Effects of Nanofiber Treatments on the Properties of Vapor-Grown Carbon Fiber Reinforced Polymer Composites

P. Cortés,[1] K. Lozano,[2] E. V. Barrera,[3] J. Bonilla-Rios[1]

[1]*Carrera de Licenciado en Ciencias Químicas, Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, N. L., México 64890*
[2]*Mechanical Engineering Department, The University of Texas Pan American, Edinburg, Texas 78539*
[3]*Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005*

ABSTRACT: Vapor-grown carbon fibers (VGCFs) were exposed to a series of chemical treatments and to electrochemical deposition of copper to modify their surface conditions and alter their electrical properties. The fibers were then mixed with polypropylene using a Banbury-type mixer obtaining composites up to 5 wt % VGCFs. Rheological, electrical, and mechanical properties were evaluated and compared to unfilled polypropylene processed in a similar manner. The composites made with HNO_3-treated VGCFs showed a lower electrical resistivity compared to the untreated samples. The composites containing VGCFs subjected to the copper electrodeposition process showed the lowest resistivity with no change in the mechanical properties. Changes in rheological properties demonstrated the effects of varying surface conditions of the VGCFs. Microscopic analysis of these composites showed a heterogeneous distribution of VGCFs forming an interconnected network with the presence of copper on the surface of the VGCFs and in the matrix. Both the interconnected network and the presence of copper led to a lower percolation threshold than those seen in a previous work where high dispersion was sought. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2527–2534, 2003

Key words: nanofiber; polymer composites; nanofiber treatment; electrical resistivity

INTRODUCTION

Currently, a great deal of interest in the development of carbon nanofiber reinforced polymer composites exists not only because of their potential for high strength but also for their electrical and thermal properties. Some of the expected near term applications are their use in aircraft and spacecraft structures and antistatic materials used for computer housing or exterior automotive parts where the reduction of static electrical charge is necessary.[1–4] The use of nanofibers such as vapor-grown carbon fibers (VGCFs) and nanotubes in conducting media is of significant interest because of the potentially high range of conduction that can be obtained with significant processing versatility. A number of studies in polymeric materials have been carried out with conductive fillers such as carbon black or carbon fibers in order to achieve a lower electrical resistivity.[5–13] Recent work has focused on the use of nanofibers for reduced resistivity and for producing multifunctional materials.[2,3,14–21] Finegan and Tibbetts[19] studied the effect of several fiber treatments on resistivity and showed that the graphitized fibers provided for low resistivity values. Sandler et al.[3] showed that a highly interconnected network of nanofibers could lead to electrical conduction with a low percolation threshold. Lozano et al.[15–17] showed that a highly dispersed network could be achieved with a higher but useful percolation threshold. In this research, we investigate two ways to reduce the percolation threshold seen by Lozano et al.[17] while providing for enhanced mechanical properties over that seen by Sandler et al.[3] To this end, VGCFs were surface modified and exposed to electrodeposition of copper to enhance their ability to achieve electrical conduction at lower concentrations but where mechanical properties are not compromised. Electrical conduction will be achieved by metal bridging between nanofibers to enhance the conductive network by a nonhomogenous deposition.[22,23] It is expected that by combining various fillers in polymers, the concentration of each component needed to achieve percolation could be decreased. Some examples of these systems are the following: VGCF/metal, VGCF/single-walled nanotubes (SWNT), multiwalled nanotubes (MWNT)/SWNT, metal/SWNT and other combinations of different types of nanotubes.

TABLE I
VGCF Treatments Used in the Processing of VGCF/PP Composites and Additives for Comparison

Initial	Treatment	Fibers Labeled as
As-received	As-received VGCF (no treatment)	ARV
As-received	Soaked in a 5.06N HNO$_3$ aqueous solution for 4 h. Rinsed with distilled water until no acid was present in the elutrant.	5H4
As-received	Soaked in 11.2N HNO$_3$ aqueous solution for 4 h. Sample rinsed similar to 5H4.	11H4
As-received	Soaked in a 11.2N HNO$_3$ aqueous solution for 64 h. Sample rinsed similar to 5H4.	11H64
5H4	Cu electrodeposition in 0.1M Cu^{2++}, 11.2N HNO$_3$ at 5 V, 1.3 A, 4 h. Sample rinsed similar to 5H4 and until no Cu^{2+} was present	5H4E4
11H64	Cu electrodeposition in 0.1M Cu^{2+}, 11.2N HNO$_3$ at 5 V, 1.3 A, 4 h. Sample rinsed similar to 5H4 and until no Cu^{2+} was present.	11H64E4
11H64	Treated in electrolyte like 11H64E4 but with no current and later rinsed until no nitric acid and Cu^{2+} were present.	11H6404
Pure Cu	Cu was cleaned with water, hexane, and dried at 90°C	PCU

When achieving conduction in filled polymers, the amount of filler, type, aspect ratio, and distribution used in the matrix are important parameters since all these determine the percolation threshold. However, the amount of filler used in the composite can cause an increase in some rheological and mechanical properties of the material and may lead to reduced strength and subsequent higher brittleness.[13] The addition of fillers tends to increase the stiffness of the composite, at the expense of toughness and elongation during forming.[24] The filler can alter the viscoelastic properties of the molten composite that play an important role in its processability and final use. Lozano et al.[16,17] showed the use of VGCFs in polymer composites where high dispersions were sought to achieve enhanced mechanical and electrical properties. In that work, the nanofiber functionalization, the composite processing, and the resulting properties were studied in relation to the VGCF concentration. That work did not study the degree of oxidation on the nanofibers and corresponding effects on the electrical properties when composites were formed.

VGCFs are produced by catalytic chemical vapor deposition that leads to two zones in the material with different aspects: an internal catalytic phase with a regular and oriented structure, and a pyrolytic phase characterized by irregular graphite layers and amorphous carbon.[25] The nanofibers used in composites for electrical applications must be free of amorphous carbon to improve the conductivity of the composite.[26,27] For this purpose, some treatments have been conducted on fibers to modify the ratio of aliphatic to aromatic carbons on the surface of the fibers.[16,17,26] VGCFs are catalytically produced from hydrocarbons that under a specific combination of temperature, pressure, and time are transformed into an amorphous carbonaceous material (precursor material) that rearranges itself in ordered clusters that grow to form the fibers. However, not all the precursor material is completely transformed into fibers and remains in between the clusters and/or the fibers; consequently

the final properties of the mixture are less than those expected for the fibers. In fact, the high electrical conductivity can be shielded because of the insulating nature of the amorphous material. The amorphous material is a mixture of hydrocarbons prone to oxidation and dissolution if the appropriate reagent is chosen. Therefore, it is expected that use of an oxidizing species of HNO$_3$ solutions to remove the amorphous carbon would lead to more highly conductive VGCFs.

In the present work, the VGCFs were treated with different concentrations of HNO$_3$ and exposure times, and an electrodeposition process was conducted to adhere copper to the fiber surface. This was carried out to improve the electrical conductivity of the composites using less nanofibers and metal compared to if they were used independently. The effectiveness of the fiber treatment and electrodeposition of copper was determined by observing the fibers under the electron microscope, and by the effect on the rheological, electrical, and mechanical properties of their composites. Electrostatic dissipative (ESD) materials were produced with the treated VGCFs and using VGCFs with Cu electrodeposition. Changes in rheological properties demonstrated the effects of varying surface conditions of the VGCFs. A combined effect of surface treatment and Cu electrodeposition led to a lower percolation where less VGCFs were needed to achieve ESD.

EXPERIMENTAL

VGCFs treatment and sample preparation

The VGCFs were purified under three conditions and consisted of soaking the as-received nanofibers in a HNO$_3$ solution with an occasional gentle stirring. The HNO$_3$ concentration and soaking time used for the production of each fiber type are listed in Table I. After soaking, the nanofibers were packed in a glass column and water rinsed until the HNO$_3$ was no longer present in the elutrant. Then the VGCFs were

dried at 90°C for 36 h in air. Nanofibers identified as 5H4E4 and 11H64E4 were produced with electrodeposition of copper on the fibers 5H4 and 11H64, respectively. In each case, the fibers were wrapped with a nonconductive porous plastic film around the cathode of an electrolytic cell. The electrolytic bath was prepared by dissolving 0.05 moles of Cu in 500 mL of a 5.02 and an $11.2N$ HNO_3 solution (pH of 1) for fibers 5H4E4 and 11H64E4, respectively. The Cu obtained from J. T. Baker Chemical was a 323 mesh ($\sim$44 μm) with a purity of 99.99 wt %. After the electrodeposition at 5 V, 1.3 amps for 4 h, the fibers were washed and dried using the procedure used for nanofibers 5H4, 11H4, and 11H64; the only difference was that the washing liquid was collected until Cu^{2+} was no longer present. The total amount of Cu on the nanofibers was determined by calculating the material balance. The Cu^{2+} left in the electrolytic bath was electrodeposited into a previously weighted platinum cathode, and the weight difference was then subtracted from the amount used in the preparation of the Cu^{2+}–HNO_3 bath solution. The results indicated that nanofibers 5H4E4 and 11H64E4 had 17.5 and 21.8 wt % Cu. This means that for 1 g of these starting VGCF materials only 0.825 and 0.782 g, respectively, were actual nanofiber material. As-received nanofibers soaked in distilled water for 4 h, with an occasional gentle stirring, were labeled as ARVW. The fibers were then rinsed with the same amount of water used to wash the HNO_3 from 11H64. Fibers labeled as 11H6404 were as-received fibers treated as if they were going to be transformed into 11H64 and after that they were soaked in the electrolytic Cu^{2+}–HNO_3 bath solution for 4 h but with zero current. The objective of these procedures was to determine whether water cleansing or the electrolytic bath solution had an effect on the electrical properties of the fibers and on their 5 wt % VGCF–PPP (i.e., 11H64PP) composites. These various treatments produced seven different types of the VGCFs that were used in the preparation of composites.

A series of composites were prepared using each of the fibers listed in Table I. Plain Polypropylene 4 MFI (PPP) was obtained from ATOFINA in Deer Park, TX. VGCFs (as-received ARV) were obtained from Applied Science, Inc. The PPP and the VGCFs were compounded in a Brabender mixer at 90 rpm for 8 min at 180°C and each batch weighted 20 g. These procedures were selected based on mixing optimization routes previously studied by Lozano et al.[16] VGCF–PP composites without electrodeposition had a 5 wt % VGCF composition and the pure copper–PP composites had a 0.1, 0.5, and 1 wt % Cu content (0.1CUPP, 0.5CUPP, and 1CUPP, respectively). The composites prepared with electrodeposited Cu had less VGCFs because the added Cu contributed to the 5 wt %. Sample 5H4E4PP had 4.125% wt and sample 11H64E4PP had 3.91% wt of VGCF. After mixing, a portion of each batch was

compression molded at a temperature of 180°C to form thin sheets weighing 14–20 g each. Torque data was recorded while compounding the composites in the Brabender mixer.

Electrical characterization

Electrical volume resistivity (ρ_v) measurements were conducted according to the ASTM 257 standard using a Keithley 247 high voltage supply. The samples were inserted in a Keithley 6105 resistivity adapter that has a special electrode configuration to assure an intimate electrode–sample contact so that no silver paint or mercury fill rings were needed for this test. The resultant current was measured with a Keithley 617 programmable electrometer. The composites showing the lowest electrical resistivity were also tested using the ANSI/EOS/ESD-S11.11-1993 method. The surface and volume resistivities (ρ_s and ρ_v) were measured with a Monroe model 262A meter and a Monroe model 268 charge plate analyzer at 25–30 and 47–50% relative humidity (RH).

Rheological and mechanical analysis

The loss and elastic moduli were obtained from frequency sweeps at 10% strain in a Rheometrics RA rheometer using 25 mm diameter by 1 mm thick disks. The measurements were conducted at 200°C, over a frequency range of 0.01–500 rad/s. The loss and elastic moduli were used to calculate the complex viscosity and, by assuming the Cox–Mertz rule, the shear viscosity was determined. Tensile test specimens were prepared and tested according to the ASTM 638D standard for testing on an Instron Universal Machine (model 5500R). The tests were conducted until failure and the elastic modulus, yield strength, and resilience were calculated for each specimen. Several samples were tested to compare the change in mechanical properties due to the combination of shear stress, temperature, and oxygen (STO) conditions present during the compounding of the VGCFs and PPP. The STO combination has been reported as a source of polymer degradation after shear working a polymer in the Banbury-type mixer,[28] and that occurs when the additive package is not well formulated and/or when an excessive shear working is applied. PPP samples were shear worked to determine if they were affected by additional shear processing. These samples were labeled SPP. Such degradation not only lowers the polymer average molecular weight, but also narrows the molecular weight distribution affecting the mechanical properties of both the PPP and its composites.

RESULTS AND DISCUSSION

VGCF treatment and rheological evaluation

The torque measurements from the high shear mixer showed a change in torque between the PPP and the
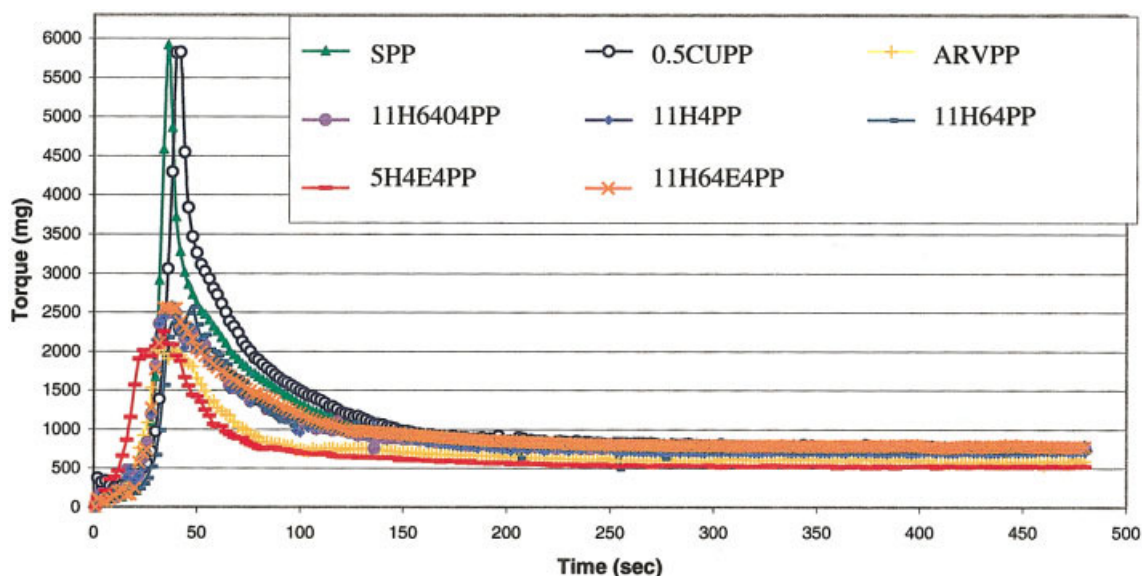
Figure 1 Torque measurements showing a change in torque, between the unfilled PP and the VGCF–PP composites. Note that for the VGCF–PP composites, the torque measurements did not vary as a function of theVGCF chemical treatments.

various VGCF–PP composites as seen in Figure 1. A change in torque as a function of chemical treatment was not observed. However, such torque values can be misleading since according to Einsten's Law, the filler should increase the viscosity of the VGCF–PP mixture, and surface treatments often affect interfacial interactions and therefore lead to an increase in viscosity.[29] Figure 2 shows the viscosity vs shear rate for PPP and the composites. Note the increase in viscosity as a function of surface treatment for shear rates lower than 100 s^{-1}. Note also that additional shear processing (sample SPP) did not alter the viscosity compared to that for PPP. All the curves converge at shear rates above 100 s^{-1}, which is the shear range observed in

the torque rheometer for mixing these composites. At lower shear rates, the viscosity of the composites are 15–25% higher than that for PPP, which is more than that expected when evaluated by Einsten's Law:

$$\eta/\eta_o = (1 + 2.5\phi_f) \tag{1}$$

where η is the viscosity, η_0 is the zero shear viscosity, and Φ_f is the volume fraction of the filler. It is expected that the VGCFs are interlocked with the polymer chains, restricting the motion of the polymer at low shear rates. When the Einsten's contribution to the viscosity is subtracted from the actual zero shear viscosity of each composite, the shear stress (τ_s) at 0.1 s^{-1}
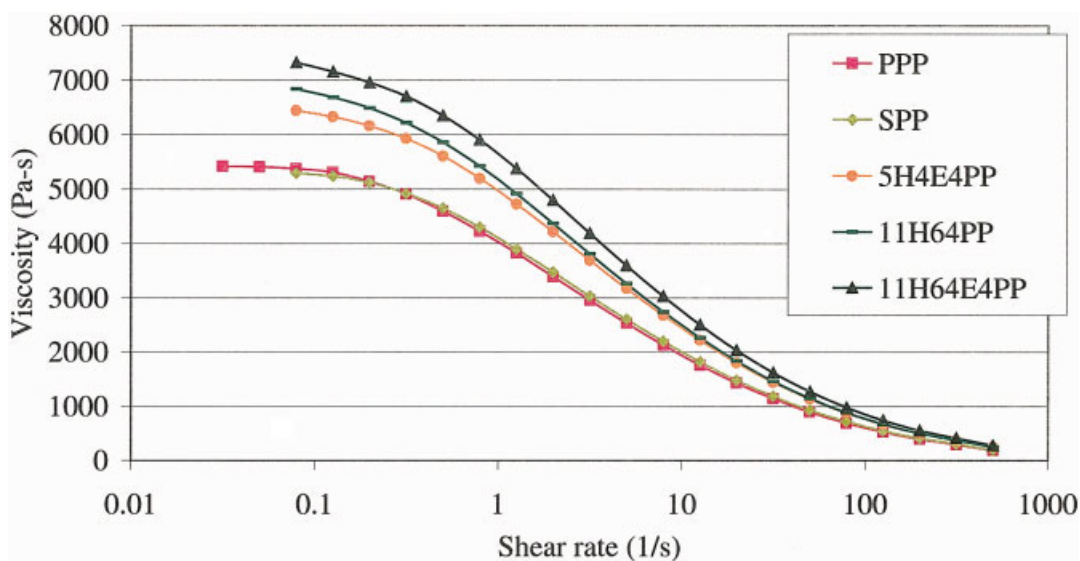

Figure 2 Viscosity curves for PPP and the composites. The curves converge at shear rates above 100 s^{-1}, which are the mixing shear rates observed in a torque rheometer and the velocities used in this study. At lower shear rates the viscosity of the composites are 15–25% higher than the PPP resin, which is more than expected by applying Einstein's Law.

TABLE II
Actual Shear Stress at 0.1 s^{-1} and that According to Einstein's Law Effect on the Zero
Shear Viscosity for a 5 wt % VGCF Content with a 2 g/cm^3 Density

Filler	Composite	Actual Shear Stress (Pa)	Calculated Shear Stress (Pa)	Difference (Pa)
No filler	PPP	500	500	0
11H64	11H64PP	675	529	146
5H4E4	5H4E4PP	690	529	161
11H64E4	11H64E4PP	720	529	191

for each composite can be calculated as $\tau_s = 0.1\tau_0$ where the difference $\tau_{composite} - \tau_{PPP}$ is related to the strength of the interaction between the filler and the polymer chains. Table II shows the τ_s values for each composite and the treatment conditions given to the VGCFs. The τ_s for 5H4E4PP is slightly higher than that for 11H64PP and the only difference is that 5H4E4PP has additional copper from the electrodeposition process. It is also important to observe that the viscosity curves of 11H64PP and 5H4E4PP converge faster at lower shear rates, which is not the case for sample 11H64E4PP. Therefore, it seems that the alignment of the polymer chains in the copper–VGCF system is more restricted. The distribution and interaction between the VGCFs and the Cu is expected to contribute to this difference. However, the filler is not significantly changing the viscosity at high shear rates since the polymer aligns with the VGCFs in the direction of the flow.[30] At low shear rates it is likely that the temperature can be increased to reduce the viscosity of the composite mixing process; however, the potential of degrading the polymer must be considered. It is more likely that this can be done for VGCF composites since an increase in polymer degradation temperature occurred when VGCFs were added.[16] Figures 1 and 2 confirm that the rheological properties of the various composites do not significantly change due to the mixing process. This indicates that the various additives protected the polymer from the STO conditions (the molecular weight distribution does not change). The addition of fibers increased the viscosity of the composites with respect to PPP, indicating an interaction of PPP and the VGCF surface. The composite made with fibers treated with HNO$_3$ for 64 h had a higher viscosity, since more surface area is available for polymer interaction.[10,31] Analyses of the surface area of the fibers made by Tibbetts et al.[32] and Alig et al.[33] indicate that the surface has low porosity, and is relatively smooth and inactive, as far as gaseous adsorption and possibly adhesion to a polymer matrix is concerned. Therefore, the oxidation by the nitric acid provides a stronger adhesion in the fiber/matrix interface.[1] Studies made in relation to the functional groups on carbon nanotubes, carbon fibers and carbon black[10,32–35] show the presence of chemisorbed oxygen complexes that also explained the higher adhesion to the matrix.

Scanning electron microscopy (SEM) analysis showed a nonhomogeneous VGCF distribution contrary to that seen by Lozano et al.[16] The resistivity and mechanical properties depend not only on the properties of the filler and its concentration in the polymeric matrix, but also on the distribution and dispersion of the filler in the matrix.[7,24] This nonuniform distribution might have resulted from incomplete mixing during the composite preparation or due to the prolonged treatment time of the nanofibers (64 h). However, Lozano et al.[16] were able to achieve a homogeneous dispersion of VGCFs in PP when longer mixing times were used (8 min compared to their 12–15 min).

Electrical properties

In this research, the VGCF content was ≤5 wt % to achieve electrical conduction due to the elimination of nonconductive amorphous material from the fiber by chemical treatment of the nanofiber surfaces. The electrodeposition process was performed to create more connections among the cleaned fibers by joining them with a Cu interconnecting cluster. HNO$_3$ cleaning and electrodeposition of Cu were used, and composite electrical resistivities were compared to results from previous VGCF/PP studies.[16,17] Figure 3 and Table III show the ρ_v measured for each composite. Composite ARVPP and the unfilled shear worked PPP (SPP) had
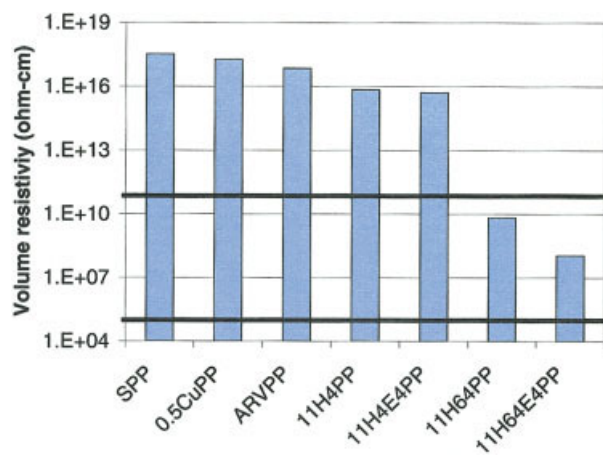

Figure 3 Volume resistivity for several composites.

TABLE III
Volume Resistivity for Composites Using the MFI 4.1 PPP Resin and 5 wt % VGCF

Filler	Composite	ρ_v (ohm cm)
No filler	SPP	3.35E + 17
0.5% Cu	0.5CuPP	1.85E + 17
As-received VGCF	ARVPP	7.25E + 16
5H4	5H4PP	7.07E + 15
5H4E4	5H4E4PP	5.23E + 15
11H64	11H64PP	6.80E + 09
11H64E4	11H64E4PP	1.12E + 08

similar ρ_v, followed by composites 5H4PP, 5H4E4PP, 11H64PP, and 11H64E4PP in order of decreasing resistivity. The effect of the HNO_3 treatment can be observed by the change in the ρ_v for 5H4PP, 11H4PP, and 11H64PP. These results indicate that soaking the fibers for 4 h in 5.02N and 11.2N HNO_3 solutions do not affect the fiber significantly since the change in ρ_v is just one order of magnitude lower with respect to that of the composite prepared with the as-received VGCF (sample ARVPP). However, when the treatment time is 64 h, using an 11.2N HNO_3 solution the ρ_v drops from 10^{17} to 10^{10} Ωcm, indicating that treatment time is certainly a factor. The ρ_v of composites 5H4E4PP and 11H64E4PP, having electrodeposited Cu on the VGCFs, showed the effect that cleaning procedure has on the electrodeposition process and confirms that the amorphous material acts as an electrical insulator.

ESD materials have ρ_s in the 1×10^5 to $10^{11}\Omega$/sq range.[18] The ρ_s of composites 11H64PP and 11H64E4PP was measured following the ANSI/EOS/ESD-S11.11-1993 standard. Table IV shows that 11H64PP is in the upper limit of the dissipative region and that composite 11H64E4PP is an ESD material. The results also indicate the heterogeneity of the composites since the ρ_s values show variations from one to three orders of magnitude. The presence of Cu powder in the PP matrix did not produce a ρ_v difference with respect to PPP. The electrodeposited Cu decreases the composite resistivity and acts on the surface of the VGCFs to connect them to each other. The ARVPP composite showed a decrease in the resistivity, as expected since the electrical resistivity of the ARVs are low.[5]

The nitric solutions removed the upper external layer resulting in composites with a low ρ_v. The external layer of the fibers is composed of amorphous carbon and its removal leaves a well-crystallized graphite structure with delocalized π electrons.[36,37] Darmstadt et al.[26] showed a decrease of aliphatic structures during surface treatment, leaving behind a graphite structure. The fibers treated with the higher HNO_3 concentration and longer exposure time had a higher amount of Cu electrodeposited than when treated with a low concentration of HNO_3 and short treatment time. In the electrodeposition process, the copper is deposited on the cathode formed by fibers due to an electrical potential difference. This deposition tends to form copper nucleation sites that are more conductive than the fibers, and the rest of the ionized Cu is deposited on these sites. These sites act as connectors and lead to a nonuniform dispersion of Cu on the fibers. If one considers this system as a precursor to MWNT and SWNT reinforced polymers, a similar behavior is expected where the percolation threshold will occur at lower concentrations, resulting also in lower resistivity values. Therefore one will expect that combinations of mechanisms (VGCF and metal, VGCF and SWNT, MWNT and metal, and etc.) to achieve conduction will result in lower cost conductive polymers with a broader range of electrical properties.

Mechanical properties

The copper electrodeposited in the VGCF was observed using energy dispersive spectrometry in conjunction with the SEM study. Figure 4 shows a heterogeneous distribution of Cu on the fibers, indicating a large concentration of nucleation centers that act as interconnectors for the nanofibers. The fracture surface of tensile test specimens of 5H4E4PP and 11H64E4PP were observed in the SEM (Figs. 5 and 6) where Cu was found dispersed in the matrix. The presence of the Cu in some parts of the matrix indicated a nonhomogeneous dispersion. The presence of Cu seen in the matrix, besides that on the VGCFs, is likely due to the breaking away of the copper from the VGCFs by the shearing process. The Cu that is con-

TABLE IV
Surface Resistivity (SR) for Composites 11H64PP and 11H64E4PP at Two Different Humidity Levels

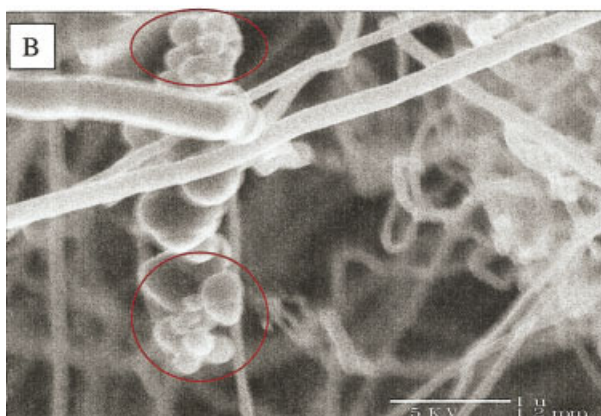| Composite	Side	SR (ohms/square) Initial Test at 50% Relative Humidity	SR (ohms/square) Second Test After 48 h at < 28% Relative Humidity
11H64PP	1	1×10^{13} to 1×10^{14}	1×10^{13} to 1×10^{14}
	2	1×10^{11} to 1×10^{14}	1×10^{12} to 1×10^{14}
11H64E4PP	1	1×10^{9} to 1×10^{11}	1×10^{9} to 1×10^{11}
	2	1×10^{10} to 1×10^{12}	1×10^{9} to 1×10^{11}

Figure 4 VGCFs treated with 11.2*N* HNO$_3$ for 64 h and electrodeposited with Cu. The circled areas indicate Cu particles attached to the VGCFs.

nected to different VGCFs hinders the dispersion of the nanofibers and further impacts the mechanical properties.

PPP, SPP, 11H64PP, 5H4E4PP (same as 5H4PP but with electrodeposited Cu added), 11H64E4PP, and ARVPP were tensile tested, and the results are shown in Figure 7. A nonhomogeneous dispersion of the fibers in the matrix was found in 11H64PP. However, indications of adhesion between the fibers and the
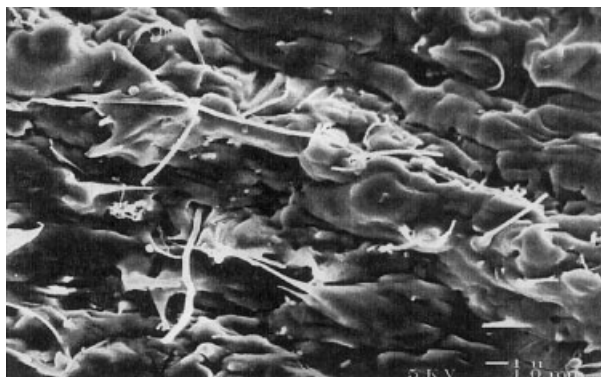

Figure 5 A fracture surface of 11H64E4PP composite showing Cu dispersed in the matrix.
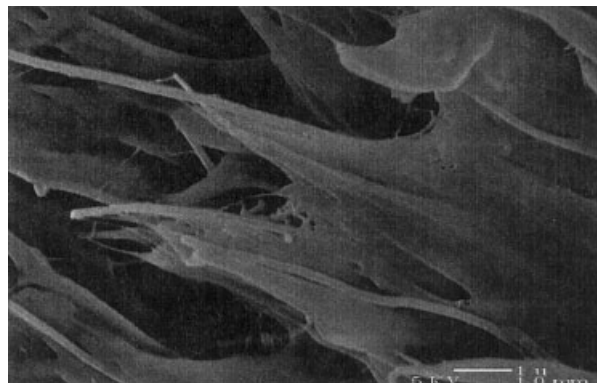

Figure 6 Fracture specimen showing adhesion between the VGCF HNO$_3$-treated fibers (11H64) and the matrix.

matrix were observed, as seen in Figure 7. The SPP had a higher Young's modulus, a lower yield strain, and a similar tensile strength to the PPP, indicating that shear work promotes links between the polymer chains, leaving a more brittle material. Samples 5H4E4PP, 11H64PP, 11H64E4PP, and ARVPP had a higher Young's modulus compared to the samples without filler (PPP and SPP). However, their yield strain and tensile strength were lower. Samples 11H64PP, 5H4E4PP, and 11H64E4PP exhibited a similar yield strain. The tensile strength of 11H64PP, 5H4E4PP, and 11H64E4PP showed similar values that were lower than the untreated samples. The modulus, on the other hand, showed an increase for the samples chemically treated or Cu electrodeposited.

CONCLUSIONS

VGCFS were exposed to a series of chemical treatments and to electrochemical deposition of copper that modify the surface conditions and electrical properties. The electrodeposited copper on the VGCFs led to composites with lower resistivity, and as consequence, the amounts of VGCF needed to reach the percolation threshold decreased. Therefore the electrodeposition together with nitric acid solution treatment is a successful process to increase the composite conductivity. The interconnected electrodeposited copper likely hindered the VGCF dispersion, which led to electrical conduction based on an interconnected network as opposed to a highly dispersed VGCF distribution. Chemical treatments and the electrodeposition process did not produce significant changes in the mechanical and rheological properties of the composites, although a decrease in tensile strength of the samples that were chemically treated and/or electrodeposited by copper was observed. Therefore as various fillers are combined, similar results observed for the electroplated VGCF/polymer system are expected.
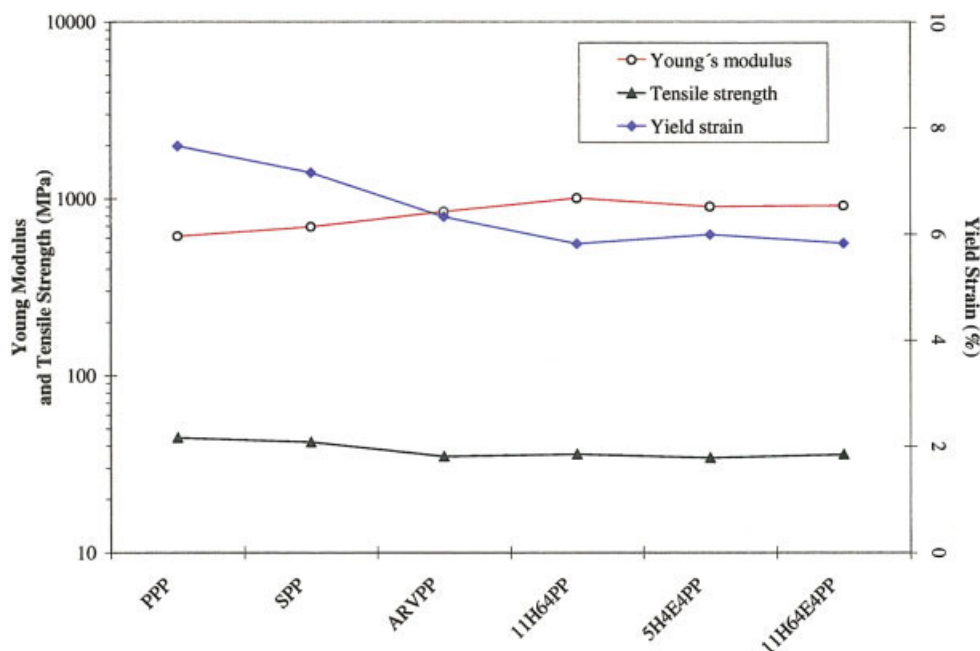
Figure 7 Tensile test data for several composites.

References

1. Chawla, K. K. Fibrous Materials; Cambridge University Press: New York, 1998; pp 227–232.
2. Barrera, E. V. J Mater 2000, 52.
3. Sandler, J.; Shaffer, M. S. P.; Prasse, T.; Bauhofer, W.; Schulte, K.; Windle, A. H. Polymer 1999, 40, 5967.
4. Hyperion Catalysis International. Plastics Additives and Compounding 2001, 3, 9, 20.
5. Andrade, J. S., Jr.; Auto, A. M.; Kobayashi, Y. Phys A 1997, 248, 227.
6. Mather, P. J.; Thomas, K. M. J Mater Sci 1997, 32, 401.
7. Mather, P. J.; Thomas, K. M. J Mater Sci 1997, 32, 1711.
8. Soares, B. G.; Gubbels, F.; Jérôme, R. 1996, 70, 60.
9. Petrovic, Z. S.; Martinovic, B.; Divjakovic, V. J Appl Polym Sci 1993, 49, 1659.
10. Accorsi, J.; Romero, E. Plastics Eng 1995, 29.
11. Zhang, H.; Yi, X.-S.; Yui, H. J Appl Polym Sci 1998, 69, 1813.
12. Kirkpatrick, S. Rev Modern Phys 1973, 45, 574.
13. Gaspari, J. D. Plastics Tech 1997, 43, 13.
14. RTP Co. Imagineering Plastics. www.rtpcompany.com.
15. Parker Seals, EMI Shielding Technology Division, Chomerics, www.chomerics.com.
16. Lozano, K.; Barrera, E. V. J Appl Polym Sci 2001, 79, 125.
17. Lozano, K.; Bonilla-Rios, J.; Barrera, E. V. J Appl Polym Sci 2001, 80, 1162.
18. Lozano, K. J Mater 2000, 52, 34.
19. Finegan, I. C.; Tibbetts, G. G. J Mater Res 2001, 16, 6, 1668.
20. Cochet, M.; Maser, W. K.; Benito, A. M.; Callejas, M. A.; Martinez, M. T.; Benoit, J. M.; Schreiber, J.; Chauvet, O. Chem Commun 2001, 1450.
21. Kymakis, E.; Alexandou, I.; Amaratunga, G. A. J Synth Met 2002, 127, 59.
22. Li, Q.; Fan, S.; Han, W.; Sun, C.; Liang, W. Jpn J Appl Phys 1997, 36, 501.
23. Chen, X.; Xia, J.; Peng, J.; Li, W.; Xie, S. Compos Sci Technol 2000, 60, 301.
24. Stobi, G. R. 996, 83,
25. Madroñero, A.; Ariza, E. J Mater Sci 1996, 31, 6189.
26. Darmstadt, H.; Sümmchen, L.; Ting, J.-M. Carbon 1997, 35, 1581.
27. Burton, D. J.; Glasgow, D. G.; Lake, M. L.; Kwag, C.; Finegan, J. C. 46th International SAMPE Symp 2001, 647.
28. Krane, S. The torque rheometer used to test engineering thermoplastics. Haake Buchler Instruments, Inc. (HBI Technical Bulletin).
29. Shenoy, A. V. Rheology of Filled Polymer Systems; Kluwer Academic Publishers: Norwell, MA, 1999; p 138.
30. Shofner, M.; Lozano, K.; Rodríguez-Macías, F. J.; Barrera, E. V. J Appl Polym Sci, submitted.
31. Lakdawala, K.; Salovey, R. Polym Eng Sci 1985, 25, 797.
32. Tibbetts, G. G.; Beetz, C. P., Jr. J Phys D: Appl Phys 1987, 20, 292.
33. Alig, R.; Ting, J. The European Carbon Conference "Carbon 96" Newcastle, UK, July 1996.
34. Peebles, L. H. Carbon Fibers. Formulation, Structure, and Properties; CRC Press: Boca Raton, FL, 1995; pp 125–126.
35. Lozano, K.; Files, B.; Rodriguez-Macias, F.; Barrera; E. V. Purification and Functionalization of Vapor Grown Carbon Fibers and Single Wall Nanotubes"; TMS Publications, 1999; p 333.
36. Knupfer, M.; Pichler, T.; Golden, M. S. Carbon 1999, 37, 733.
37. Morrison, T.; Neilson, B. R. Química Orgánica; Addison-Wesley: Reading, MA, 1990.