The morphology of PS/CNF nanocomposites was studied through scanning electron microscopy (SEM). Contact angles decreased in all cases, indicating a change in hydrophobicity of the modified CNFs. This change was confirmed in the CNF dispersion tests in several solvents. SEM micrographs show the difference between the original and the PS coated CNF. In addition, fractured samples show the effect of this treatment, in the sense that the CNF seem to be completely embedded in the polymer matrix, which clearly indicates the high compatibility between the PS and the modified (PS coated) CNF. As a consequence, a much better dispersion of the treated CNF was observed. Finally, the tensile modulus of PS/CNF composites increased slightly with respect to PS when using untreated CNFs, but more than doubled when using plasma treated CNFs. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1893–1899, 2008

Key words: carbon nanofibers; polymer nanocomposites; plasma polymerization; CNF functionalization

INTRODUCTION

The success of nanoparticles as reinforcing agents in polymer composites are of course due to the intrinsic mechanical properties of the said nanoparticle, but it is mostly due to their great surface area to volume ratio. And a requisite for this great surface area to be effective in reinforcing is the compatibility between the nanoparticles and the polymer matrix. Nonetheless, incompatibility is the most common issue when dealing with polymer–nanoparticle composites. In this respect, a great effort has been dedicated to study the effect of modifying with specific functional groups, either the nanoparticles[1–4] or the polymer matrix,[5,6] in order to attain a much better compatibility between them. Another line of study is the use of a third substance which would act as a compatibilizer between them.[7–10]

As well as compatibility, another very important factor that directly affects the properties of the polymeric nanocomposite is the degree of dispersion of the nanoparticles. In this respect, the positive effect of shear during mixing has been demonstrated in attaining optimum levels of dispersion.[11] When the mixing process is carried out in solution, it has been reported that the use of ultrasound has produced very good levels of dispersion.[12,13]

One of the methods that can be used to modify the nanoparticles is the plasma technique. This is a relatively simple, rapid, and dry method that has been used to modify the surface of different substrates. Though it was originally implemented to modify the surface of polymeric substrates,[14,15] this technique has been successfully used during the last decade for the surface modification of different filler particles, such as; zinc, iron, and aluminum oxide nanoparticles, nanoclays, and carbon nanofibers (CNFs) and nanotubes.[1,16–19]

The mechanism of plasma polymerization tends to be a radical polymerization process,[20,21] especially when the plasma power is high. However, when the plasma power is low, the reaction tends to go through an ionic polymerization process.[22] These latter authors showed that the plasma polymerization of styrene goes mostly through a radical polymerization process.

Also, it has been reported, after XPS and SIMS, plus MS studies, that the aromatic structure of styrene remains almost intact after the plasma polymerization process.[23,24]

The purpose of the present work was to study the effect of the plasma reactor conditions on the surface modification (surface coating) of the CNF, via plasma polymerization of styrene, and the effect of this modification on the tensile properties of polystyrene (PS)/CNF composites.

EXPERIMENTAL

Materials

The polymer used was general purpose PS, from Resirene, México, with Mw of 168,000 and M_w/M_n equal to 4.3. The CNFs were from Applied Sciences and are designated as Pyrograf III; these are 60–150 nm in diameter, 30–100 çm in length, and have a density of 1.95 g/cm^3 and a surface area of 55 m^2/g. The styrene used to modify the CNFs, i.e., to produce an ultrathin PS layer coating on the CNFs, was obtained from Sigma-Aldrich.

Methodology

The CNFs were coated with an ultrathin PS layer as styrene monomer was being polymerized in the plasma reactor, in the vapor phase, and deposited on the surface of the CNFs.

The plasma reactor used was designed by the authors and consists mainly of a power controller coupled to a radiofrequency generator of 13.56 MHz, a vacuum pump, a gas flux control valve and a 500 mL glass flask. Figure 1 shows a photograph of the plasma reactor used.

The glass flask is held over an electrical heater with constant agitation in order to achieve a homogeneous PS coating over the CNFs. A copper wire that acts as an electrode is coiled around the glass flask. One of the ends of the copper wire is connected to the radiofrequency generator (Advance Energy RFX600). The vapor phase polymerization of PS and coating of the CNFs was carried out as follows: 1.5 g of nanofibers were introduced in the glass flask and put under vacuum. The initial system internal pressure was 0.3 Pa. Then, the styrene monomer flow was fixed while the pressure was kept constant at 2.5 Pa. This pressure gave a constant styrene flow, into the reactor, of 0.15 cm^3 (1.25 mmol) per min. The CNF were treated for different times (30, 60, and 120 min), with different power intensities (50, 100, and 150 W).

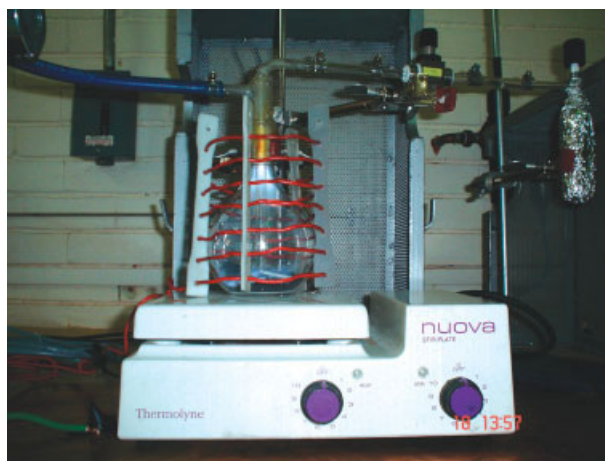The plasma reactor used in this study has a different configuration than the one used by Gao et al.[13]

Figure 1 Plasma reactor used for the CNF modification. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Preparation of the nanocomposites

All nanocomposites were prepared in a Brabender torque rheometer mixing chamber, using cam type rotors, at 190°C and 85 rpm for 15 min. In all cases, the 75 mL chamber was filled up to 93%, i.e., with 70 mL. The PS/CNF nanocomposites were prepared containing four different CNF concentrations (0.5, 1.0, 3.0, and 5.0 wt %), previously treated in the plasma reactor for three different periods of time at three different power intensities. The mixing procedure was as follows: the PS was introduced into the mixing chamber and the processing started. Once the PS ''melted,'' the CNF was introduced during a period of 2 min; thereafter, the mixing was continued for 13 more min to complete the 15 min mixing time. Finally, the nanocomposites were extracted, ground, and compression molded to obtain 150 × 150 × 3 mm^3 plates, from which tensile test specimens (ASTM D-638) were cut.

Characterization

The contact angle of a drop of water over a compressed and uniform layer of the unmodified and modified CNFs was measured with a Rame-Hart goniometer. A 50 μL syringe was used to deposit a 5 μL drop of water over the bed of CNF. Three measurements were made for each case.

The unmodified and modified nanofibers were also tested for dispersion in several solvents with different polarity indexes: water, ethanol, acetone, chloroform, and THF, with a relative polarity of: 1, 0.654, 0.355, 0.259, and 0.207, respectively.[25] Then, 3 mg of the differently treated nanofibers were immersed into 10 mL of solvent and agitated. After
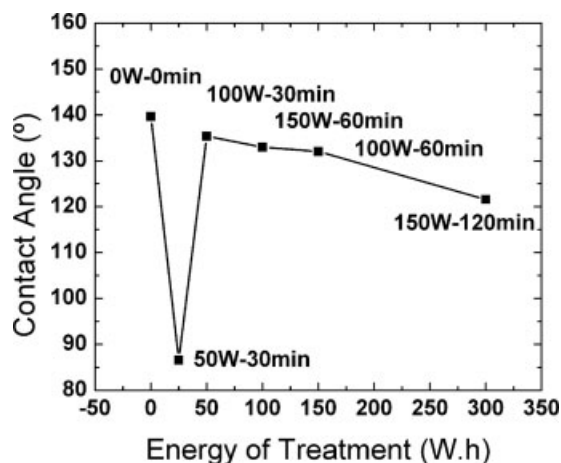
Figure 2 Contact angles of water on the untreated and treated CNFs.

a given time, photographs were taken and the degree of dispersion was established.

Fractured tensile specimens were studied through a Jeol JSM7401F Scanning Electron Microscope to assess the nanocomposite morphology and the ''adhesion'' between the CNF and the polymer matrix.

Tensile properties were measured in a United Tensile Tester 3M-10 machine, fitted with a 450 kg load cell at an extension rate of 5 mm/min. All tests were performed in accordance to ASTM D638. Six test specimens were tested for each data point and the average was taken as the result.

RESULTS AND DISCUSSION

Figure 2 shows the contact angles of the untreated, as well as that of the plasma treated CNFs. The contact angle of the untreated nanofibers is about 140°, whereas that of the nanofibers with the PS coating due to the plasma treatment is less than that. This suggests that the plasma treatment changed the ''normal'' hydrophobic character of the CNFs to a slightly hydrophilic character. This may be

explained, assuming that the aromatic groups of the PS, now coating the CNFs, interact more easily with the water, decreasing so the contact angle. In addition, it is observed that when the time and the power intensity are in the lower range studied, i.e., 30 min and 50 W, the contact angle is the lowest, whereas when increasing either the time or the power intensity, the contact angle increases, but anyhow, remains below that of the untreated CNFs. This can be explained considering that at 30 min and 50 W the styrene monomer polymerizes, and scarcely crosslinks, to form an ultrathin PS layer on the nanofibers, which permits the water molecules to diffuse freely along this PS film. When the plasma treatment is for longer times or at higher power intensities, however, the styrene monomer polymerizes, but tends strongly to crosslink due to increased density of energetic electrons.[26–28] This crosslinked coating appears to be impermeable enough to the diffusion of water, so the interaction between water and the treated nanofibers is diminished and the contact angle increases (increases with respect to the nanofibers treated for 30 min at 50 W).

On the other hand, Figure 3 presents a photograph of the vials containing the untreated and the plasma treated CNFs dispersed in chloroform. It can clearly be observed that the untreated nanofibers sediment almost immediately, whereas the plasma treated ones (for 30 min, 100 W; and 120 min, 150 W), remain fairly dispersed after standing for 24 h. In general, it was observed that dispersion was poor or even nil in high polarity solvents, as water, whereas dispersion was much better in low polarity solvents, such as ethanol, THF, and chloroform, especially the plasma treated nanofibers. There was no difference in dispersion for either the untreated or treated nanofibers, the nanofibers always remained on the water surface.

Figure 4 presents a photograph of the vials containing the untreated and the plasma treated CNFs dispersed in acetone. The difference is clearly
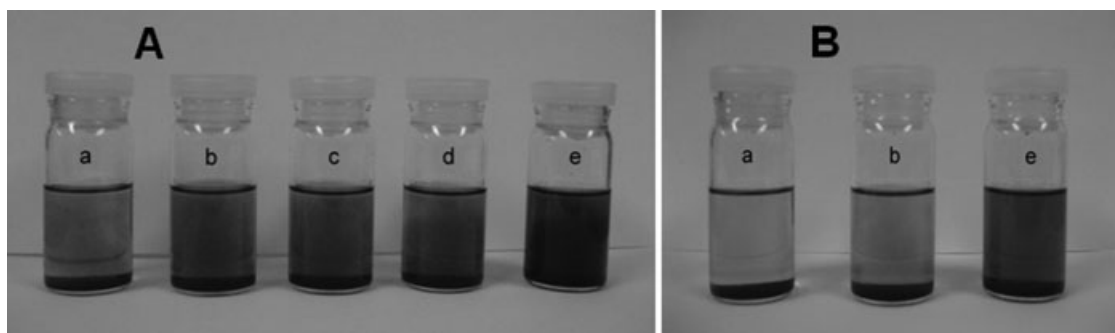

Figure 3 Dispersion of CNFs in chloroform. (A) At the beginning and (B) after 24 h. (a) Untreated CNFs and treated for: (b) 30 min, 50 W; (c) 30 min, 100 W; (d) 60 min, 150 W; and (e) 120 min, 150 W.
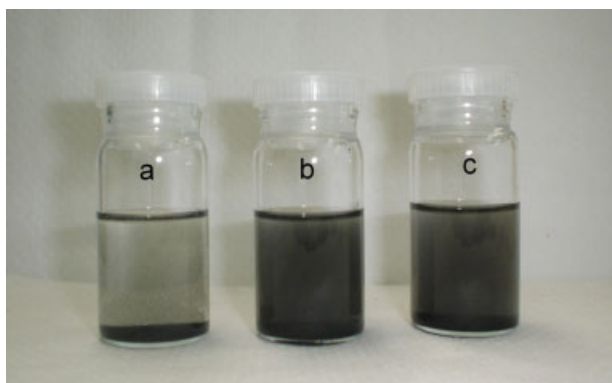
Figure 4 Dispersion of CNFs in acetone: (a) untreated; and treated for: (b) 30 min, 50 W; and (c) 120 min, 150 W. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed. The untreated CNFs sediment almost immediately, whereas the plasma treated CNFs remain as dispersion for more than an hour, suggesting an interaction between the solvent and the CNFs.

Dispersability tests do not give a quantification of the degree of modification; however, they give a fair idea whether the modification on the CNFs was or not achieved.

Figure 5 presents a pair of scanning electron micrographs (SEM) of fractured tensile specimens of PS/untreated CNF composites. Figure 5(A) clearly shows the presence of nanofiber agglomerates. This poor dispersion is originated in part by the lack of compatibility between the CNFs and the PS matrix. This poor compatibility is observed in Figure 5(B), where the nanofiber is seen completely loose, without any attachment to the PS matrix.

Figure 6, on the other hand, presents a pair of SEM micrographs of PS/treated CNF composites. Contrary to that observed with the untreated nanofibers, the nanofibers appear very well dispersed, as shown in Figure 6(A); no nanofiber agglomerates are observed. In addition, a high compatibility between the CNFs and the polymer matrix can be presumed

from Figure 6(B), in which the nanofibers seem to be completely embedded in the PS matrix.

The plasma treatment favors a much better dispersion of the nanofibers, as observed in Figure 7(A,B). Undoubtedly, the dispersion degree achieved with the modified CNF, as observed in Figure 7(A,B), is clearly superior, compared to the dispersion attained with untreated nanofibers, as shown in Figure 5(A).

In addition, Figure 7(C) shows the tearing of the fractured polymer matrix around the nanofibers. This is an indication of the good stress distribution on the whole composite during the application of the tensile stress, which in time, is the result of the good dispersion of the CNFs and the excellent adhesion between the polymer matrix and the nanofibers.

In addition, taking a closer examination at Figures 5–7 it can be observed that the fracture of the sample with treated CNFs appears to be slightly ductile, with a network structure, similar to the one reported by Bernadette,[29] whereas the fracture of the sample with untreated CNFs tends to be fragile, as PS.

The above results show that the ultrathin PS layer deposited on to the CNFs during the plasma treatment clearly helps in compatibilizing the nanofibers with the PS matrix.

This plasma treatment, in addition to increasing the compatibility, creates an ultrathin PS coating on the CNFs, which renders the nanofibers surface to have identical characteristics to those of the PS matrix. This results in a much greater adhesion and interaction between both phases, facilitating the load transfer from the continuous polymer matrix to the dispersed nanofibers.

This effect can be observed in the micrograph in Figure 8, where a single CNF in the upper right hand side, clearly appears to have been telescoped (do not forget that these micrographs were taken on the surface of fractured tensile specimens), that is, this single nanofiber has apparently lost the outer grafene layers as a result of absorbing part of the tensile stress applied during testing.
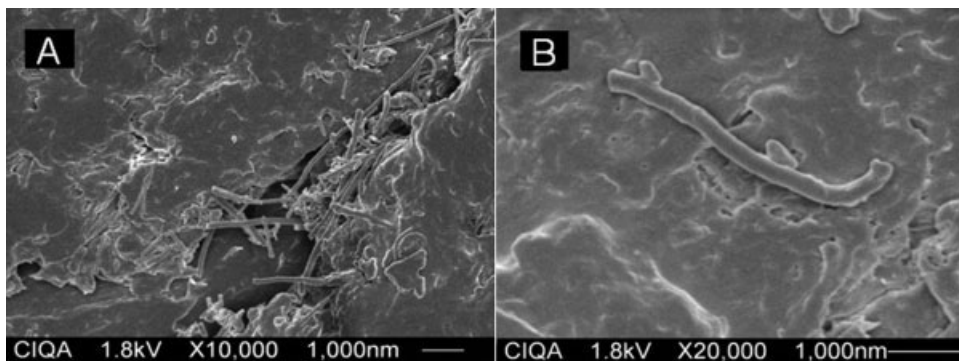

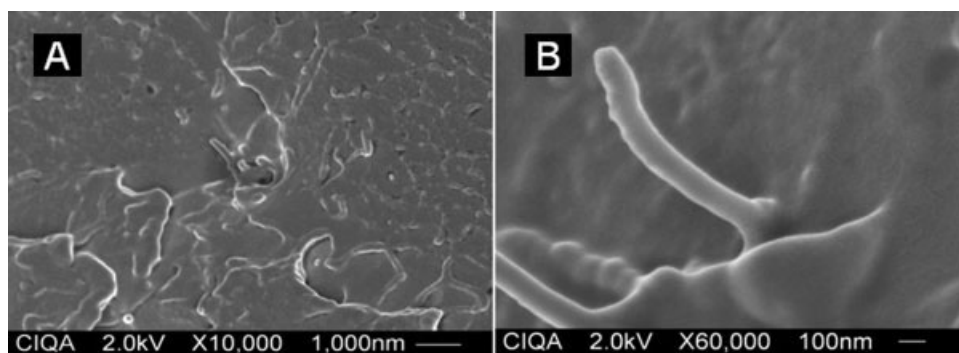**Figure 5** SEM micrographs of PS, 5 wt % untreated CNF composites. (A) ×10,000 and (B) ×20,000.

Figure 6 SEM micrographs of PS, 1 wt % treated CNF composites. The nanofibers were treated for 30 min at 50 W. (A) ×10,000 and (B) ×60,000.

Considering the scale in the micrograph in Figure 8, and calculating the difference in the nanofiber diameter (before and after telescoping, i.e. before and after the tensile testing), it can be estimated that about 100 layers of grafene were detached from the nanofiber core.

This estimate is based upon the average distance between concentric layers, which is equal to 0.34 nm, as determined through HRTEM by Shi et al.[30] For this detachment to happen, the strength at the interphase should have been greater than the van der Walls forces that join the grafitic nanofiber layers.

The effect on the mechanical properties, of the plasma treatment on the CNFs, is observed in Figures 9 and 10. Figure 9 shows the variation of tensile strength with deformation for PS and PS composites with 3 and 5 wt % [Fig. 9(A,B) respectively] of untreated and treated CNFs. The addition of CNFs reduces the elongation at break, from 3% for the pure PS to approximately 1–2% for the nanofiber composites, as well as the tensile strength, from 35 MPa for the pure PS to approximately 30 MPa for the nanofiber composites.

However, the tensile modulus, shown in Figure 10, more than doubles with the addition of plasma treated CNFs. The modulus goes from 1.25 GPa for the pure PS, to 2.55 and up to 2.90 GPa for the composites with 3 and 5 wt % of plasma treated CNFs, respectively. It is also observed that the modulus of
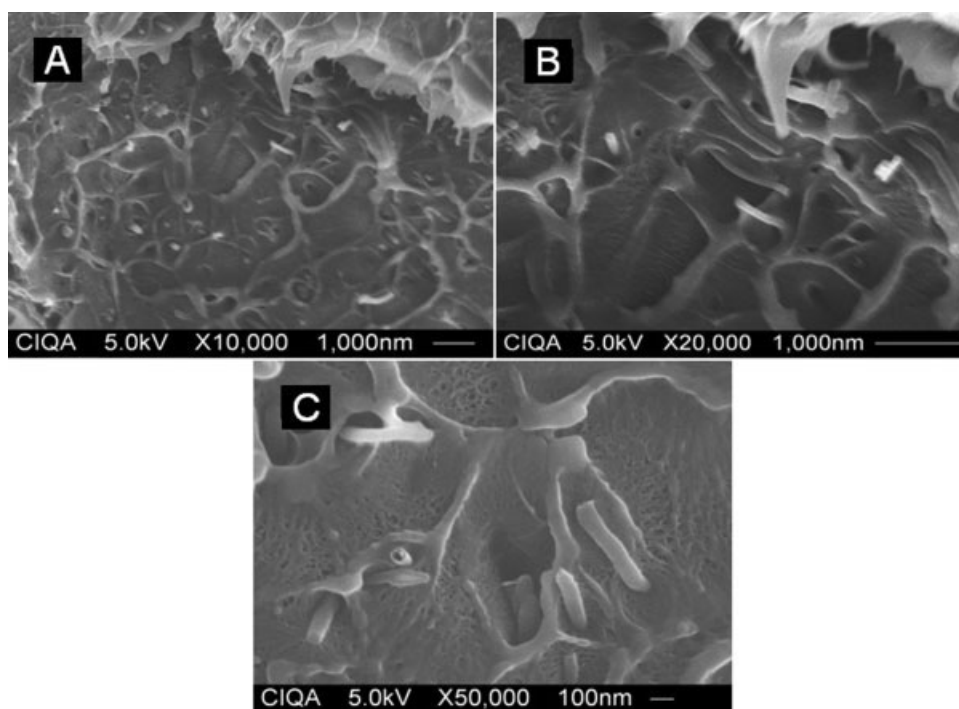

Figure 7 SEM micrographs of PS, 5 wt % treated CNFs. The nanofibers were treated for 60 min at 150 W. (A) ×10,000; (B) ×20,000; and (C) ×50,000.
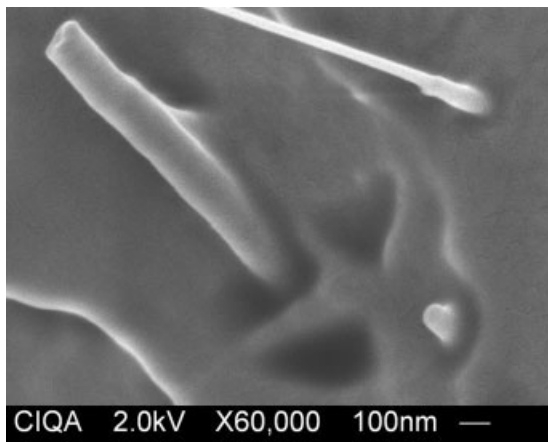
Figure 8 SEM micrograph of PS, 1 wt % treated CNFs. The nanofibers were treated for 30 min at 50 W.

pure PS is not modified by the addition of untreated CNFs.

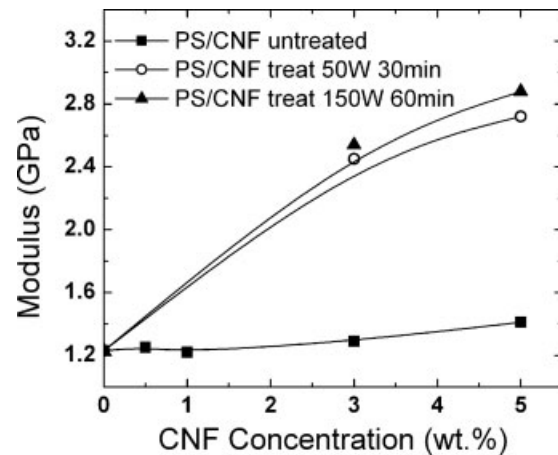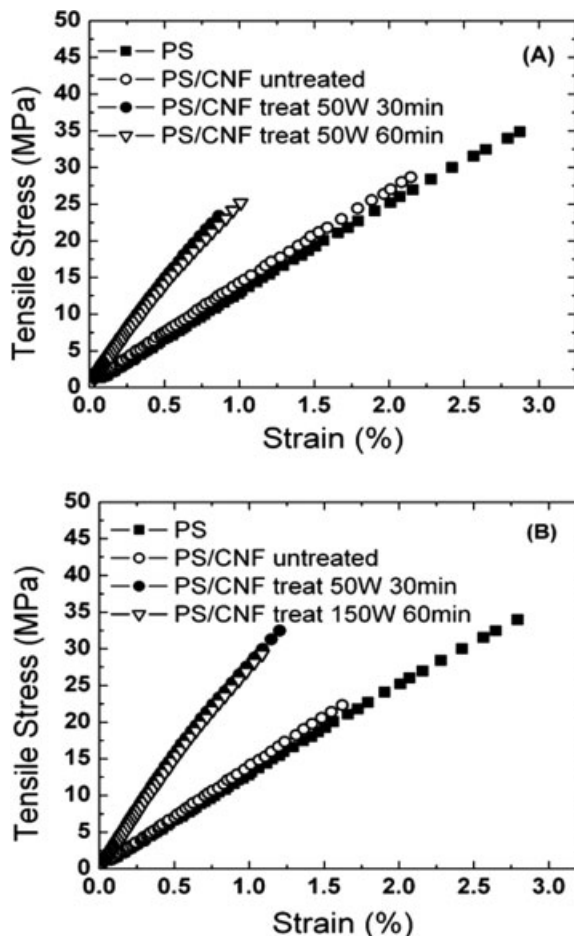All conditions examined during the plasma treatment (different power intensities and different

Figure 9 Tensile stress–strain of pure PS, and PS composites with untreated and treated CNFs. (A) with 3 wt % CNFs and (B) with 5 wt % CNFs.

Figure 10 Tensile modulus of PS composites with untreated and treated CNFs.

times), resulted in PS/treated CNF composites with approximately the same large modulus. These results follow the same tendency as reported by Shi et al.,[30] who prepared their nanocomposites in solution.

CONCLUSIONS

It is clear that the ultrathin PS coating deposited on to the nanofibers via plasma treatment changes the distinct hydrophobic character of the CNFs into slightly hydrophilic. The treated CNFs showed poor dispersion in high polarity solvents, whereas showed a better dispersion in low polarity solvents.

This plasma treatment greatly enhances the nanofiber dispersion within the PS matrix.

In addition, this treatment clearly helps in compatibilizing the nanofibers with the PS matrix. This compatibility is exemplified in the SEM micrographs of the fractured nanocomposite samples, where the treated CNFs appear totally embedded in the PS matrix.

SEM micrographs showed the excellent interfacial adhesion between the PS matrix and the treated CNFs, which produced a telescoping effect on the nanofibers, when subjecting the nanocomposite to a tensile stress, suggesting that the strength of the interfacial adhesion is superior to the forces that maintain the CNF graphitic layers together. This interfacial adhesion is also responsible for the much improved tensile modulus of the nanocomposite.

As a result of this compatibility, the tensile modulus highly increases from approximately 1250 to 2900 MPa. This is of great importance for applications requiring a greater modulus, and may open an opportunity for nanocomposites based in commodity plastics in some demanding engineering applications.

After examining the results, it is concluded that the longest plasma treatment times, as well as the

highest plasma treatment powers, do not noticeably affect the Young modulus of the PS/CNF composites studied. In similar future work, therefore, it is recommended to use the lower parameter values.

References

1. Shi, D.; He, P. Rev Adv Mater Sci 2004, 7, 97.
2. Tijmen, G. R.; Adrianus, J. V. P.; John, W. G.; Diederik, C. K. Chem Eur J 2002, 8, 5.
3. Hill, D.; Lin, Y.; Qu, L.; Kitaygorodsky, A.; Connel, J. W.; Allard, L. F.; Sun, Y. P. Macromolecules 2005, 38, 7670.
4. Qu, L.; Veca, L. M.; Lin, Y.; Kitaygorodsky, A.; Chen, B.; McCall, A. M.; Connel, J. W.; Sun, Y. P. Macromolecules 2005, 38, 10328.
5. Soung, H. P.; Sang, D. K. Polym Bull 1994, 33, 249.
6. Inagaki, S. T.; Ishii, K. J Appl Polym Sci 1993, 48, 1433.
7. Yoshida, K.; Greener, E. H. J Dentistry 1994, 22, 57.
8. Wang, M.; Bonfield, W. Biomaterials 2001, 22, 1311.
9. Xiu-yong, S.; Zi-Kang, Z.; Jie, Y.; Xiao-dong, M. Chem Mater 2002, 14, 71.
10. Min, X.; Tao, Z.; Bing, G.; Jieli, W.; Qun, C. Macromolecules 2006, 39, 3540.
11. Lozano, K.; Barrera, E. J Appl Polym Sci 2001, 79, 125.
12. Huang, W.; Lin, Y.; Taylor, S.; Gaillard, J.; Rao, A.; Sun, Y. Nano Lett 2002, 2, 231.
13. Gao, Y.; He, P.; Lian, J.; Wang, L.; Qian, D.; Zhao, J.; Wang, W.; Schulz, M. J.; Zhang, J.; Zhou, X.; Shi, D. J Macromol Sci Phys 2006, 45, 671.
14. Westerdahl, C. A. L.; Hall, J. R.; Schramm, E. C.; Levi, D. W. J Colloid Interface Sci 1974, 47, 610.
15. Kogoma, M.; Kasai, H.; Takahashi, K.; Moriwaki, T.; Olazaki, S. J Phys D Appl Phys 1987, 20, 147.
16. Weinkauf, D. H.; Harper-Nixon, D.; Wyatt, J.; Jeon, H. S. Abstr Am Chem Soc 2002, 224, U618.
17. Harper-Nixon, D.; Weinkauf, D. H. Abstr Am Chem Soc 2002, 224, U299.
18. Shi, D. L.; He, P.; Lian, J.; Wang, L. M.; Ooij, W. J. Mater Res 2002, 17, U299.
19. Shi, D. L.; Wang, S. X.; Ooij, W. J.; Wang, L. M.; Zhao, J. G.; Yu, Z. Appl Phys Lett 2001, 78, 1243.
20. Schulze, R. D.; Friedrich, J. F. SEERS in Sampling Mode: A Tool to Investigate Dynamics in Pulsed R.F. Plasma, In 2nd Workshop on Self Excited Electron Plasma Resonance Spectroscopy, Dresden, Germany, December, 2000.
21. Yasuda, H. Plasma Polymerization; Academic Press: London, 1985.
22. Orhan, B. Ö.; Hacaloglu, J.; Akovali, G. Eur Polym J 1991, 27, 1405.
23. Leggett, G. J.; Rather, B. D.; Vickerman, J. C. Surf Interface Anal 1995, 23, 22.
24. Beck, A. J.; Jones, F. R.; Short, R. D. J Chem Soc Faraday Trans 1998, 94, 559.
25. Christian, R. Solvents and Solvent Effects in Organic Chemistry, 3rd ed.; Wiley-VCH Publishers: Germany, 2003.
26. Lam, D. K.; Baddour, R. F.; Stancell, A. F. J Macromol Sci Chem 1976, 10, 421.
27. Tibbit, J. M.; Shen, M.; Bell, A. T. J Macromol Sci Chem A 1976, 10, 1623.
28. Kobayashi, H.; Shen, M.; Bell, A. T. J Macromol Sci Chem 1974, 8, 373.
29. Bernadette, A. H. Carbon nanofibre-polymer composites for electronic applications. Doctoral thesis, University of Akron, 2006, 162.
30. Shi, D.; Lian, J.; He, P.; Wang, L. M.; Xiao, F.; Yang, L.; Schulz, M. J.; Mast, D. B. Appl Phys Lett 2003, 83, 25.