

Improving nanofiber dispersion and adhesion in polypropylene composites

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The effects of different carbon nanofiber surface functionalizations, as well as the use of two compatibilizers, on the physical and mechanical properties of polymer samples are investigated.

In the last several years, the use of carbon nanofillers—especially carbon nanotubes (CNTs) and carbon nanofibers (CNFs), but also graphite and graphene—has become a popular method for the reinforcement of polymers. CNFs and CNTs have very similar characteristics (e.g., their high aspect ratios, as well as their mechanical, electrical, and thermal properties), but CNFs are a more economical option.^{1,2} Even at low concentrations, the fillers can be used to significantly improve the mechanical, thermal, and electrical properties of the polymers,^{3–5} and they are thus attractive for a variety of technological applications.^{6,7} To realize high-performance composites in this way, it is particularly important to achieve homogenous dispersion of the fillers and for there to be strong interactions at the interface between the fillers and the host polymer.⁸ It can be extremely challenging, however, to achieve the necessary dispersion of carbon nanofillers within non-polar polymers, such as in the widely used polypropylene (PP).

To date, PP has been mixed with various nanofillers to improve its mechanical properties.^{9,10} Although polymer/CNF composites with excellent mechanical properties of polymer/CNF composites have been fabricated with the use of a functionalized CNF formulation,^{11,12} the addition of an appropriate compatibilizer or filler modification is required to achieve adequate filler dispersion. Such modifications improve the dispersion of the fillers by enhancing the interface interaction between the two composite components (i.e., by wetting the fibers and causing increased adhesion of the fillers to the polymer matrix during processing of the composites).^{13,14} CNF-reinforced polymer composites such as these combine the toughness of the original polymer matrix with the stiffness and strength of CNFs.^{15,16} The composites are

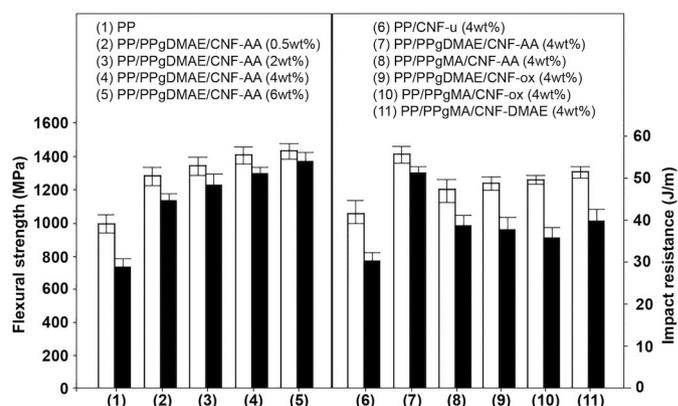


Figure 1. Measured flexural strength (white) and impact resistance (black) of neat polypropylene (PP) and PP/carbon nanofiber (CNF) composites. The composites consist of a PP matrix and untreated CNFs (CNF-u), oxidized CNFs (CNF-ox), or CNFs treated with either an acrylic acid plasma (CNF-AA) or dimethyl amine ethoxy ethanol (CNF-DMAE), at a concentration of 0.5, 2, 4, or 6wt%. The composites also contain a functionalized compatibilizer, i.e., PP grafted with either maleic anhydride (PPgMA) or DMAE (PPgDMAE).

therefore widely used in a range of applications (e.g., in the automotive and aerospace industries).

In this work,¹⁷ we chose to study PP/CNF composites because of their importance in industry. Specifically, we have examined the influence of surface functionalization of CNFs, as well as the use of functionalized PP as a compatibilizer, on the physical and mechanical properties of PP/CNF composites. For the experiments, we treated the CNFs in one of three ways: with a reactive plasma of either acrylic acid or of dimethyl amine ethoxy ethanol (DMAE), or by oxidation with a sulfuric acid/nitric acid mixture. In addition, we used PP grafted with maleic anhydride (PPgMA) or modified with DMAE¹⁸ (PPgDMAE) as the two compatibilizers in our work. We also used melt-mixing and

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compression-molding processes to prepare our nanocomposites, i.e., that contained the untreated (CNF-u), oxidized (CNF-ox), acrylic-acid-plasma-treated (CNF-AA), or DMAE-treated (CNF-DMAE) CNFs in concentrations of 0.5, 2, 4, and 6wt%.

Some of our flexural-strength and impact-resistance measurements for the PP and PP/CNF samples are illustrated in Figure 1. These results highlight that, for the PP/PPgDMAE/CNF-AA composite, increased CNF-AA content gives rise to a substantial increase in the flexural strength and impact resistance of the material (with maximum values measured for CNF-AA concentrations of 4 and 6wt%). Indeed, we observe the maximum increase in flexural strength and impact resistance (of 40 and 80% compared with the neat PP sample, respectively) for the 6wt% filler content sample. These results thus demonstrate that effective load transfer can be achieved with this compatibilizer/CNF combination. Indeed, the PPgDMAE compatibilizer improves the filler dispersion by enhancing the interactions between the acid groups in the treated CNFs and the amine groups in the compatibilizer polymer matrix. Moreover, we find that the PPgDMAE/CNF-AA combination exhibits both the highest flexural strength and toughness values of all the compatibilizer/CNF composite combinations, which confirms the favorable filler–polymer matrix interactions in this compound. Our measurements also show that the PPgMA/CNF-DMAE combination provides an acceptable performance, but the composites that contain CNF-ox show less of an improvement in flexural strength and

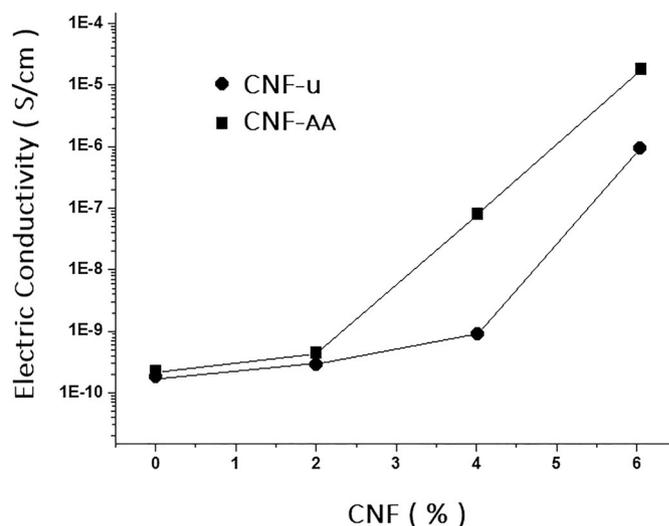


Figure 3. Electrical conductivity of the PP/CNF-u and PP/PPgDMAE/CNF-AA composites at different fiber loadings.

toughness. We attribute this to the reduced fiber aspect ratio that occurs because of the oxidation treatment.

We have also obtained scanning electron microscope (SEM) images for our samples. We show the images for the PP/CNF-u and PP/PPgDMAE/CNF-AA samples (both with 4wt% filler contents), for example, in Figure 2. For the PP/CNF-u sample, at low magnification—see Figure 2(a)—we observe an apparently good filler dispersion, with no visible filler aggregates. However, at higher magnification for the same sample—see Figure 2(b)—we see areas that contain holes (i.e., which contained fibers before the sample was fractured), and where there is no adhesion between the CNFs and the polymer matrix. This image is thus evidence that the compatibility between the fillers and the matrix is limited to certain areas, which in turn gives rise to only a fair improvement of the composites’ mechanical properties compared with neat PP. In contrast, we observe a more homogeneous filler dispersion for the PP/PPgDMAE/CNF-AA composite: see Figure 2(c). In addition, noticeable adhesion of the fillers to the polymer matrix can be seen at higher magnification: see Figure 2(d). Our SEM results thus illustrate that the inclusion of a compatibilizer (i.e., PPgDMAE)—in combination with the CNF-AA fibers—enhanced the fiber adhesion, which was responsible for the remarkable increase in the mechanical properties that we measured.

Lastly, we present the electrical conductivity of the PP/CNF-u and PP/PPgDMAE/CNF-AA composites in Figure 3. These measurements indicate that the conductivity of the PP/CNF-u samples changes only

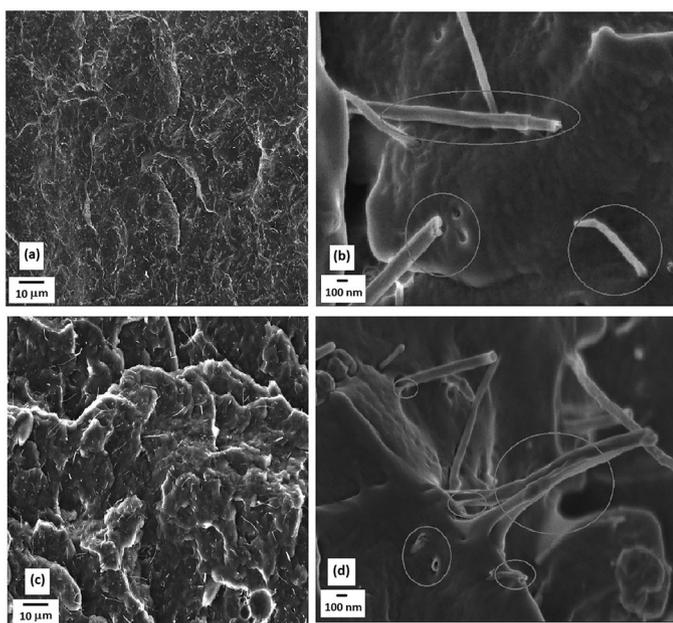


Figure 2. Scanning electron microscope images of the fractured surfaces of the (a,b) PP/CNF-u and (c,d) PP/PPgDMAE/CNF-AA composites (both with 4wt% filler content).

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slightly at CNF loadings of 2 and 4wt% (compared with a loading of 0.5wt%), but that at a loading of 6wt%, the conductivity increases abruptly. We therefore assume that the percolation threshold for this composite occurs above 4wt%. For the compatibilized PP/PPg/DMAE/CNF-AA composites, however, we note a dramatic change in conductivity even at lower filler loadings. This sharp increase in conductivity thus indicates that the percolation threshold occurs at a lower filler content and that it is related to the improved filler dispersion (promoted by this compatibilizer/filler combination). In other words, incorporating PPgDMAE as the coupling agent, with CNF-AA fibers, promotes greater matrix–fiber adhesion, which improves the filler dispersion and causes a reduction in the electrical percolation threshold. Our result also indicates that the electrical conduction mechanism is strongly influenced by the filler dispersion (i.e., which is promoted by this compatibilizer).

In summary, we have investigated the effects of various CNF functionalizations and two different compatibilizers (PPgDMAE and PPgMA) on the physical and mechanical properties of PP/CNF nanocomposites. For instance, we have shown that the flexural strength and impact resistance of the samples can be substantially improved, particularly with the PPgDMAE/CNF-AA combination. We have also used SEM images to examine the filler dispersion and adhesion within our composites, and we found that the use of the PPgDMAE and CNF-AA promotes greater matrix–fiber adhesion and improved filler dispersion. We are now continuing to study the use of these compatibilizer/fiber modification combinations in other polymer matrices and to compare the properties of our composite prototypes with other nanocomposites.

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