Development of Wood-Substitute Composites from FGD Sulfite-Rich Scrubber Material and Waste Plastic Bottles While Taming Potential Mercury Reemission

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ABSTRACT

Generally two types of scrubber materials are produced, depending upon the scrubber technology used, by coal burning power plants during wet scrubbing of SO_2 from the flue gases. These are classified as flue gas desulfurization (FGD) sulfate-rich and FGD sulfite-rich scrubber materials. While the sulfate-rich scrubber material has found large-scale application in the manufacturing of wallboard products, the utilization of about 16 million tons of sulfite-rich scrubber material produced annually has had very limited success. With a view to alleviate the environmental and monetary concerns associated with sulfite-rich scrubber material disposal, we have been attempting to develop value-added products which would consume large quantities of scrubber material while generating viable marketable products. In this paper, we describe our results on the development of wood-substitute composites from sulfite-rich scrubber material and high density polyethylene (HDPE). Because the success of our materials would not only depend on the technical merit of the final product but also equally on the cost of the composites, we focused on developing our composites from waste plastic bottles. The DSC measurements at $30^oC<T<200^oC$ indicated the waste plastic melted at 124^oC, and the melting transition was unaffected when scrubber material was incorporated into our composites. Because the fabrication temperature was $T > 125^oC$, we mitigated the potential reemission of mercury from the scrubber material by developing our products at moderate pressures. The success of our products was ascertained by undertaking SEM, DSC, dynamic mechanical analyzer (DMA), and flexural strength measurements.

INTRODUCTION

Coal combustion byproducts (CCB), generated by coal-burning power plants, provide millions of tons of underutilized material each year.[1-4] Over 100 million tons of CCBs are produced every year in the USA alone, and only about 30 percent are being utilized.[2] While the FGD gypsum generated during flue gas scrubbing is used by the wallboard

manufactures as well as for agricultural and cement purposes, there is currently almost no use for the sulfite rich FGD scrubber material. Millions of tons of sulfite rich FGD scrubber material are land filled each year.

Unique crystalline structure of sulfite rich FGD scrubber material, however, can be exploited to develop structural composites, e.g., artificial wood. Traditionally, the engineered wood composites are molded from a thermoplastic polymer, such as polypropylene,[5,6] PVC,[7,8] or polyethylene[9-11] and wood fillers. However, to reduce costs, the fillers such as nanoclay[12] and even sand[13] have been successfully incorporated in various polymer matrices. While the wood fillers, such as wood pulp, wood chips, or other cellulose-based fibers provide a wood-like structure to the composite, additional additives may provide different desirable properties. For example, the compressive strength of the material was improved by 50% after mixing fly ash particles with the post consumer polyethylene terephthalate (PET) polymer.[14]

There are abundant amounts of wasted thermoplastics, generated mostly by consumers, from food packaging. Polymers such as PET, HDPE, and LDPE are commonly used to package various fluid and food items. These waste thermoplastics can serve as a matrix for wood-substitute composites. Most of the milk currently sold at stores in the United States is packaged in HDPE bottles, which we used for this study as our polymer matrix. HDPE also showed favorable results in the other studies, when it was used in conjunction with such fillers as sand[12] and nanoclay[13]. The strength of the pure HDPE matrix is much higher than the typical strength of wood-plastic composites, which are typically accepted to be in the range of 10 MPa – 18 MPa[15]. Mixing and processing of such thermoplastic polymer with the sulfite-rich scrubber in order to form a wood substitute composite, however, will require elevated temperatures and pressures. This can be a potential problem, as the mercury captured in the scrubber material during the FGD process may be released as those parameters are varied. Therefore, in this study, we also examined how the processing conditions of our composites affected the mercury behavior in FGD scrubber material.

EXPERIMENTAL PROCEDURES

Sulfite-rich scrubber material was obtained from one of the Illinois bituminous coal burning power plants. The material was air dried for at least 24 hours prior to analysis and composite fabrication. Agricultural crop material was used as a fiber reinforcement in some of our composites. Crop material was first ground with a large scale hammer mill to obtain a particle size of ~ 2 to 3 cm in length, and then it was further ground in a cyclone mill to obtain micron-sized particles. Recycled HDPE polymer was obtained from post-consumer milk containers. The plastic bottles were initially shredded using a cutting mill fitted with a screen with 8 mm mesh size. The shredded milk bottles are shown in Fig. 1. Following that, the particles were further reduced with the help of a cyclone grinding mill, which resulted in HDPE beads with the average size of about 100 μm in diameter.

Figure 1. Picture showing the shredded material obtained from the milk bottles.

The melting transition of recycled HDPE as well as the composite mixtures was evaluated using a Perkin-Elmer differential scanning calorimeter (DSC), i.e., DSC7. The DSC measurements were performed at $30^{\circ}C < T < 200^{\circ}C$ with a constant heating rate of $20^{\circ}C/min$. Based on the DSC results, the composites were fabricated via compression molding at $T \geq 170^{\circ}C$. Raw materials were thoroughly mixed with a motorized high shear mixer and were molded in the 50 mm diameter high pressure stainless steel die. A 30 ton automated hydraulic press was used to formulate our composites at 1.2 MPa. A series of composites were prepared by changing the HDPE-to-additive ratio.

Flexural strength was determined according to ASTM D790 standard method, which is a maximum sustained stress by the sample at break, and is calculated using the following equation:

$$\sigma = \frac{3Fl}{2bh^2},$$

where F, l, b, and h are the load at failure, span length, width, and thickness, respectively. Strain values were determined from the displacement data:

$$r = \frac{6Dd}{L^2},$$

where D is the mid-span deflection, d is the depth of beam, and L is the support span. Load and displacement data were used to generate stress vs. strain curves.

Mercury analysis of sulfite-rich scrubber was performed on the air-dried material. In a first experiment, small samples of FGD scrubber material were oven heated from room temperature to 250°C in 25°C increments after which the samples were cooled to room temperature and were subjected to Hg analysis. Mercury concentration in the material was determined using a Milestone DMA80 system. In the second experiment, a number of scrubber samples were hot pressed at 3 MPa in the same stainless steel die that was used for the composite fabrication. This effectively simulated the conditions under which our composites were made. The samples were pressed at the following temperatures: 140°C, 155°C, 170°C, 185°C, 200°C, 215°C, 230°C, and 245°C. After hot-pressing, the scrubber materials were subjected to mercury analysis.
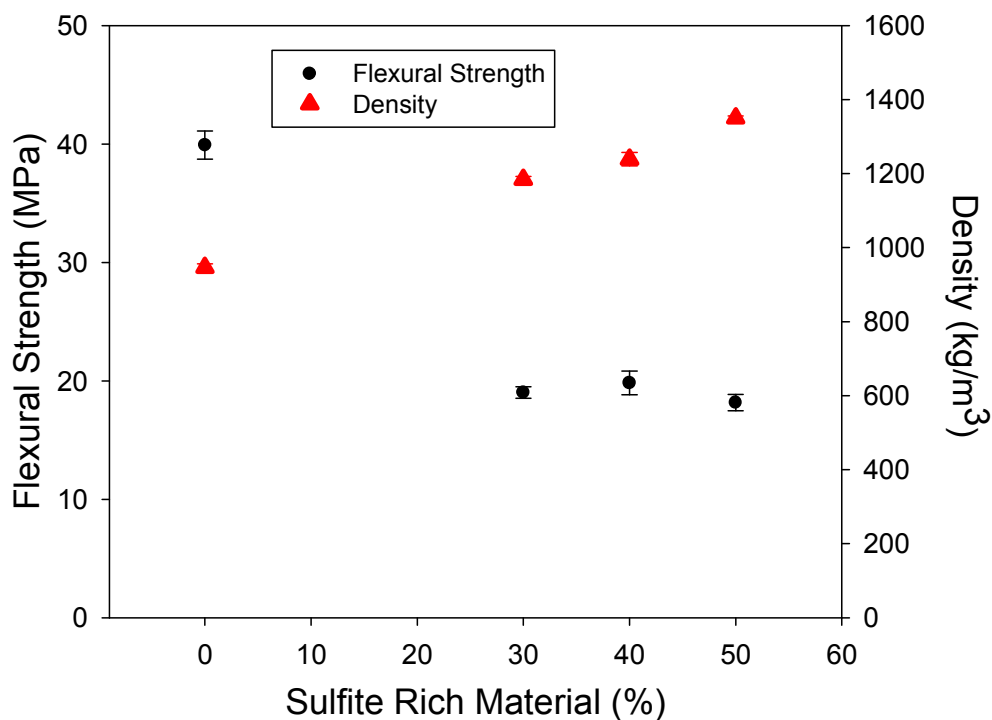
RESULTS AND DISCUSSION

The melting temperature of HDPE polymer, obtained from shredding waste milk bottles, was determined with the help of DSC. In the 65°C < T < 160°C temperature range, a single endothermic peak was observed with an onset temperature of 124°C. This peak is associated with the melting transition of HDPE. Because both sulfite-rich scrubber material and cellulosic material, obtained from agricultural crops, have different thermal characteristics, it is important to understand whether the addition of these additives into HDPE would modify the polymer's melting behavior. Therefore, we recorded the DSC temperature scans of the composites fabricated from 30 wt% of FGD material, 30 wt% of cellulosic material, or 50 wt% of the FGD and cellulosic materials' mixture (mixed with a ratio of 4:1). The results are summarized in Table 1. The enthalpy, ΔH, associated with the melting transition of HDPE should remain invariant if no interaction occurs between the polymer and additives. As can be seen from Table 1, the observed ΔH of the composites made from scrubber material, cellulosic material, or a mixture of scrubber and cellulosic materials has a much reduced observed enthalpy. However, if HDPE is the only material which contributes to the observed endothermic peak, which is the case here, then the ΔH must be normalized according to the weight of HDPE in the composites. The normalized enthalpy of the melting transition was determined and is listed in Table 1. The normalized enthalpy shows variations in its values depending upon the additives. However, the observed variation in the normalized enthalpy is within the experimental uncertainty. Therefore, it is reasonable to argue that the addition of either scrubber material or cellulosic material does not affect the melting transition of HDPE. No significant shift in the melting transition temperature was observed which further indicates that our additives did not modify the melting transition of HDPE.

Even though the thermal characteristics of HDPE were not significantly altered with the addition of the FGD scrubber and cellulosic materials, the strength, the bulk density, and appearance of the composites were changed. Figure 2 shows how the flexural strength and the density of the composites changed as the sulfite-rich scrubber material was incorporated into the HDPE matrix. We observed a decrease in the flexural strength, and a slight increase in the bulk density values as the concentration of FGD material was increased. However, even with the 50% of material added, the strength values remained above those that are acceptable for engineered wood composites.

Table 1. DSC analysis of the HDPE melting transition for various HDPE, FGD scrubber material, and cellulosic material sample combinations.

Sample Composition (%)			Peak Values (°C)			Observed Enthalpy, {ΔH} (J/g)	Normalized Enthalpy, {ΔH} (J/g)
HDPE	Scrubber Material	Cellulosic Material	Onset	End	Peak		
100	0	0	124	138	133	235	235
70	30	0	128	143	139	157	224
70	0	30	124	135	132	169	241
50	40	10	124	135	131	120	240

Figure 2. Flexural strength and density changes in the composites as a function of FGD material content.

The addition of small amounts of crop cellulosic fibers, however, should not only lower the density of composites but should also alter the physical appearance of the composites to give them a more wood-like appearance. It should be noticed from Figure 3 that the modulus of elasticity was significantly affected by the addition of both FGD scrubber material and cellulosic crop fibers. Figure 3a shows the stress versus strain curves for the pure HDPE sample. A large strain before the break values indicated that the material is very elastic and not susceptible to breaking until very large

strain values are reached. Figure 3b shows how this was altered with the addition of FGD scrubber material.
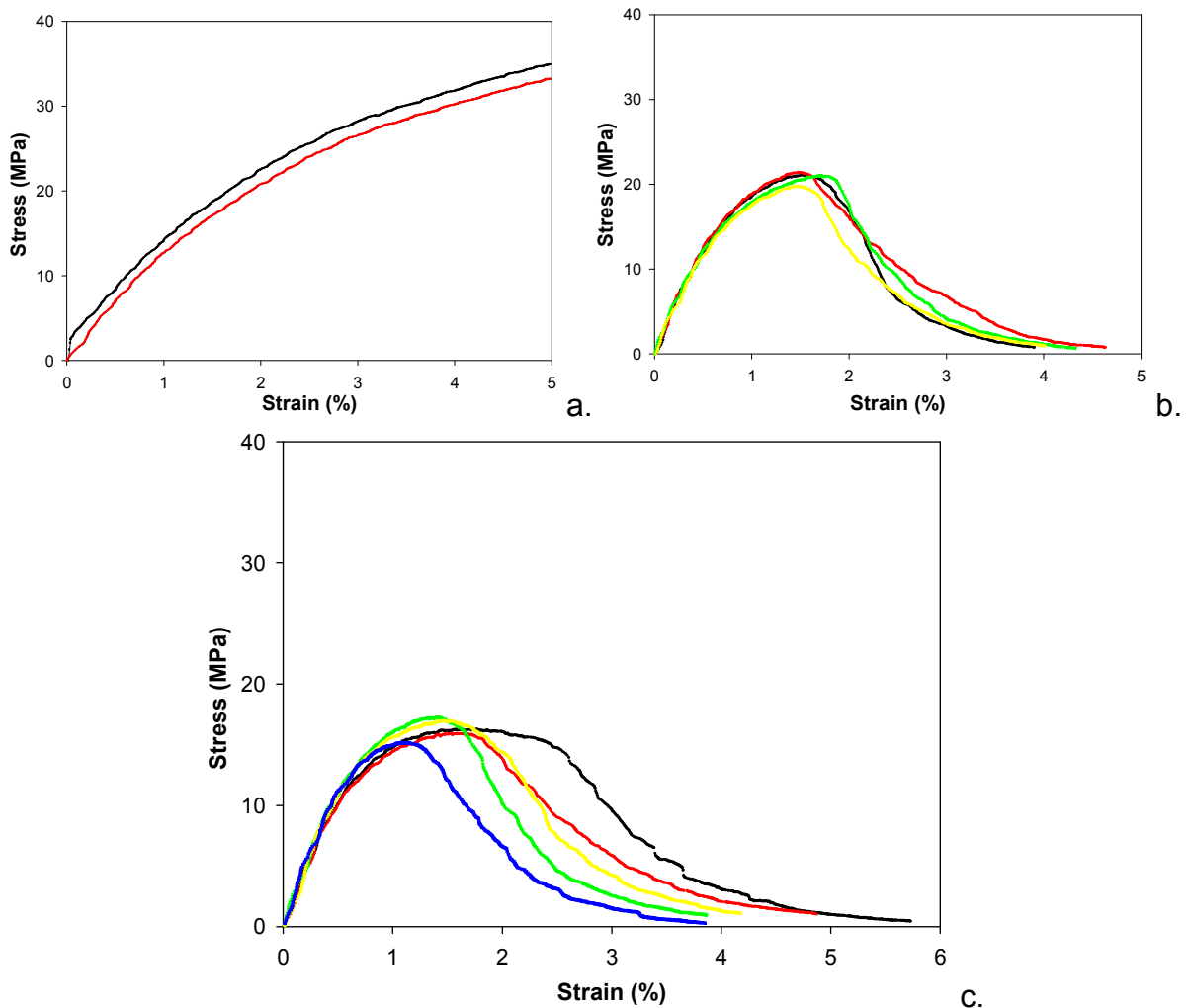
Figure 3. Stress versus strain behavior of a) 100% HDPE, b) HDPE reinforced with 30% of sulfite-rich scrubber material, and c) composite reinforced with 40% of FGD scrubber material and 10% of cellulosic fiber.

The modulus of elasticity was increased with the addition of FGD material into HDPE matrix. This is indicated by the steeper slope as compared to the pure polymer data. After the incorporation of sulfite crystallites and cellulosic fibers, the stress vs. strain behavior more closely resembles that of natural wood. While material does fail at higher strain values, the failure is gradual. Such stress versus strain behavior indicates that our wood-substitute composites can be processed using regular woodworking equipment and can be used with the same hardware (such as screws or nails) just like natural wood. Calcium sulfite crystals that comprise the FGD sulfite-rich scrubber material are relatively soft and will not damage the composite fabrication equipment. This is another advantage of adding this material to the wood-substitute composites.

In the next step, we evaluated how the mercury concentrations in the sulfite-rich FGD material were affected by the elevated temperatures and pressures that are required for our composites. Figure 4a shows that if FGD scrubber material is heated without applying any pressure, the mercury starts to escape from the sample at around 150°C. About 30% of the mercury captured in the scrubber material was re-emitted by 250°C. Because our composites are fabricated at temperatures ≥ 170°C, this could be a potential problem. However, our pressure experiments suggested that even very moderate pressures on the sample had a dramatic effect on the potential mercury re-emission at 150°C ≤ T ≤ 250°C. This can be clearly seen from Figure 4b.

a.

b.
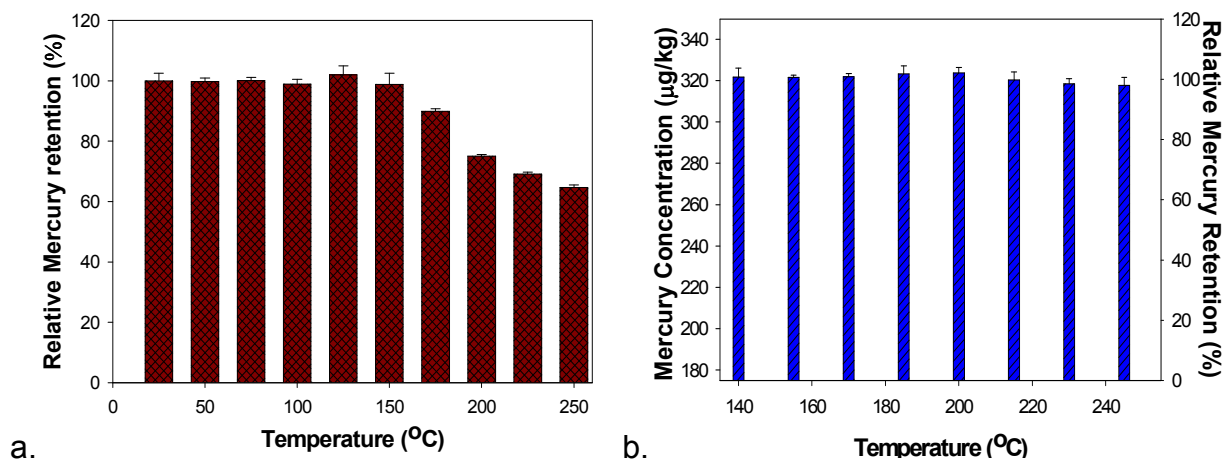
Figure 4. Mercury concentrations of the FGD material heated in the oven (a), and hot-pressed under 3 MPa (b).

SUMMARY AND CONCLUSIONS

Sulfite-rich scrubber material, generated during the FGD process, was successfully incorporated into recycled HDPE polymer matrix to fabricate wood-substitute composite materials. Composites were further enhanced with the addition of small amounts of natural fiber material. Thermal measurements indicated that the melting temperature of the polymer was not affected by the addition of FGD sulfite-rich scrubber material and/or cellulosic fibers. Flexural strengths of composites containing up to 50% of additives ranged between 15 MPa – 25 MPa, which is comparable to other engineered-wood composites. Stiffness of the material was increased with the addition of sulfite-rich scrubber material, and composites fabricated using these additives showed similar flexural behavior to that of natural wood. Mercury emission from the FGD scrubber material was found to be inhibited by elevated pressures.

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REFERENCES

[1] V. M. Malhotra, P. S. Valimbe, and M. Wright, Fuel, **81**, 235, 2002.

[2] Kalyoncu, R.S., "U.S. Geological Survey Minerals Yearbook", **2001**

[3] CARRC Topical Report, U. S. DOE (DE-FC26-98FT40321), April, 2003.

[4] A. D. Randolph, D. J. Kelly, and B. Keough, "Calcium Sulfite and Calcium Sulfate Crystallization. Volume 1.: Effect of Crystallizer Type on Gypsum Size Distribution", EPRI Report 1013-3, 1986.

[5] Danyadi, L., Renner, K., Szabo, Z., Nagy, G., Moczo, J., Pukanszky, B., *Polymers for Advanced Technologies* **17,** 967-974 (2006).

[6] Jayaraman, K., *Composites Science and Technology*, **63,** 367-374 (2003).

[7] Jana, S.C., Prieto, A., *Journal of Applied Polymer Science* **86,** 2159-2167 (2002).

[8] Pilarski, J.M., Matuana, L.M., *Journal of Vinyl and Additive Technology* **11(1),** 1-8 (2005).

[9] Li, T., Yan, N., *Composites: Part A* **38,** 1-12 (2007).

[10] Colom, X., Carrasco, F., Pages, P., Canavate, J., *Composites Science and Technology* **63,** 161-169 (2003).

[11] Mohanty, S., Verma, S.K., Nayak, S.K., *Composites Science and Technology* **66,** 538-547 (2006).

[12] Faruk, O., Matuana, L.M., *Composites Science and Technology* **68,** 2073-2077 (2003).

[13] Herrera-Franco, P., Valadez-Gonzalez, A., Cervantes-Uc, M., *Composites: Part B* **28B,** 331-343 (1997).

[14] Li, Y., White, D.J., Peyton, R.L., *Resources, Conservation and Recycling* **24(2),** 87-93 (1998).

[15] Klyosov, A.A., "Wood-Plastic Composites", Wiley-Interscience, Hoboken, New Jersey, **2007**