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Reducing the water uptake of environmentally friendly polypropylene composites

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Spent coffee ground particles are treated with a fatty acid derivative in a novel hydrophobic method that improves particle dispersion and impact properties.

The increasing environmental concerns of recent years, as well as problems related to the depletion of oil (petrol) reserves, have stimulated research on and the development of environmentally friendly materials. This work has mainly been conducted within the field of polymers and polymer composites because these materials have high petroleum dependencies.[1,2] Although previous work has shown that natural fibers for such composites provide some advantages over conventional fillers, e.g., glass (fibers, spheres, or flakes), alumina, calcium carbonate, sulfates, phosphates, or silicates,[3,4] there are also problems associated with these natural fillers.

The advantages of natural fillers include lower densities, cost reductions, lack of toxicity, balanced mechanical performances, as well as the lower environmental impacts.[3,4] Nevertheless, poor particle dispersion and low natural filler–polymer interactions occur when natural fillers are used. In addition, the highly hydrophobic nature of most plastics is not compatible with the highly hydrophilic nature of lignocellulosic (i.e., dry plant matter) fillers.[5,6] Another problem connected with natural lignocellulosic fillers is dimensional instability. This is caused by high water uptake levels, which are promoted by the high hydroxyl content of cellulose and can cause undesirable swelling.[7,8]

In our work, we manufactured environmentally friendly ('green') composites that are based on polypropylene (PP) and 20wt% spent coffee ground (SCG) wastes. We use extrusion-compounding and subsequent injection molding to make these composites. This is a novel hydrophobizing treatment in which we use a fatty acid derivative from palmitic acid to reduce the water uptake and to improve particle dispersion.

We also compared the effects of our treatment with two conventional approaches for the reduction of water uptake levels, i.e., silanization with (3-glycidyloxypropyl)trimethoxysilane, as well as the use of a compatibilizer agent that is based on the polypropylene-*graft*-maleic anhydride copolymer (PP-*g*-MA). A summary of the mechanical features of our PP-SCG composites—in terms of the treatments and/or compatibilizers—is shown in Table 1. These results reveal that the composite with previously treated SCG particles (i.e., with palmitoyl chloride) has balanced flexural properties with similar values to other treatments. For instance, the flexural strength is within the same range as for other treatments, and the flexural modulus is slightly lower. This composite, however, also displays a higher impact energy. This is because our pre-treatment of the SCG powder gives rise to improved particle dispersion and makes it less likely that particle aggregates will form (which tends to occur with hydrophilic materials). Hydrophobized SCG particles are thus able to interact with the highly hydrophobic PP matrix, and this has a positive effect on the impact energy because micro-crack growth is restricted.[9]

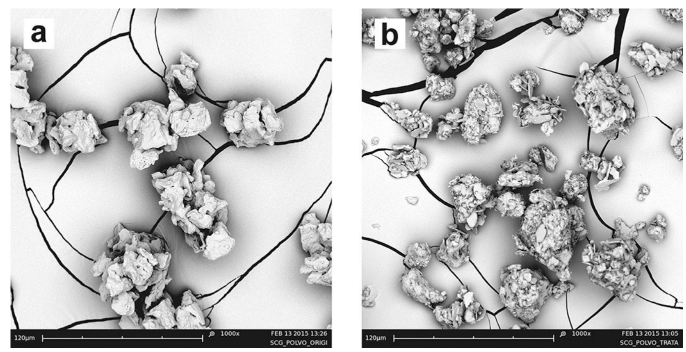

Figure 1. *Scanning electron microscope images of spent coffee ground (SCG) particles at a magnification of 1000. Untreated SCG particles are shown in (a) and SCG particles that have been pre-treated with palmitoyl chloride are shown in (b).*

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Table 1. Mechanical properties of polypropylene-SCG composites that contain 20wt% SCG. The properties are given for untreated samples as well as for those that have undergone various pre-treatments. SCG MA: SCG particles pre-treated with a compatibilizer agent (PP-graft-maleic anhydride). SCG SIL: SCG particles subjected to silanization with (3-glycidyloxypropyl) trimethoxysilane. SCG PALM: SCG particles pre-treated with palmitoyl chloride.

	Samples				
Property	**Unfilled PP**	**SCG**	**SCG MA**	**SCG SIL**	**SCG PALM**
Flexural strength (MPa)	37.0 ± 0.2	33.4 ± 0.3	31.7 ± 0.2	32.4 ± 0.3	31.9 ± 0.2
Flexural modulus (MPa)	1034 ± 78	1176 ± 26	1121 ± 41	1222 ± 35	989 ± 27
Impact energy (Jm^{-2})	2.6 ± 0.1	1.1 ± 0.1	1.5 ± 0.3	1.0 ± 0.1	1.7 ± 0.1

We obtained scanning electron microscope images of untreated SCG particles—see Figure 1(a)—and of SCG particles that we subjected to a pre-treatment with palmitoyl chloride: see Figure 1(b). From these images, we can see clearly that aggregates in the untreated SCG particles are larger than those in the pre-treated (i.e., hydrophobized) SCG particles. The formation of these aggregates (or particle clusters) occurs because hydroxyl groups in cellulose tend to interact with each other. With our hydrophobization technique, however, we can neutralize hydroxyl groups in cellulose and hemicellulose. We used an esterification reaction for the hydrophobization of the SCG particles, wherein palmitic acid molecules were anchored on the hydroxyl groups of the cellulose and hemicellulose. In this way, the hydroxyl groups became blocked and were unable to interact.

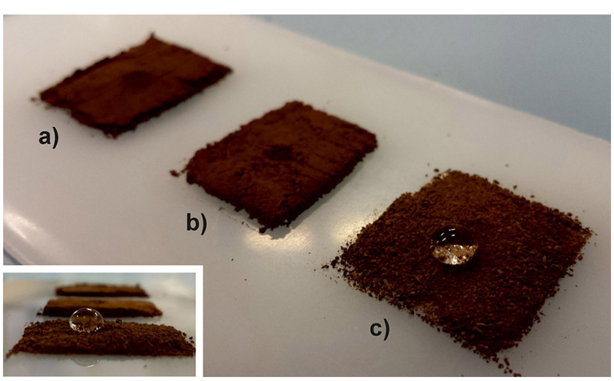

Figure 2. Photograph illustrating the behavior (over 60s) of a water droplet on different SCG samples. The sample labeled (a) contains untreated SCG particles, the sample labeled (b) contains SCG particles that have been silanized with (3-glycidyloxypropyl)trimethoxysilane, and the sample labeled (c) contains SCG particles that have been hydrophobized with palmitoyl chloride.

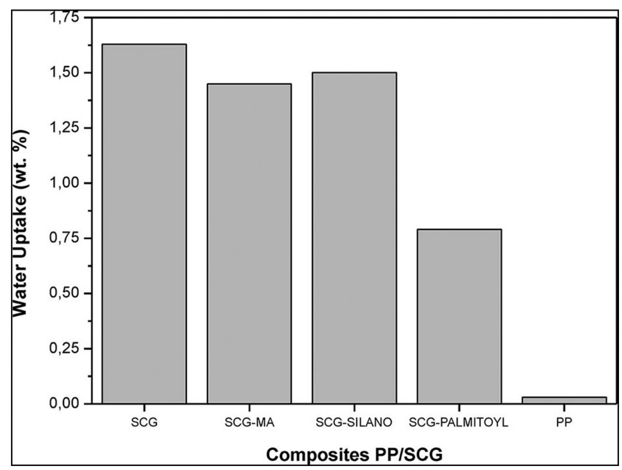

Figure 3. Plot showing the total water uptake (over three months) of SCG particles, PP, and PP-SCG composites that involve different pre-treatments or compatibilizers. SCG-SILANO: SCG particles subjected to silanization with (3-glycidyloxypropyl) trimethoxysilane. SCG-PALMITOYL: SCG particles pre-treated with palmitoyl chloride.

In addition, the fatty acid formed a very thin hydrophobic layer on the SCG particles. The apparent hydrophobic behavior of our SCG particles that have been treated with palmitoyl chloride is illustrated in Figure 2. One of the main advantages of our hydrophobizing treatment was the remarkable improvement in the water uptake level of our samples (see Figure 3). With our treatment, we were able to reduce water uptake from about 1.6% for untreated SCG particles to about 0.75% for hydrophobized SCG particles that have been treated with palmitoyl chloride.

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We have shown that PP composites that include SCG particles are attractive and environmentally friendly materials. We were able to address the water uptake problem that was associated with lignocellulosic fillers by pre-treating the SCG particles with palmitoyl chloride. Our pre-treatment method is therefore an effective technique for the realization of highly hydrophobic natural lignocellulosic fillers for green composites with PP matrices. Our hydrophobizing treatment has a positive effect on particle dispersion and gives rise to improved impact properties. Furthermore, our treatment method substantially reduces water uptake levels and therefore improves overall dimensional stability and the amount of moisture-related swelling that occurs in these composites. Our future work will include evaluation of the effects of different fatty acids on hydrophobic properties and dispersion ability. We will also continue to investigate even more environmentally friendly processes with low-impact solvents.

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