

Recycled Carbon Fiber Filled Polyethylene Composites

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ABSTRACT: Composites of recycled carbon fiber (CF) with up to 30 wt % loading with polyethylene (PE) were prepared via melt compounding. The morphology of the composites and the degree of dispersion of the CF in the PE matrix was examined using scanning electron microscopy, and revealed the CF to be highly dispersed at all loadings and strong interfacial adhesion to exist between the CF and PE. Raman and FTIR spectroscopy were used to characterize the surface chemistry and potential bonding sites of recycled CF. Both the Young's modulus and ultimate tensile stress increased with increasing CF loading, but the percentage stress at break was unchanged up to 5 wt % load-

ing, then decreased with further successive addition of CF. The effect of CF on the elastic modulus of PE was examined using the Halpin-Tsai and modified Cox models, the former giving a better fit with the values determined experimentally. The electrical conductivity of the PE matrix was enhanced by about 11 orders of magnitude on addition of recycled CF with a percolation threshold of 7 and 15 wt % for 500- μm and 3-mm thick samples. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2015–2021, 2008

Key words: carbon fibers; polyethylene; composites; compounding; recycling

INTRODUCTION

The use of carbon fiber (CF) composites in aeronautical and certain automotive applications has been increasing over the last three decades. Such composites provide improved mechanical, fatigue, and corrosion properties, that are lighter in weight and easier to assemble compared to metals. As a consequence of the increased use of CF composites, the aeronautics industry in particular, is forced to dispose of large quantities of scrap CF composite by dumping in landfill sites. The recovery of CF from the composite material has been attempted using a range of processes, including chemical, mechanical, thermal, and even its use as a fuel after incineration has been investigated. Liu et al.¹ reported a thermochemical method for recycling of CF filled epoxy composites from rocket engine shells. Optimum recovery of CF was obtained, with no damage to the fibers, using an 8M nitric acid solution and a decomposition temperature of 90°C for a 4% nitric acid solution. Recycled CF obtained from such processes can then be used to reinforce thermoplastics and thermosets or improve the electrical conductivity of insulating polymers, a more attractive

proposal than using high cost virgin CF. The incorporation of virgin CF into a range of polymers and polymer blends, including high density polyethylene (HDPE),² polypropylene (PP),^{2,3} Nylon 6,6,⁴ styrene-butadiene-styrene (SBS),⁵ epoxy,⁶ ethylene-vinyl acetate copolymer (EVA),⁷ and HDPE/PMMA blends⁸ have been widely reported. However, the published literature on composites of recycled CF and polymers is limited. Kouparitsas et al.⁹ used a grinding and sifting procedure to recover CFs from an epoxy/CF composite, then melt blended the recycled CF (20 wt % only) with an ionomer. The elastic modulus and tensile strength of the recycled CF filled ionomer decreased slightly and the elongation at break increased when compared with virgin CF filled ionomer at the same loading. More recently, Markov et al.¹⁰ described the preparation, mechanical properties, and electrical conductivity of recycled CF filled glass fiber (GF) reinforced HDPE. The CF was reclaimed from prepregs using a pyrolysis technique at 700°C, purified and then laminates manufactured by first impregnating GF rovings with a HDPE/CF suspension that was prepared using sonication assisted solution mixing. The electrical conductivity of the GF/PE matrix was significantly increased on addition of CF, the authors reporting a percolation threshold of about 15 wt % for a 2-mm thick laminate (12 layers).

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The importance and novelty of this topic cannot be over stated, in that, the ability to melt blend with polymers, recycled CF recovered using a cost-effective process and having properties similar to virgin CF could provide composite materials that would find widespread use in automotive, aerospace, and civil engineering applications. In this article, we report the preparation of recycled CF filled PE composites, at loadings up to 30 wt % CF by melt compounding. The morphology of the composites and degree of dispersion of the CF is examined and correlated with the tensile mechanical and electrical properties of the filled materials.

METHODS

Materials and composite preparation

The CF used in this study was recycled from an epoxy/CF composite used in Formula 1 motor racing cars. The fiber was reclaimed using CARBON-CLEAN[®] technology, a thermochemical process that recovers 95% of the CF. The unsized CF obtained was subsequently milled to produce fiber with a density of 1.8 g cm^{-3} , a nominal length of $250 \mu\text{m}$ and diameter of $7 \mu\text{m}$, as shown in Figure 1. The CFs used were polyacrylonitrile based and have a Young's modulus and tensile strength of 200 and

3 GPa, respectively. The milled CF was dry blended with the PE before melt processing. The PE used was a linear medium density metallocene catalyzed polymer [density = 940 kg m^{-3} , MFR ($190^\circ\text{C}/2.16 \text{ kg}$)], Borecene RM7403, kindly supplied by Borealis (Norway). Composites of CF and PE were prepared at loadings of 0, 1, 3, 5, 8, 10, 15, 20, 25, and 30 wt % CF using a Dr. Collin 25-mm corotating intermeshing twin screw extruder fitted with a 3-mm strand die and a screw speed of 200 rpm. The temperature settings over six zones from the feed section to die head increased from 190 to 205°C resulting in a melt temperature of 212°C . The extrudate was quenched in a water bath at 20°C , pelletized and dried.

Characterization

Tensile test specimens were manufactured from the compounded blends using an Arburg 320S Allrounder 500-350 injection molding machine with a clamping force of 500 kN (50 tons) and a back pressure of 20 bar. This machine had a general-purpose screw of diameter 45 mm and L : D ratio of 18 : 1. The barrel temperature profile from the feed section to the nozzle was maintained at $180\text{--}200^\circ\text{C}$ during the manufacture of the various samples and the mold maintained at a cooling temperature of 35°C using a

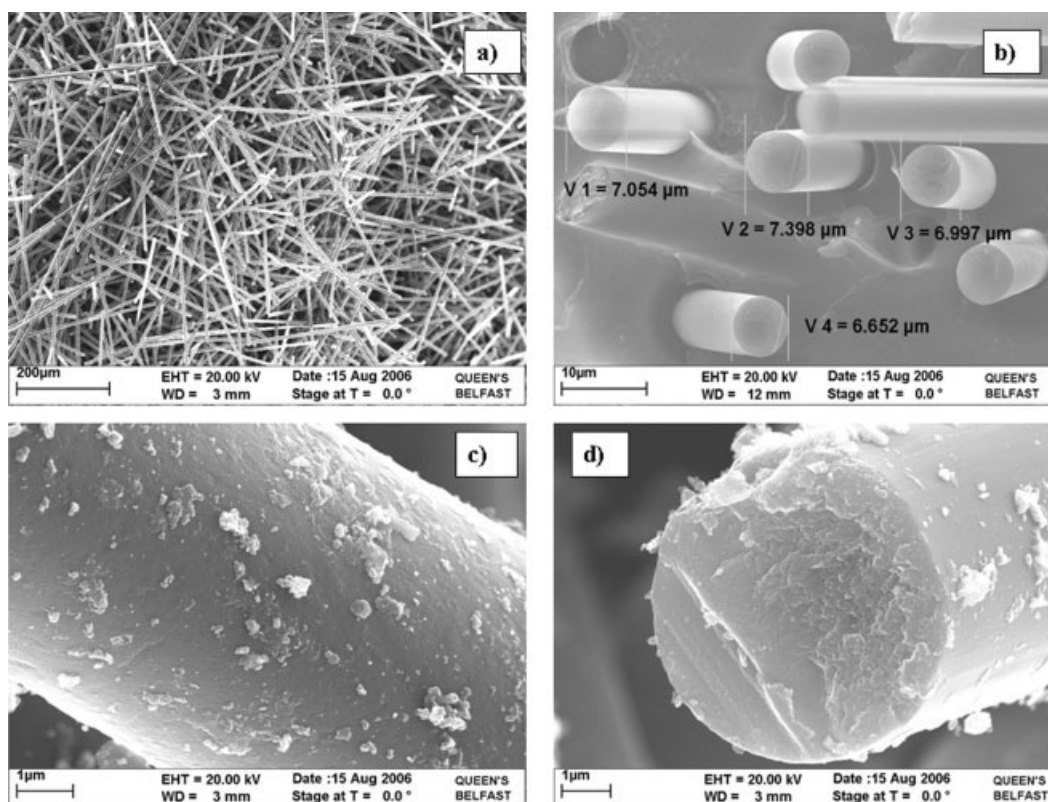


Figure 1 SEM images of (a) recycled CF, (b) CF having an average diameter of about $7 \mu\text{m}$, (c and d) showing residue along length and tip of fibers.

Stephens (UK) mold-heating unit. The temperature was maintained within $\pm 2^\circ\text{C}$ of the required temperature setting. The elastic modulus, tensile strength, and elongation at break of the composites were measured using an Instron 4411 Universal Tester to standard tensile test conditions according to ASTM D638M. The morphology of the CF and the degree of dispersion of the CF in the PE matrix was examined using a Leo Supra-25 scanning electron microscope on cryo-fractured gold coated molded samples at an operating voltage of 20 kV. The surface of the recycled CFs was examined using both Raman and Fourier transform infrared (FTIR) spectroscopy. The Raman spectra of the chopped recycled CF were obtained using an Avalon Instruments Raman station (AVRS002A) with 100 mW laser at wavelength of 785 nm, exposure time of 30 s and measurements taken were an average of 30 exposures. Numerous spectra were recorded along the length of the fibers using a Raman probe. FTIR spectra were collected using a Perkin-Elmer Spectrum 1000 microspectrometer in the spectral range $700\text{--}4000\text{ cm}^{-1}$ using a resolution of 2 cm^{-1} and an average of 50 scans recorded. The CF was dried in a convection oven at 80°C for 24 h prior to all spectroscopic analysis. Volume resistivity measurements were performed on two different thicknesses of sample, 500 μm and 3 mm, for all composites. Five hundred micrometer thick films

were obtained by compression molding extruded pellets of each composite using a circular template (diameter 60 mm, thickness 500 μm) placed between the platens and 3-mm thick discs (diameter 60 mm), specimens were obtained by injection molding the composites using the parameters described earlier. All tests were performed using a Keithley electrometer (Model 6517A) equipped with a Keithley resistivity test fixture (Model 8009). The sample of interest is placed between two circular electrodes and the volume resistivity measured by applying a DC voltage potential across opposite sides of the sample and measuring the resultant current through the sample, the test conforms to ASTM D-257 standard.

RESULTS AND DISCUSSION

The morphology and geometry of the recycled CF is shown in Figure 1. The fibers recovered were bundled, had an average length around 250 μm and diameter of 7 μm , see Figure 1(a,b). There was evidence, as shown in Figure 1(c) that residual organic material remained after treatment, although this tended to be confined toward the end and on the tips of fibers. The extent of the dispersion of CF in the PE matrix was also investigated using SEM. By way of example, Figure 2 shows the SEM images for

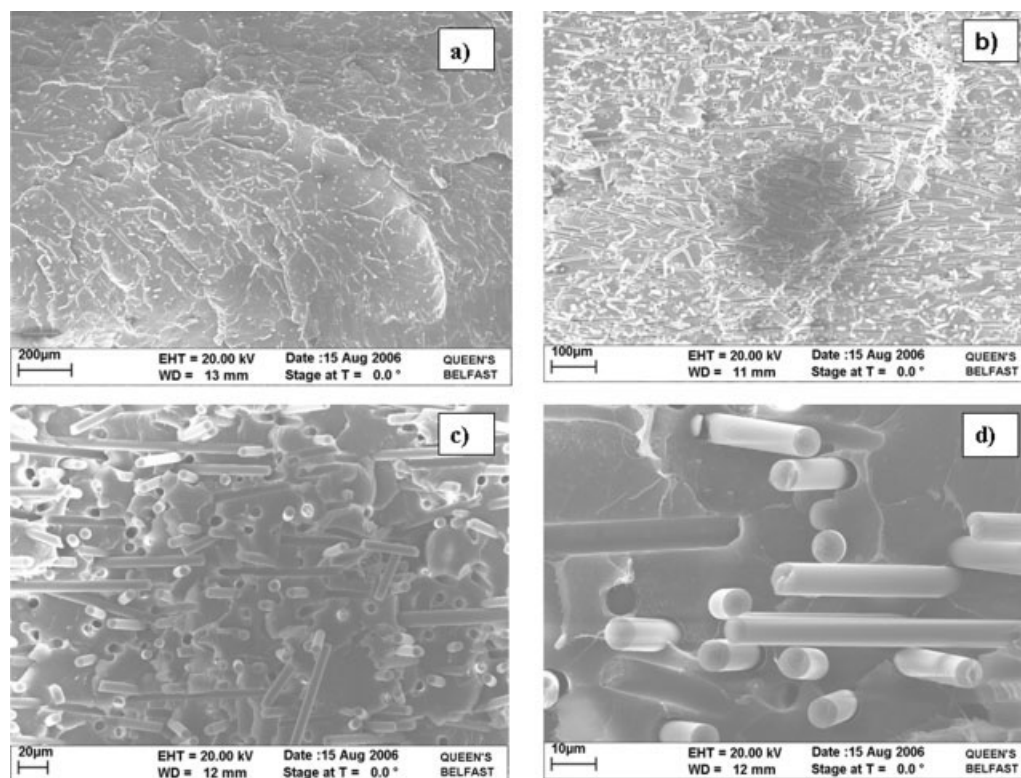


Figure 2 Representative SEM images of the composite materials showing a highly dispersed CF phase for (a) 3 wt % and (b) 30 wt % CF loading, (c) randomly oriented and distributed CF and (d) strong interfacial adhesion between CF and matrix.

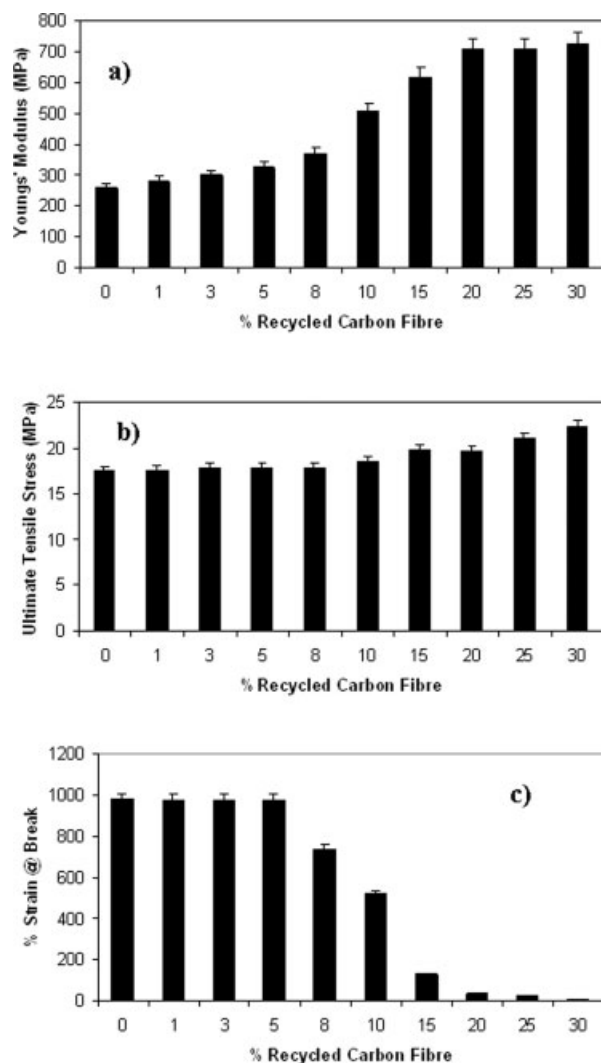


Figure 3 Variation in (a) Young's Modulus, (b) ultimate tensile stress, and (c) percentage strain at break as a function of CF loading.

the 3, 25, and 30 wt % composites. It is clear that the CF is highly dispersed in the polymer, see Figure 2(a,b), and this was evident across the length scales and for all compositions. Interestingly, there seems to be some interfacial attraction between the CF and polymer. After cryofracturing an excess of 80% of the CF remained embedded in the PE matrix, see Figure 2(c), closer inspection of the surface revealed little or no breakage of fibers and wetting of the CF by the PE, as shown in Figure 2(d). The tensile mechanical properties of PE and the composites were measured and are shown in Figure 3. The Young's modulus of PE increased with successive additions of CF from 258 MPa for PE itself to 724 MPa for the composite with 30 wt % CF, an increase of 180%. Similarly, the ultimate tensile stress increased with CF addition, by a total of 27.5% from 17.5 MPa for PE alone to 22.3 MPa to the 30 wt % filled compos-

ite. The increase in tensile modulus and strength with increasing CF loading are typical of those reported previously for virgin CF filled PE and PP composites.^{3,11,12} The increase in strength and stiffness obtained maybe explained in terms of interfacial interactions and chemical bonding between polymer and functional groups on the surface of the fiber. The surface functionality of the recycled CF was investigated using both Raman and FTIR spectroscopy, see Figure 4(a,b), respectively. The Raman spectrum shown for the recycled CF is typical of that report for graphitic carbon.^{13–15} The peak at 1316 cm^{-1} , known as the D band, corresponds to the A_{1g} mode and is derived from defect sites in the CF. The peak having a mean position at 1605 cm^{-1} is assigned the G band or E_{2g} mode and at 2622 cm^{-1} , the G' band, is also characteristic of crystalline graphite. No additional peaks associated with polar functional groups were detected. In contrast, the FTIR spectrum of recycled CF showed clear evidence for the presence of polar groups. The peaks having mean positions at about 3450 , 2913 , and 1620 cm^{-1} are derived from hydroxyl ($-\text{OH}$), carboxylic acid ($-\text{COOH}$) and carbonyl ($-\text{C}=\text{O}$) functionality and are formed due to the degradation of the epoxy resin during the CARBONCLEAN[®] process, a combined thermal and chemical treatment of the epoxy/CF

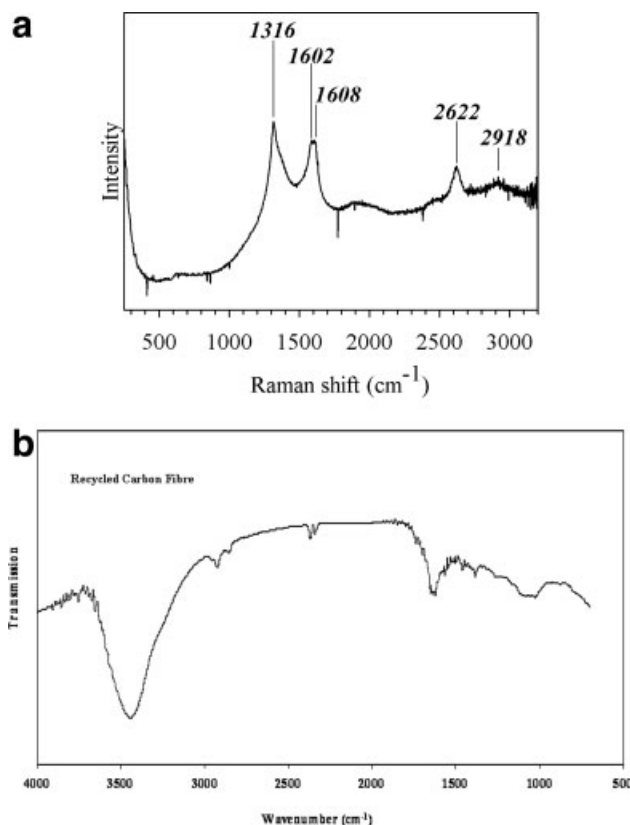


Figure 4 (a) Raman and (b) FTIR spectrum of recycled CF.

TABLE I
Elastic Modulus of CF Composites Calculated
Experimentally and Using a Modified Cox and
Halpin-Tsai Models

CF (wt %)	E_{EXP} (GPa)	E_{MCOX} (GPa)	E_{HT} (GPa)
0	0.258	–	–
1	0.280	0.33	0.30
3	0.299	0.54	0.38
5	0.325	0.81	0.47
8	0.371	1.31	0.61
10	0.509	1.72	0.72
15	0.618	3.00	1.02
20	0.707	4.74	1.40
25	0.708	7.12	1.84
30	0.724	10.37	2.42

MCOX, modified Cox model; HT, Halpin-Tsai model.

composite. The presence of these groups on the surface of the recycled CF provides a mechanism for good wetting between polymer and CF,^{16–18} and as such account for, in part, the increase in strength and stiffness of the composites with increasing CF loading. Residual undegraded epoxy resin was also evident along the length and the tip of the fibers, see Figure 1(c,d), this residue may also aid dispersion of the CF in PE during melt mixing. The percentage strain at break (a relative measure of toughness) remained unchanged when up to 5 wt % CF was added, but fell by 26 and 49% with 8 and 10 wt % CF addition, respectively. Further larger loadings of CF, above 20 wt %, resulted in a dramatic reduction in the strain at break, confirming embrittlement of the composites at higher loadings of CF.

The elastic modulus of the composites was determined using the Halpin-Tsai¹⁹ and modified Cox models.^{4,20} For the Halpin-Tsai model for randomly oriented fibers, the modulus of the composite (Y_c) can be calculated using:

$$\frac{Y_c}{Y_m} = \frac{3}{8} \left[\frac{1 + \zeta \eta_L V_f}{1 - \eta_L V_f} \right] + \frac{5}{8} \left[\frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \right] \quad (1)$$

where

$$\eta_L = \frac{Y_f/Y_m - 1}{Y_f/Y_m + \zeta} \quad (2)$$

and

$$\eta_T = \frac{Y_f/Y_m - 1}{Y_f/Y_m + 2} \quad (3)$$

Y_c , Y_m , and Y_f are the moduli of the composite, matrix, and fiber, respectively, V_f is volume fraction of fiber and ζ is a constant shape factor, normally between 1 and 2. The modified Cox's model can also be used to calculate the Young's modulus (E_c) of the

PE/CF composites with randomly oriented fibers from:

$$E_c = (1 - V)E_m + q \left(1 - \frac{\tan h \beta}{\beta} \right) V E_f \quad (4)$$

where

$$\beta = \frac{l}{d} \sqrt{\frac{E_m}{(1 + \nu)E_f \times \ln(\pi/4V)}} \quad (5)$$

and $E_m = 258$ MPa, $E_f = 200$ GPa, V is the volume fraction, q is an orientation factor and is assumed to be 1/6 for randomly oriented fibers, and ν in Poisson's ratio = 0.4 for PE. The modulus of the composites was calculated using both models and compared with the values determined experimentally, see Table I. In general, there is a better fit between the experimental values and those obtained using the Halpin-Tsai model for all compositions. However, there is good agreement between both models and the experimental data at low loadings of CF, about 5 wt % and below. Both models fail to predict accurately the increase in stiffness with incremental increases in CF loading in the composites, most notably at higher concentrations of CF. The discrepancy in the modulus values obtained experimentally with those determined using the modified Cox and Halpin-Tsai models can be explained in terms of the limitations of the theories both models are based on. The modified Cox model deals with low aspect ratio fibers, assumes the matrix transfers load to the fibers via a shearing mechanism, the fibers behave elastically and the polymer matrix responds in a linear viscoelastic manner.^{20–22} In general, modulus values determined using semiempirical expressions, such as the Halpin-Tsai equation, tend to be in better agreement with those obtained experimentally, particularly at low fiber volume fractions. However, the Halpin-Tsai model too has limitations in its applicability, in that, there is an assumption that the polymer and fiber are perfectly bonded and the fibers have uniform geometry, the latter directly related to the constant shape (or reinforcement) factor, ζ .^{23,24}

The volume resistivity of the composites for both a 500- μ m thick film and a 3-mm molded sample was measured as a function of CF loading and is shown in Figure 5. Below the percolation threshold the resistivity of the composites decreases with increasing CF content, until further successive CF loading a percolation threshold is attained. After a percolation threshold was achieved, the volume resistivity of the PE matrix had decreased by about 11 orders of magnitude, from 10^{18} ohm cm^{-1} to 10^7 ohm cm^{-1} , now more conductive than what would be required for antistatic applications. As expected,

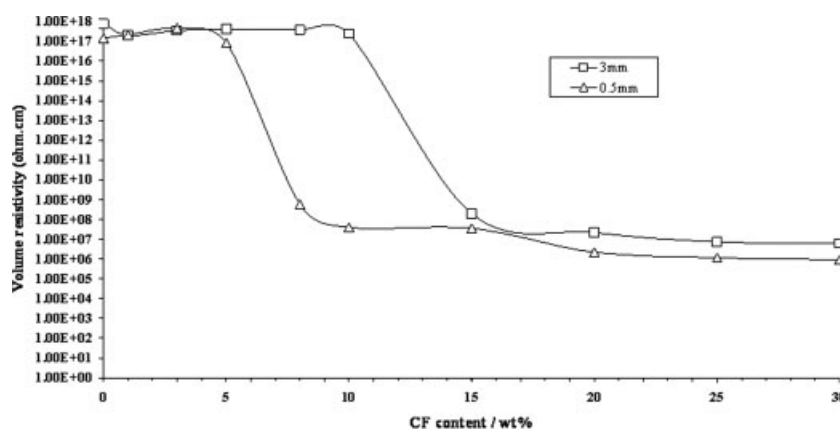


Figure 5 Volume resistivity of CF filled PE composites.

the percolation threshold for the thin film was attained at a lower CF loading (7 wt %) compared with the 3-mm thick plaque (12.5 wt %). At and just above these loadings a conductive network of CF fibers has formed facilitating electron hopping between fibers. Subsequent addition of CF above the percolation threshold increases the conductivity to a much smaller extent. This small change in conductivity above the threshold can be expressed using percolation theory as:

$$\sigma \propto (p - p_c)^t \quad (6)$$

where t is the critical conductivity exponent, p is volume fraction of filler and p_c is the critical concentration of fibers. For a single percolation process with randomly oriented and distributed fibers in three dimensions, t should be less than 2, although this is dependant on the aspect ratio of the fibers.²⁵ The t exponent for both the thin film and thicker plaque were determined by taking the slope of a plot of log resistivity against $\log(p - p_c)$, see Figure 6. The value obtained for the 500- μ m film was 1.92, but for the thicker sample (3 mm), $t = 1.19$, indicative of the

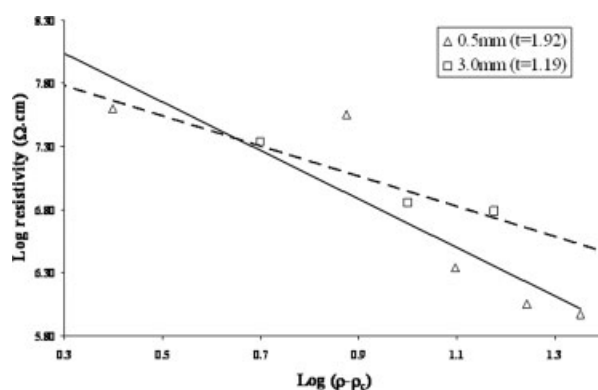


Figure 6 Electrical resistivity of PE-CF composites as a function of $p - p_c$.

nonuniversality of t because of the variable interfacial connectivity between fibers, which is more likely to occur with thicker samples.²⁶

CONCLUSIONS

CF reclaimed from CF filled epoxy prepregs can be readily melt blended with PE. The CF was highly dispersed in the PE matrix at all loadings. The Young's modulus and tensile strength of the composites increased by 180 and 27.5%, respectively, with increasing CF loading, suggesting that some degree of interfacial adhesion is present between the CF and PE. Good interfacial adhesion and wetting between PE and the recycled CF is possible, in part, due to the presence of polar functional groups, observed in the FTIR spectrum of this CF, along the length of the CF. The modulus predicted using the Halpin-Tsai model was in reasonable agreement with those measured experimentally, although the values obtained for both the Halpin-Tsai and modified Cox models deviated to a larger degree at higher CF loadings. The percentage strain at break was unchanged with up to 5 wt % CF, fell by 50% for the composite with 10 wt % addition, then decreased rapidly for the composites with up to 30 wt % CF, as the composites became embrittled. The electrical conductivity of the PE was enhanced by ~ 11 orders of magnitude on addition of the recycled CF and a percolation threshold observed at ~ 7 wt % for a 500- μ m film and 15 wt % for a 3-mm thick plaque. The critical exponent (t) determined for both sample thicknesses was below the theoretically predicted value of 2, implying a single percolation process.

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