Journal of Applied Polymer Science

Green nanocomposites filled with spent coffee grounds

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ABSTRACT: This study evaluated physical properties of the nanocomposites reinforced by used coffee grounds. Coffee grounds were ball-milled and filtered in an effort to secure nanoparticles for the fabrication of polyvinyl alcohol (PVA)/coffee nanocomposites. We analyzed the particle size distribution of coffee particles and investigated mechanical and optical properties of the prepared nanocomposites. Carbon black (CB)-filled nanocomposites were also prepared to understand the physical behavior of the nanocomposites reinforced with coffee grounds and to explore the possibility of replacing CBs with nanosized coffee grounds used as a composite filler. It was found that the tensile strength and Young's modulus of PVA/coffee grounds nanocomposites were significantly enhanced compared with those of the PVA/CB nanocomposites. In addition, morphological observation for the nanocomposites was carried out using scanning electron microscopy (SEM). © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42043.

KEYWORDS: composites; mechanical properties; nanoparticles; nanowires and nanocrystals

Received 21 May 2014; accepted 11 January 2015
DOI: 10.1002/app.42043

INTRODUCTION

Environmentally benign materials have attracted enormous attention since it is important to reduce the environmental footprint in the ecosystem and to develop a more sustainable material lifecycle.[1–3] In terms of composites, much effort has been made to investigate green composites composed of natural and biodegradable fillers or matrices.[4–8] However, such green composites have yet to be materialized for their promising potential as an advanced material for the next generation compared with conventional composites that comprise engineering fillers such as talc, carbon nanomaterial, glass fiber, and carbon fiber.[9–12]

Coffee, one of the most popular and established beverages, is prepared with roasted coffee beans. Approximately, 6,600,000 tons of coffee grounds (CG) are produced annually worldwide, but a great majority of the amount is simply discarded.[13,14] It is reported that coffee grounds comprise a large number of organic compounds such as fatty acids, lignin, cellulose, hemicellulose, and so on. As a result, many attempts have been made to use the coffee waste as a valuable bioresource.[15–17] While some of the coffee waste is reused as compost, animal feed, sugar source, metal ion sorbent, and biodiesel source, the development of more robust strategies and techniques for converting such coffee waste into a new resource material remains a major challenge.[18–20] From an environmental perspective, reutilizing the waste could lead to the reduction of environmental burdens such as the decrease in carbon dioxide.

In general, a nanocomposite, a multiphase solid material filled with nanosized particles, shows remarkably superior mechanical properties due to the exceptionally high surface to volume ratio of incorporated fillers compared to that of conventional composites.[21] Furthermore, such a high surface/volume ratio enables a reduction in the amount of fillers needed for the required physical features of the composites. For example, the addition of carbon nanotubes of as little as 1 wt % can lead to striking improvements in various properties such as mechanical, electrical, thermal, and dielectric properties.[22,23] However, natural reinforcing agents, such as coffee wastes, minerals, and cellulose fibers, originally have micron size fillers since the fillers are not fragmented into every single piece.[24,25] For instance, while composites filled with coffee grounds, such as the surface products, are commercially available, particle size of the coffee needs to be reduced to a submicron level. In this sense, embodying the size effect of nanofillers in the green composites is crucial for replacing manufactured fine fillers-based composites and for expanding their application areas toward optics, electronics, and automobiles. To the best of our knowledge, this is the first report that addresses the physical properties of composites incorporated with nanosized coffee grounds.

In the current study, we prepared natural nanoparticles reinforced composites and films. Coffee wastes were used as a

Additional Supporting Information may be found in the online version of this article.

Table I. Elemental Composition of Exhausted Coffee Ground and Carbon Black

Element	Proportion (%)	
	Coffee ground	Carbon black[26]
C	33.58	74.3
H	8.2	1.9
N	1.36	-
O	39.34	19.2

nanofiller, and PVA was used as a matrix. For comparison, carbon black-filled composites were also prepared. The size of the fillers was controlled and analyzed. The deodorant performance, mechanical, and optical characteristics of specimens were evaluated. In addition, a morphological observation was conducted to identify the dispersion state of the fillers.

EXPERIMENTAL

PVA was purchased from Sigma-Aldrich (363146, Mw 85,000–124,000), and carbon blacks (CB) were supplied by Orion Engineered Carbons (HB 20B BDS). The coffee powders were employed as reinforcing fillers, and CB was selected for comparison. Used coffee grounds were obtained locally and ball-milled. First, the coffee waste was extracted several times with hot water and then dispersed into distilled water. The solution was filtered using a glass filter with a mesh size of 700 nm. The filtered solution was then dried, and the resulting coffee grounds were weighted. PVA was dissolved in distilled water at 60°C, and the prepared fillers were distributed into the solution with a stirring mixer. The composite films were then cast with varying weight percentages of fillers (i.e., 1 wt %, 2 wt %, and 3 wt %). In addition, highly particles filled PVA composites (50 wt %) were prepared for a deodorization test.

In this study, constituents of the used coffee grounds were investigated using an elemental analyzer (Thermofinnigan, EA1110 and EA1108). Prior to the test, the samples were completely oven-dried. The deodorization performance of composite specimens was evaluated through a deodorizing experiment. About 3 L of ammonia gas was collected into a 5-L gas bag, and the concentration of ammonia was monitored. The initial gas concentration of ammonia was 100 ppm. After two hours, the following deodorization performance was evaluated: deodorization performance $(\%) = (C_b - C_s)/C_b \times 100$, where C_b denotes the gas concentration of blank, and C_s refers to the gas concentration under specimen existence. For the experiment, the applied temperature and humidity were 30°C and 40%, respectively.

Table II. Deodorization Performance of The Specimens Prepared in This Study

Sample	Deodorization (%)
PVA/Coffee	98.9
PVA/CB	89.5
PVA	45.4

The size distributions of coffee grounds and CBs were analyzed using a Nanotrac (Microtrac,) light scattering instrument. Red and blue light wavelengths were employed, and volume-weighted size distribution ($q3$) was obtained based on the Mie scattering theory.

Tensile tests were conducted at room temperature using a universal testing machine (Instron, 5584). The crosshead speed was set to 5 mm/min. In each case, at least five measurements were carried out for repeatability. The dimensions of specimens were 1.5 × 5 cm^2. For morphological observation, the specimens were fractured in a liquid nitrogen environment. The fracture surface of tensile specimens was characterized morphologically using scanning electron microscopy (JEOL, JSM-5410LV). All specimens were coated with gold using an ion sputter coater (JEOL, JFC-1100E). Transmittance measurements were carried out using a UV-visible spectrometer (PerkinElmer, Lambda 1050).

RESULTS AND DISCUSSION

Elemental analysis of the coffee ground and carbon black used in this study is demonstrated in Table I. For the coffee ground, the four elements, C, H, N, and O were mainly detected, and their elemental compositions were 33.58, 8.2, 1.36, and 39.34, respectively. Compared with the results in the literature,[16] the specimen showed relatively low carbon content. Since carbon

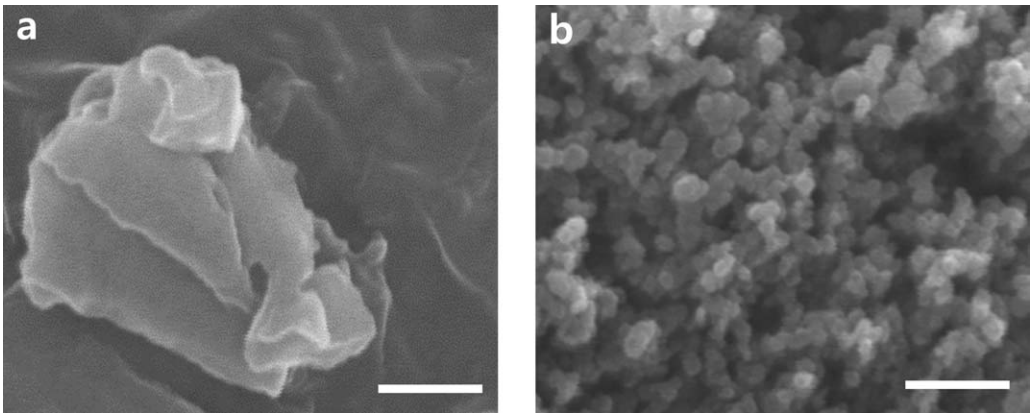

Figure 1. FE-SEM images: (a) coffee ground and (b) carbon black. The scale bars indicate 400 nm.

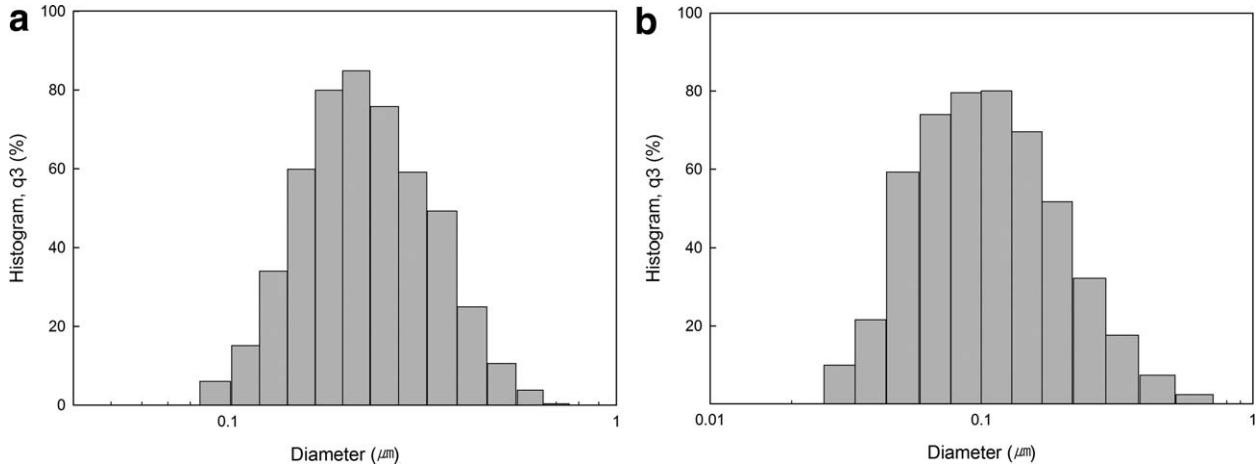

Figure 2. Particle size distribution: (a) coffee grounds and (b) carbon blacks.

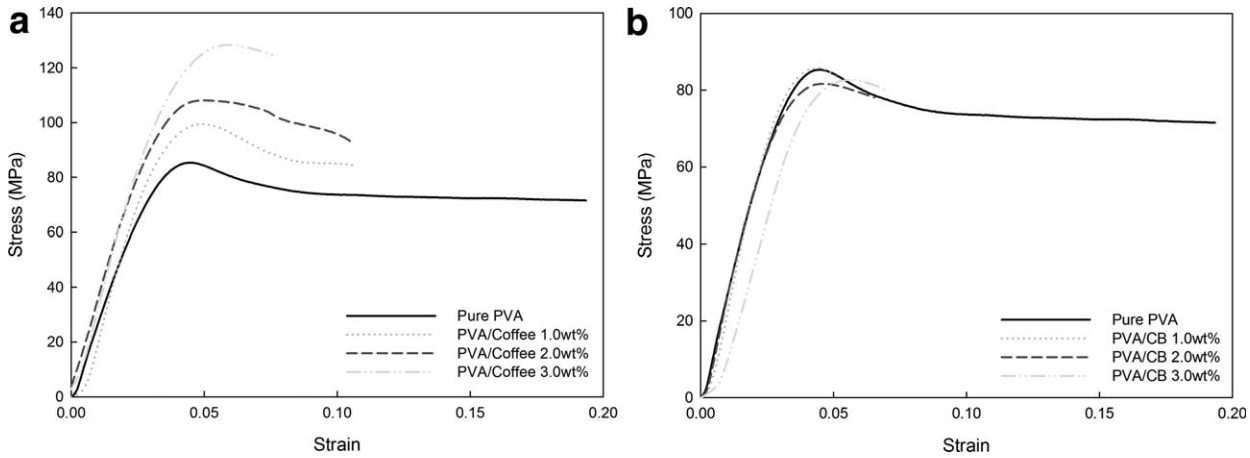

Figure 3. Results of tensile tests for (a) coffee grounds and (b) carbon blacks reinforced composites.

black is one of the most popular fillers, we adopted it for comparison with the coffee ground. Figure 1 shows FE-SEM mages of the coffee ground and carbon black used in this study. The images revealed that the coffee ground and CB had less than 1 μm and 100 nm, respectively. Table II shows the results of deodorization tests for the PVA/coffee and PVA/CB composites. The PVA/coffee specimen is found to have the highest deodorization performance.

Figure 2a presents the particle size distribution of the used coffee grounds prepared via ball-milling and filtering. These results indicate the volume-weighted size distribution, $q3$. The average diameter of the coffee grounds was 240 nm, which is a fairly

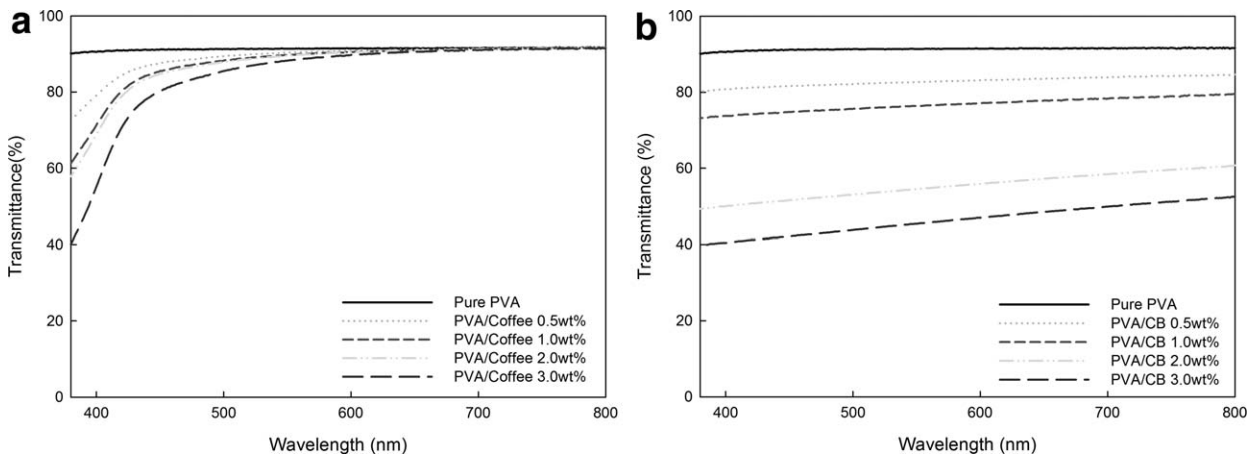

Figure 4. Transmittance behavior of (a) coffee grounds and (b) carbon blacks reinforced composites.

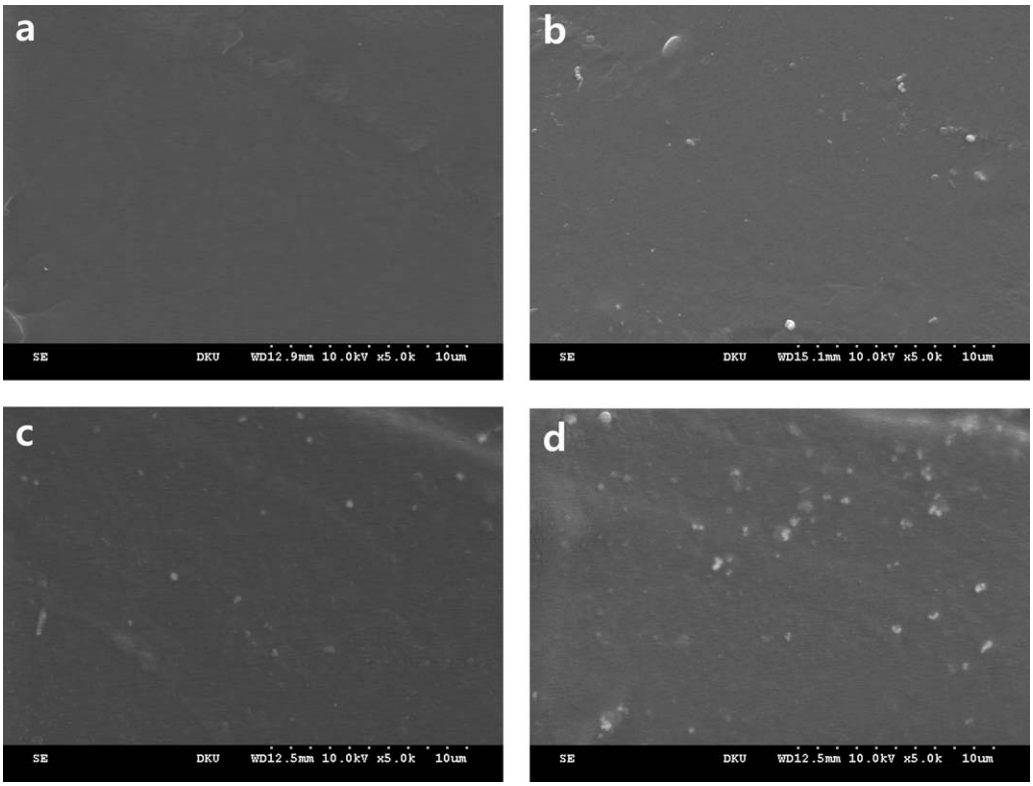

Figure 5. FE-SEM images of the specimens prepared: (a) pure PVA, (b) PVA/Coffee 1 wt %, (c) PVA/Coffee 2 wt %, and PVA/Coffee 3 wt %.

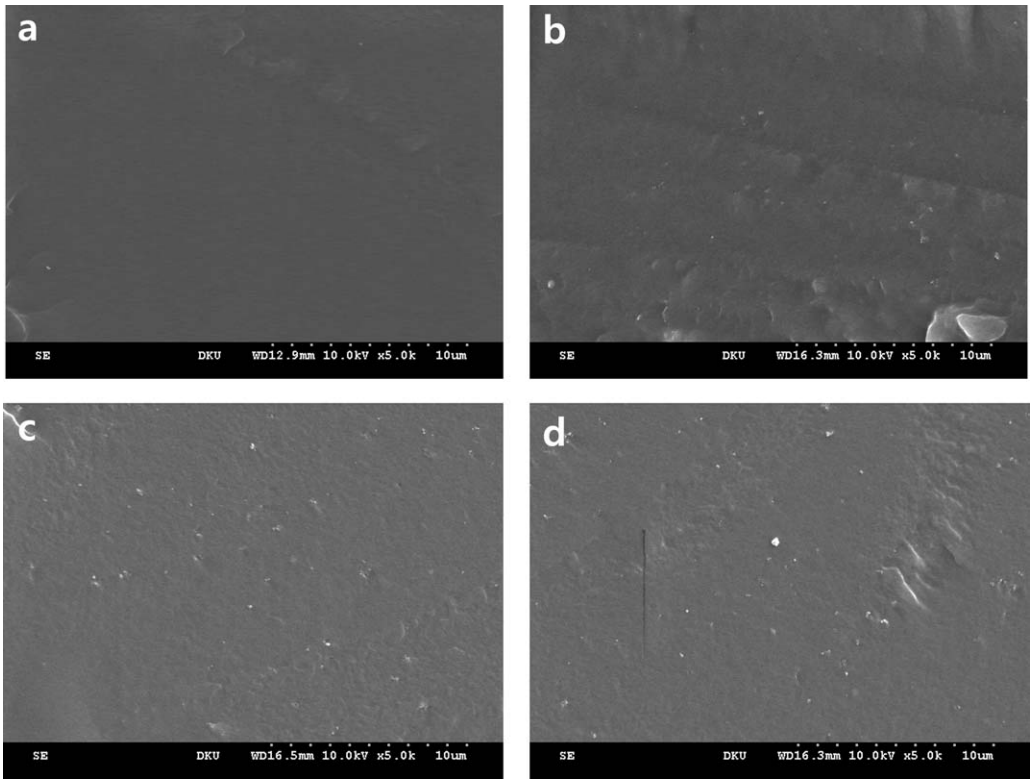

Figure 6. FE-SEM images of the specimens prepared: (a) pure PVA, (b) PVA/CB 1 wt %, (c) PVA/CB 2 wt %, and PVA/CB 3 wt %.

small sized natural filler. The particle size distribution of CB is shown in Figure 2b. Its average particle size was 110 nm. It is shown that the coffee grounds have broader particle size distribution than CB, which indicates that the natural fillers have lower uniformity in size.

Figure 3 shows the results of tensile tests carried out in this study. In PVA/coffee nanocomposites, as the weight fraction of fillers increases, the tensile strength and Young's modulus increase significantly. In particular, the increase in the strength is meaningful enough to infer the good dispersion state of nanoparticles in the composites. However, the addition of coffee grounds leads to a decrease in the elongation at break, which is a typical result of conventional composite materials. It is found that there is no significant distinction between the mechanical properties of PVA/CB nanocomposites demonstrated in Figure 3b, depending on the weight fraction of the filler. More results for the mechanical tests are presented in Supporting Information.

Since the coffee grounds naturally have hydrophilic characteristics, they are compatible with hydrophilic polymers such as PVA. Furthermore, considering the result of elemental composition presented in Table I, the coffee ground contains larger oxygen and nitrogen than the CB, which can lead to the hydrogen bonding between reinforcing agents and polymer matrix. These might be the main reason why the coffee ground-reinforced composites provide better mechanical behaviors than the CB-reinforced composites.

Figure 4 presents the transmittance behaviors of the composite films. It is found that the PVA/coffee nanocomposites provide very different optical features from the PVA/CB nanocomposites. Even if the PVA/coffee and PVA/CB nanocomposites showed decreasing transmittances with increasing weight fraction of the filler, the former samples show quite good transmittance, especially in the high wavelength regime, even with a 3% filler weight fraction. From this, we infer that the PVA/coffee nanocomposites have better dispersion of particles in the composites than the PVA/CB nanocomposites. In addition, the PVA/coffee nanocomposites show a larger dependence on the wavelength. On the other hand, since incident light with a long wavelength can penetrate a material, the resulting transmittance generally increases with respect to wavelength.

Figure 5 presents FE-SEM images of the fracture surface for the PVA/coffee nanocomposites. As the content of fillers increases, more objects are observed. Considering the average particle size of coffee grounds, the detected objects appear to be aggregated particles. In other words, while the PVA/coffee nanocomposites have good dispersion of particles at a low-weight fraction of reinforcing agents, the higher filler content yields greater aggregation of the fillers in the composite. Furthermore, the size of the coffee ground particles is larger than that of the CB particles. In the current study, the PVA/CB nanocomposites are a control sample for the PVA/coffee nanocomposites. Surprisingly, no significant distinction is observed between the FE-SEM images shown in Figure 6. This implies that the CB particles are dispersed most probably at the nanoscale level even if they do not have a sufficiently strong interfacial adhesion with the matrix. As a consequence, the mechanical properties of the PVA/CB nanocomposites are inferior to those of the PVA/coffee nanocomposites. Overall, this study is expected to show a promising potential and corresponding strategy to employ coffee grounds as a possible reinforcing agent in the composites.

CONCLUSIONS

In this study, we introduced used coffee grounds as a nanosize filler for fabricating polymer nanocomposites. The coffee grounds were ball-milled and filtered, and their particle distribution was analyzed. For comparison, carbon black-filled nanocomposites were also fabricated, revealing that the PVA/coffee nanocomposites had better deodorizing, mechanical, and optical behavior than the PVA/coffee nanocomposites. The coffee grounds prepared had larger average particle size and a broader spectrum of particle size. The PVA/coffee composites give significantly improved mechanical features including tensile strength and Young's modulus compared with the PVA/CB composites. In addition, the microstructure of both nanocomposites was observed from morphological analysis.

ACKNOWLEDGMENTS

This work was supported by the research fund of Dankook University in 2014.

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