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Surface treatments for improving the mechanical properties of carbon nanofiber/thermoplastic composites

I. C. FINEGAN*, G. G. TIBBETTS
Materials and Processes Laboratory, General Motors R&D Center, 30500 Mound Road, Warren, MI 48090-9055, USA
E-mail: tibbetts@apsci.com

D. G. GLASGOW, J.-M. TING‡, M. L. LAKE
Applied Sciences, Inc., P.O. Box 179, Cedarville, OH 45314, USA

Nanofiber-matrix adhesion was studied after surface treating carbon nanofibers using a variety of methods. Among as-grown fibers, those produced with longer gas phase feedstock residence times were less graphitic but adhered to the polypropylene matrix better, giving improved tensile strength and modulus. A modest degree of oxidation was also found to increase adhesion to the matrix and increase composite tensile strength, while extended oxidation attacked the fibers sufficiently to decrease composite properties. Two chemical treatments were found to be ineffective in increasing tensile strength or modulus. © *2003 Kluwer Academic Publishers*

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1. Introduction

The demand for high-performance, inexpensive polymeric composites is raising new challenges for materials engineers. In particular, exciting new possibilities are being investigated for developing composite materials with discontinuous fibers of short length [1–4]. An important advantage of such short-fiber-reinforced composites is ease of manufacturing, since they may be produced without the special care required to orient fibers in long fiber composites.

The incorporation of carbon nanofibers (CNF) [4] in a polypropylene thermoplastic matrix can give composites of considerably improved strength and stiffness [5]. Furthermore, CNF/polypropylene composites may be continuously fabricated by extrusion or injection molding, permitting both high-volume production and recycling [5].

Fiber-matrix adhesion is governed by the chemical and physical interactions occurring at the fiber-matrix interface. An extensive literature exists describing the surface treatment of conventional carbon fibers by such methods as oxidation in the gas and liquid phases and anodic etching [6]. Good nanofiber-matrix adhesion is necessary in order to produce composites with acceptable mechanical properties. If the fiber-matrix adhesion is poor, the composite may fail at the interface, reducing both the longitudinal and transverse tensile strengths of the composite.

In the following report, the mechanical properties of CNF/polypropylene composites are analyzed in an attempt to optimize the CNF/surface treatment. The strength and stiffness of the composites were evaluated from tensile tests. The fiber-matrix adhesion was qualitatively studied by scanning electron microscopy (SEM) with more quantitative data from DMA (Dynamic Mechanical Analyzer) tests. The use of DMA to investigate the fiber-matrix interphase in polymer composites has been recently explored [3]. Here it will demonstrated that DMA offers a direct approach to evaluating the fiber-matrix adhesion based on the contribution of the interphase to the tanδ damping peak [1]. Finally, it will be shown that a modest fiber surface oxidation treatment can increase the tensile strength of carbon nanofiber/polypropylene composites.

2. Experiment

The PYROGRAF carbon nanofibers used in this study were produced at the pilot plant of Applied Science, Inc., (ASI), in Cedarville, OH. Fe-based particles formed from the decomposition of iron pentacarbonyl extruded carbon filaments as they flowed through a methane filled tubular reactor; they were later thickened to approximately 0.2 μm in diameter by carbon vapor deposition from the methane [4]. The following fiber designations refer to differing reactor gas mixtures used in production:

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[*] Present address: Central Michigan University, Mt. Pleasant, MI, 48859, USA.

[‡] Present address: The National Cheng Kung University, Tainan, Tiawan, Republic of China.

- Clean (described in [5], ASI code PR-1): Relatively low feedstock gas flow rate. Cleanest fiber product with least aromatics.
- PR-18: Somewhat higher gas flow rate. Used primarily in rubber mixtures.
- PR-5: Still higher gas flow rate.
- Best Shot (described in [5], ASI code PR-11): Highest gas flow rate of methane-based fibers. Most aromatics on fiber surfaces. This mixture was designed for highest feasible fiber production rate.
- Coal-based fibers: These utilize a mixture of ground coal to supplement the natural gas and hydrogen sulfide.
- Acetylene-based fibers: These are made by using acetylene gas as the primary carbon feedstock instead of methane.

A more graphitized fiber may be produced by high temperature heat treatment:

- Graphitized fibers: Best Shot fibers were heated to 3000°C for 1 h and gradually cooled in an inert gas atmosphere.

Four different wet chemical treatments were tested:

- Diamine salt of carboxylic acid, high (DH): Clean (PR-1) fibers were oxidized at 450°C for 60 min. 150 g of the oxidized fibers were mixed with a solution of 5 g of Armak 1192 (Akzo Nobel Chemicals) in 10 liters of propanol for 60 min. The fibers were dried in air overnight, followed by an oven drying at 38°C. Armak 1192 is a proprietary compound comprising two amine groups positioned near the end of a long hydrocarbon chain, each amine being fully neutralized by a large fatty acid The 3 hydrocarbon chains are designed to bond with nonpolar surfaces such as hydrocarbons, while the amine groups bond to polar groups such as the oxygenated groups on the fiber surface. This latter bonding probably occurs by displacement of the fatty acid on Armak by the stronger acid group on the fiber surface.
- Diamine salt of carboxylic acid, low (DL): Prepared similarly to DH, except that only 2 g of Armak 1192 was used.
- Epoxy, high (EH): Clean (PR-1) fibers were oxidized at 450°C for 60 min. 150 g of the oxidized fibers were mixed with a solution of 2 g Epon 828 (Shell Chemicals) in 7 liters of propanol for 6 min and then dried overnight at 38°C.
- Epoxy, low (EL): Prepared similarly to EH, except only 0.5 g of the Epon 828 was used.

Finally, some samples of fibers were oxidized after production, using different procedures to increase the surface area, energy, and reactivity:

- Air-Etched fibers are Clean fibers oxidized in air at 450°C for 16 min and forced through a 0.16 cm sieve by a stainless steel wiper blade in order to reduce the clump size of the as-grown fibers with minimum damage to the fibers.
- CO_2 oxidized fibers are Best shot fibers oxidized with CO_2 in a tube furnace at temperatures from 850 to 950°C for from 15 min to 2 h at flow rates from 2 to 9.2 l/min; specific conditions for several runs are tabulated in Table I.

Each of these materials except for the Air-Etched and sieved sample was ball milled for 2 min using a Spex 8000 mixer mill to reduce the clump size of the as-grown fibers. This allows good permeation of the fibers by the polypropylene melt; the procedure is described more completely in reference [5].

X-ray diffraction measurements on the fibers were performed in the standard Bragg-Brentano ($\theta \rightarrow 2\theta$) configuration on a powder diffractometer. Bundles of fibers were pressed into an off-axis oriented quartz plate smeared with petroleum jelly. The jelly was both an adhesive for the fibers and a means of calibrating the scattering angle, since it exhibited sharp paraffin (110) and (200) diffraction lines.

Injection molding of mini-tensile specimens (ASTM Test Method D638 Type V) using CNF/polypropylene was performed with a benchtop CSI MiniMAX Molder which has been described previously [5]. The apparatus was equipped with a rotor, which may be submerged in a 12.7 mm diameter heated cup. Mixing was imparted by the rotary as well as by the vertical motion of the rotor. As with the ball-milling experiments, extreme care was used to employ a similar mixing procedure for all samples. Samples with high fiber fractions required as much as 10 min mixing because the bulky fibers had to be gradually added to the melt in order not to overflow the cup. Samples with a low fiber volume fraction were

TABLE I Analytical data for CO_2 oxidized best shot fiber

Run no.	Time (min)	Temp. (°C)	CO_2 flow (L/min)	Surface area (m^2/g)		Surface energy, γ_s^D (mJ/m^2)	Weight loss (%)	
				Total	External		Initial	Adjusted
1	15	850	2	24	16	152	−0.27	−6.96
2	120	850	2	83	28	106	24.27	19.19
3	15	950	2	43	23	179	4.83	−2.44
4	120	950	2	123	46	79	47.6	43.58
5	15	850	9.2	26	15	156	−4.7	−11.70
6	120	850	9.2	65	34	116	18.2	12.75
7	15	950	9.2	91	53	248	40.0	35.41
8	120	950	9.2	120	47	361	74.8	72.82

subjected to the same thermal regime. Further details on the injection procedure were presented in [5].

The specimens were mounted in the grips of an MTI tensile testing machine and stretched at 1 mm/min until failure occurred. The modulus was determined from the slope of the initial section of the stress-strain curve, while the tensile strength was determined from the ultimate load before separation of the two sections of the 2.54 cm dogbone.

Micrographs of fracture surfaces of the composites made from Air Etched and Graphitized/polypropylene composites were taken with the SEM.

A TA Instruments DMA 2880 dynamic mechanical analyzer was used to probe the dynamic characteristics (damping and stiffness) of Air Etched, Clean and Graphitized/polypropylene composites. The DMA is an analytical instrument used to measure the modulus (stiffness) and damping (energy dissipation) of the samples [7]. It has been demonstrated [8] that the DMA may be used to measure the modulus and tan δ of carbon nanotubes.

The samples are rectangular beam specimens cut from the central part of the injection molded samples for testing in the DMA (double cantilever, bending mode). The specimen rectangular bars were of length 30.4 mm, width 15 mm, and thickness 3 mm. The temperature was 21°C and the frequency was 1 Hz. Dual cantilever beam testing was performed on the DMTA. It has been shown that there is a relation between the fiber-matrix adhesion and tan δ [3]. Although the addition of carbon nanofibers as a reinforcement to Polypropylene can change the glass transition temperature of the composite formed, the damping measurements of the composite were done at room temperature, where such changes should be minimized. More details on the methodology used to measure the dynamic properties of carbon/nanofiber composites is given in [9].

3. Results and discussion

Fig. 1 shows the tensile strength and stiffness for carbon nanofiber/polypropylene composites using reinforcing fibers produced by several methods and having the various surface treatments described in the previous section. These data show that it is possible to triple both the modulus and strength of the polypropylene resin (open circle) by adding only 15 vol% carbon nanofiber. It also underscores the fact that some of the fiber production methods and surface treatments produce much better composites than others.

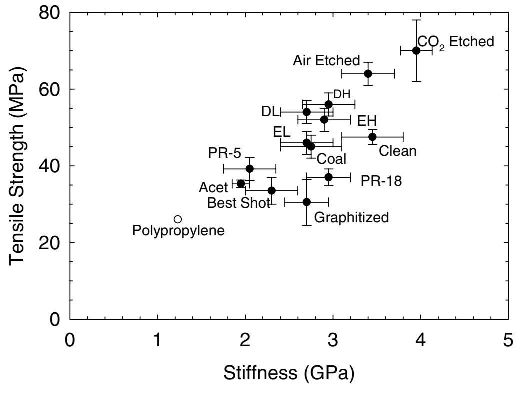

Figure 1 Tensile strength versus modulus for 15 vol% composites using different types of CNF in polypropylene. The open circle shows the properties of polypropylene.

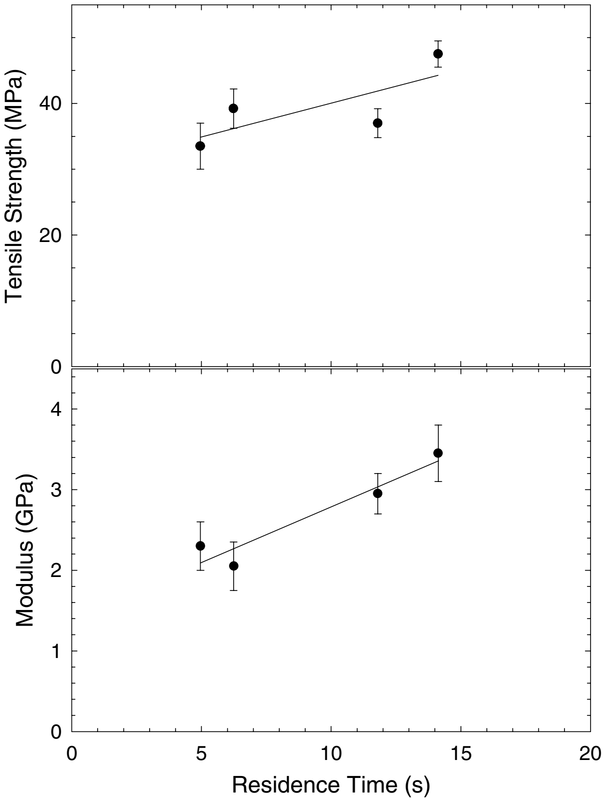

Figure 2 Tensile strength and modulus of composites fabricated from 15 vol% CNF produced with different gaseous feedstock residence times.

First the reinforcing properties of the as-grown fibers are compared. Fig. 2 shows a relationship between the

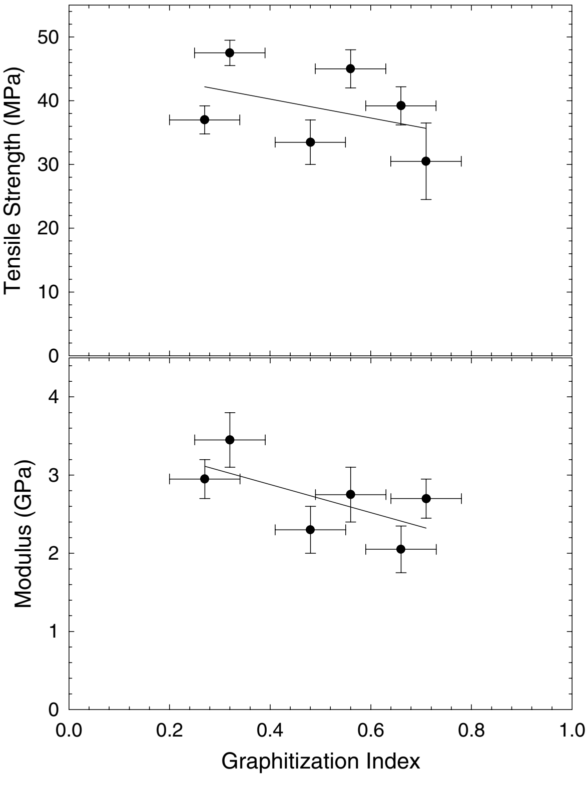

Figure 3 Tensile strength and modulus of composites fabricated from 15 vol% CNF produced with different gaseous feedstock residence times.

gas phase residence time (reactor volume/gas flow rate) of the feedstock mixture used to grow several varieties of fibers and the tensile strength (top graph) and modulus (bottom graph) of a 15 vol% composite fabricated from the fibers. Fibers grown under higher flow conditions, with shorter gas phase residence times, evidently produce composites with poorer mechanical properties.

Fig. 3 helps to rationalize this observation. It shows the tensile strength versus the graphitization index. Graphitization index g may be calculated from the d_{002} lattice spacing (nm) determined from the X-ray diffraction Bragg-Brentano scans.

$$g = \frac{0.344 - d_{002}}{0.344 - 0.3354}$$

This number varies from 0 for completely disordered carbons to 1 for single crystal graphite. The plot shows that more graphitic fibers of higher graphitization index tend to make composites having both lower tensile strength and modulus. The data in Fig. 3 exhibit greater scatter than those in Fig. 2 because of the error in measuring graphitization in these low density fibers due to the difficulty in precisely defining the sample plane. Overall, fibers grown under conditions of lower feedstock residence time are more graphitic and adhere more poorly to polypropylene, an observation consistent with earlier results [10].

Scanning electron micrographs show a significant difference in the fiber-matrix adhesion for the Air-Etched and Graphitized CNF/polypropylene composites. Figs 4 and 5 show that Graphitized fibers project much further from the fracture surface than Air-Etched fibers do, implying that the interfacial shear strength of the Graphitized fibers is much less than that of the Air-Etched. It is evidently much easier for the graphitized fibers to pull out of the matrix as the composite fractures. This result is consistent with the higher strength of the Air-Etched/polypropylene versus the Graphitized/polypropylene composite. Note that the polymer does appear to wet the fiber surfaces in both cases (Fig. 5), implying that the low interfacial strength is not merely a question of surface wetting. It can be

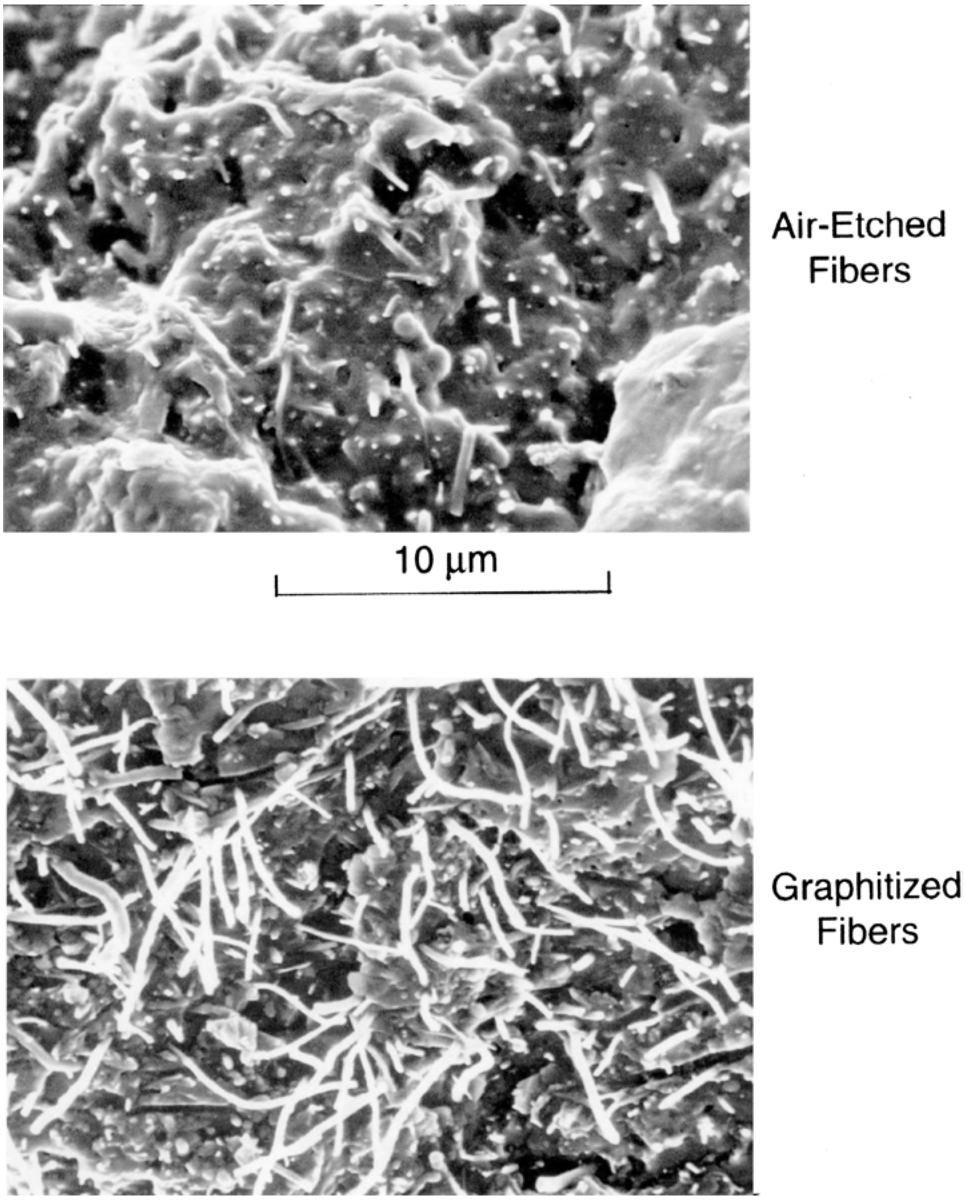

Figure 4 SEM micrographs of the fracture surfaces of polypropylene composites fabricated from Air-Etched and Graphitized fibers.

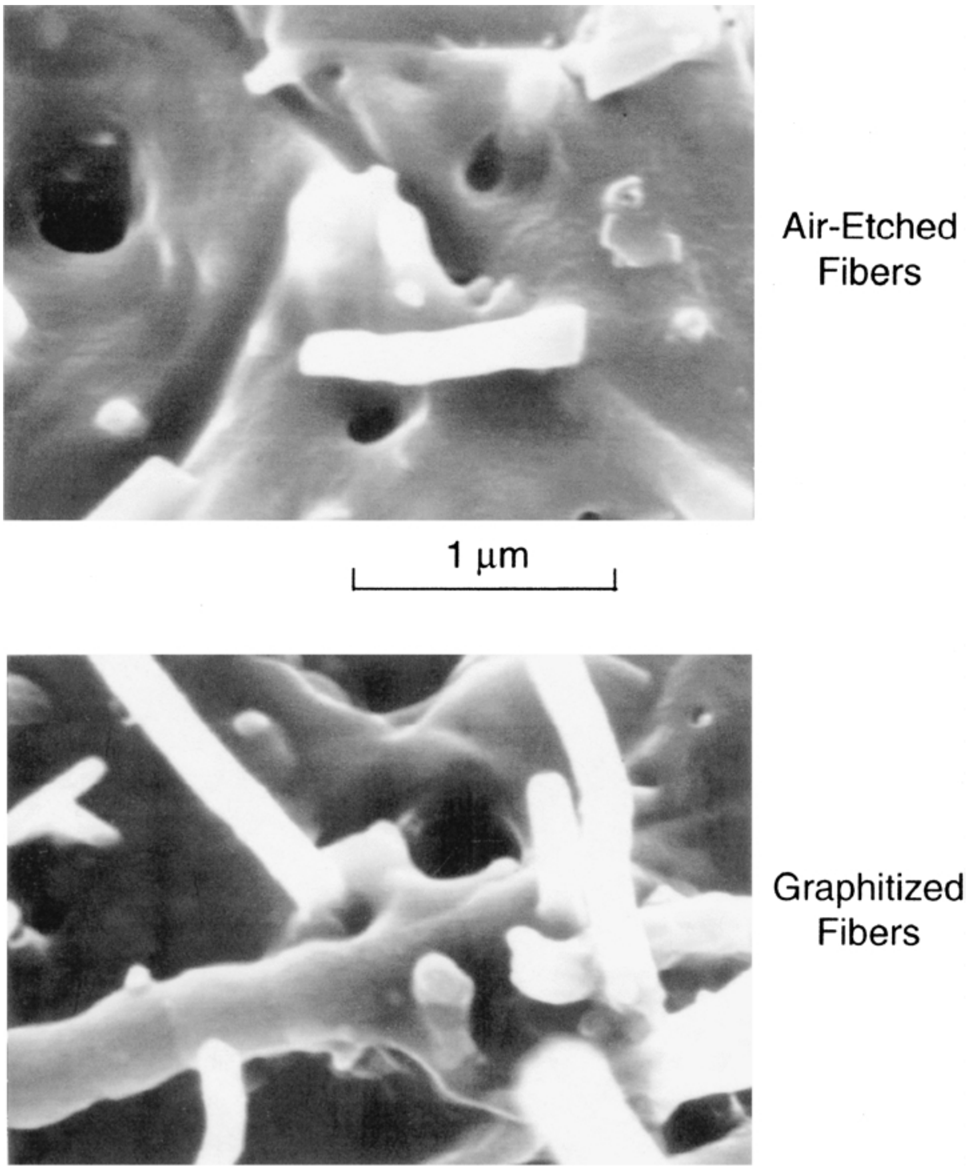

Figure 5 Higher magnification SEM micrographs of the fracture surfaces of polypropylene composites fabricated from Air-Etched and Graphitized fibers.

concluded from the micrographs presented in Figs 4 and 5 that a higher graphitization index will decrease the fiber-matrix interphase adhesion and decrease composite strength and stiffness in polypropylene.

Fig. 1 also gives little encouragement to the notion that composite tensile properties may be somewhat improved by applying properly reactive chemical coatings to the oxidized fibers. Compared to the Air-etched fibers, both the Epon 828 and the Armak 1192 seemed to very modestly decrease the stiffness while significantly decreasing the tensile strength of the composites in which they were used. These observations are consistent with the interpretation that the added liquid processing steps simply degraded the fiber lengths.

Perhaps the most salient feature of the data of Fig. 1 is the higher strength (70 MPa) and stiffness (4 GPa) observed for the fibers which were CO_2 oxidized at 850°C compared to the graphitized carbon nanofiber (strength 30 MPa and stiffness 2.6 GPa). The air etched and sieved CNF (65 MPa strength and 3.4 GPa stiffness) does not have quite as good properties as the CO_2 etched, but is still far superior to the graphitized material.

A more systematic examination of the tensile strengths of composites made from fibers with differing surface oxidizing treatments is presented in Fig. 6. The abscissa in Fig. 6 represents the total surface energy (mJ/g) of each type of fiber (obtained from Table I); it is determined by independent measurements of the external surface area of the treated fibers (m^2/g) times the surface energy of the fibers (mJ/m^2). It is evident from Fig. 6 that a modest amount of oxidation of the surface increases the tensile strength of the composite, while too much etching can decrease it. The optimum etch was carried out in a tube furnace using CO_2 at 850°C for 15 min at a 9.2 l/min flow rate.

Fig. 7 shows the variation of the loss factor (tan δ) of the Graphitized fiber, Air-etched, and Clean fiber/polypropylene composites versus fiber volume fraction. As fiber volume fraction increases, the loss factor decreases compared to the unreinforced polypropylene. Furthermore, the slope of the damping versus fiber volume fraction curves increases as adhesion between

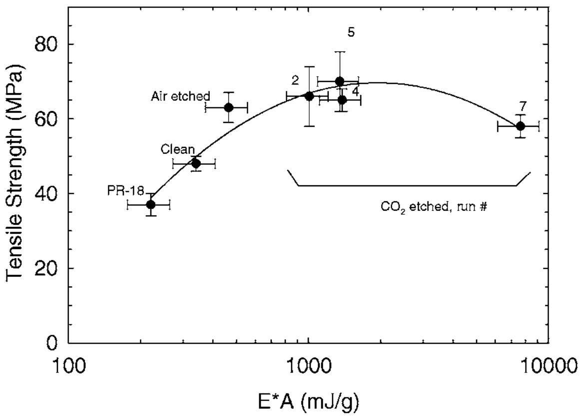

Figure 6 Tensile strengths of various 15 vol% CNF/polypropylene composites as a function of fiber total surface energy (fiber surface energy *x* external surface area).

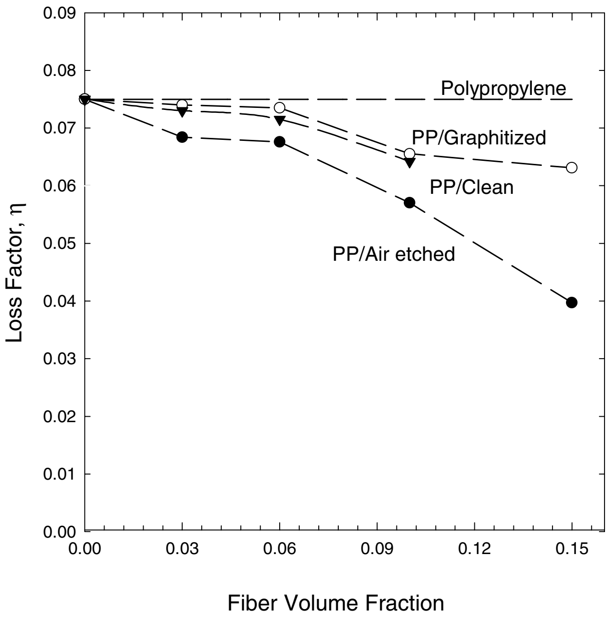

Figure 7 Loss factor vs fiber volume fraction for CNF/polypropylene composites at room temperature.

the fiber and the matrix increases. A higher slope (slope = 0.25) for the Air-Etched/polypropylene composites manifests a higher interphase adhesion than the Clean/polypropylene (slope = 0.13) and Graphitized/polypropylene (slope = 0.13) [1]. The loss factors decrease precisely in the same order as mechanical properties increase. It can be thus concluded from Fig. 7 that there is a significant difference between the loss factor, η, of the polypropylene matrix alone, and the loss factor obtained by reinforcing the polypropylene matrix with carbon nanofibers.

4. Conclusions

The data obtained for the tensile strength and modulus of composites made from various varieties of fibers with various surface treatments on them may be rationalized by a few principles:

- More graphitic fibers adhere poorly to the polypropylene matrix compared to less graphitic fibers.
- Fiber matrix adhesion may be improved by moderately oxidizing the fibers either in air or CO_2. This oxidation seems to become more effective as it increases the product of the external surface area and the surface energy of the fibers; however, excessive etching can be destructive.
- Two chemically active coatings did not increase the tensile stiffness, while perhaps somewhat decreasing the strength.

The evaluation of the fiber-matrix adhesion using scanning electron microscopy and DMA are consistent with direct measurements of mechanical properties. The dynamic mechanical analyzer is an easy and direct probe of the degree of adhesion between carbon nanofiber and a polypropylene matrix.

Better fiber-matrix adhesion increases the mechanical properties of CNF/polypropylene composites. A tentative optimum formula for etching and activating the surface to provide maximum composite properties was determined: it requires CO_2 at 850°C for 15 min at a 9.2 l/min flow rate.

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