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The potential of paper mill sludge for wood–plastic composites

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ABSTRACT

Recent studies have demonstrated the potential of primary sludge (PS) as reinforcing fibers and secondary sludge (SS) as binder or co-binder in wood–plastic composites (WPC). A comparative study was conducted using paper mill sludge produced by three different pulping processes at two SS to PS ratios. The objectives were to determine the impact of PS and SS on the development of high density polyethylene (HDPE) WPC properties. Sludge produced by thermomechanical pulping (TMP), chemithermomechanical pulping (CTMP), and Kraft pulping were used at three different proportions (20%, 30%, and 40%) for composite manufacturing. The use of mixed sludge containing 30% SS resulted in lower tensile, flexural, and impact performance of the WPC compared to mixed sludge containing only 10% SS for the three pulping processes. Sludge type had a significant impact on the WPC physical and mechanical properties. Kraft sludge produced the best WPC properties, followed by CTMP and TMP sludge. Increasing the sludge proportion produced increasingly negative impacts on water absorption and thickness swelling, but improved the flexural and tensile properties.

1. Introduction

The pulp and paper industry requires large quantities of water to operate. The wastewater must then be treated to reduce the total suspended solid content and the oxygen demand prior to disposal (Gilbride and Fulthorpe, 2004). The sludge is the solid residue generated by the water treatment plant. Each ton of paper produces about 45 kg of dry sludge (Son et al., 2004). Sludge disposal can account for up to 60% of the total water treatment cost (Mahmood and Elliott, 2006). Certain fine particles that are mechanically removed from the wastewater are called primary sludge (PS). These suspended solids contain mostly cellulose, hemicelluloses, and lignin, as well as other possible residues such as bark and additives used as filler in paper production (Mahmood and Elliott, 2006; Chen et al., 2002). The remaining suspended solids are sent to a secondary treatment plant for bacterial digestion. The mixture of biosolids and the remaining suspended solids is called the secondary sludge (SS). The large numbers of bacteria in the SS make it difficult to dewater and dry, because a large portion of the water is trapped inside the living cells, and therefore tends to jellify (Mahmood and Elliott, 2006; Tchobanoglous et al., 2003; Mabee, 2001). Bacteria are made up of approximately 80% water and 20% dry material, of which 90% is organic and 10% inorganic. An approximate formula for the organic portion is $C_5H_7O_2N$ (Cheremisinoff, 1996). The nitrogen content in the simplified molecular structure is a particular feature of SS. When the SS is digested in the presence of oxygen, the aerobic process generates mainly heat, water (H_2O), and carbon dioxide (CO_2).

When a secondary treatment plant operates in the absence of oxygen, the digestion produces methane (CH_4) and carbon dioxide (CO_2). This anaerobic process considerably reduces the biomass produced by the digestion of suspended solids (Baudez, 2001). The mixture of PS and SS is called mixed sludge. Paper mills usually dispose of mixed sludge by burning and landfilling (Beauchamp et al., 2002). However, burning nitrate-rich paper mill sludge in industrial boilers has been criticized because it generates powerful greenhouse gases such as nitrate oxide (NOx) and provides low calorific value. In Canada, the public has begun complaining about land filling because of the unpleasant smell of the active bacterial culture in the sludge and the potential to produce elements that are toxic to fauna and flora (Pearson, 2005). Studies have recommended composting, ethanol production, and other thermal treatments such as pyrolysis, vitrification, and gasification for sludge disposal, but these alternatives are either economically unviable or liable to generate other sub-products that could be protested by environmentalists (Beauchamp et al., 2006; Mahmood and Elliott, 2006). Due to the very high volume of sludge worldwide, there is growing interest in either increasing agricultural use of sludge or processing sludge for use in producing other products (Chen et al., 2002). For example, Ou-Yang and Wu (2002) observed a 50% higher plant

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growth rate when composted paper mill sludge was added to peat as a container medium for seed germination. They also noted that the sludge application rate should be adapted according to the paper sludge composition, which varies across mills.

Recent studies (Geng et al., 2007; Migneault et al., 2010, 2011a,b) have assessed the potential of recycling paper mill sludge as filler and co-binder in medium density fiberboard manufacturing. Geng et al. (2007) reported that medium density fiberboards made with up to 20% primary and deinking sludge met the American National Standards Institute minimum requirements. Migneault et al. (2010) found that thermomechanical pulping (TMP) sludge was suitable for medium density fiberboards and met the minimum requirements using up to 25% sludge content with a secondary to primary sludge ratio up to 3:7. Medium density fiberboards made with sludge from chemico-thermomechanical pulping (CTMP) and Kraft pulping did not meet the American National Standards Institute minimum requirements. Soucy (2007) studied the mechanical properties of WPC made with pulp from three different processes and found that Kraft fibers made stiffer WPC compared to TMP fibers. Migneault et al. (2009) reported that increasing CTMP fiber length improved the mechanical properties of injected and extruded WPC. Injection molding and extrusion are the two most commonly used thermoplastic processing methods, and they dominate the plastic products market (Trotignon et al., 1996). Injection molding uses WPC pellets with a maximum of 40% wood content, whereas the extruded product can contain up to 60% wood content (Maine, 2007). In both processes temperatures in excess of temperatures are generally used 120 °C. At these temperatures all living cells are killed (Regnault, 1990). Since these processing methods kill all the microorganisms and pathogens in the sludge, they provide a promising alternative to sludge disposal.

World production of high-density polyethylene (HDPE) was 29.8 million metric tons in 2007. About 10–15% of the HDPE is converted into construction products. HDPE is increasingly replacing traditional materials such as wood, glass, concrete, and paper in the construction industry, but its use is limited by its dependence on oil prices (Borruso, 2008). WPC have been proposed as an environmental solution for replacing a large proportion of plastic products, and the demand for it is expected to grow worldwide (Merle-Lamout and Pannetier, 2012; Ismail and Bakar, 2005a). The most commonly used thermoplastic polymer for manufacturing WPC is polyethylene, followed by polyvinyl chloride and polypropylene.

PS has proven to be a good reinforcing fiber source due to its high fiber content, whereas SS is used more as an adhesive or co-binder due to its high protein content (Zerhouni et al., 2012). Other paper mill additives found in PS and SS, such as clay and calcium carbonate, are currently used as filler in the plastic industry, and should be suitable for traditional plastic processing. For example, polypropylene is usually filled with mica, talc, calcium carbonate, and glass fibers to lower the price and strengthen the properties. More recently, several natural fibers such as wood, cellulose, jute, and bamboo have been investigated due to their low price, low density, high stiffness, and low abrasion during processing compared to traditional mineral fillers (Qiao et al., 2004).

Several studies have discussed the potential of SS, bacteria, and biofilm as binder and co-binder in material fabrication. Vu et al. (2009) described the molecular structure of some extracellular polysaccharides found in the biofilm of certain microorganism structures. They showed that alphaproteobacteria produce polymeric cellulose with a beta 1,4 bond, such as in wood cellulose. Cellulose is produced primarily by bacteria of the genera Acetobacter, but also by the genera Agrobacterium, Pseudomonas, and Rhizobium. Gerardi (2006) found that approximately 20% of the bacteria in an activated sludge process constituted gram-negative cocci and rods. This 20% also included species of the genera Acetobacteria and Pseudomonas. Haag et al. (2006) showed that glues derived from extracellular polysaccharides are VOC free and form sufficiently strong bonds at low and moderate relative humidity, achieving shear strength comparable to that of commercial polyvinyl acetate-based adhesives. Zerhouni et al. (2012) obtained higher internal bond strength from handsheets made with a higher SS:PS ratio and dried at 180 °C. The higher bond strength was attributed to a higher number of hydrogen bonds within the handsheet under these conditions. Recently, Xing et al. (2013) made particleboard panels using SS and urea-formaldehyde resins. All their tested formulations met most American National Standards Institute minimum requirements with significantly lower formaldehyde emissions.

Only a few studies to date have examined the use of paper mill sludge as filler, co-binder, or reinforcing fibers in WPC. Son et al. (2001) studied the effect of extrusion temperature and sludge particle size on the properties of sludge-filled thermoplastic. They observed that increased particle size resulted in improved mechanical properties, which could be explained by the high cellulosic content of the PS and the smaller particle size (fines) of the organic content in the SS. They also found improved dimensional stability with higher extrusion temperature and lower water absorption. Ismail and Bakar (2005a,b, 2006) studied the properties of a thermoplastic blend of polypropylene filled with paper mill sludge. Their results showed several similarities with conventional WCPs made with thermoplastics processes: (1) increased sludge content, water sorption, and Young modulus but reduced tensile strength and strain; (2) surface modifications such as sludge esterification and acetylation also improved most of the composites' physical and mechanical properties; and (3) the addition of sludge to a thermoplastic polymer reduced the cristallinity but did not affect the melting temperature.

The use of sludge for WPC application would benefit both the industry, by providing a new fiber source, and the environment, by reusing an industrial waste for high value products. However, the chemical composition of sludge varies depending on the pulping process, the sludge treatment processes and the chemical composition varies among SS to PS ratios. Consequently, using sludge in the manufacture of WPC is challenging and might lead to variable WPC properties. The sludge chemical composition is expected to play a major role in the WPC properties development. Thus, using sludge samples from different processes and at different SS to PS ratios is associated with important variations in both morphological and chemical properties of the sludge material used in WPC manufacturing. Thus, this study compares the physical and mechanical properties of HDPE WPC made with sludge from three different pulping processes and two SS to PS ratios. The objectives were to (1) investigate the role of PS and SS in the development of the WPC properties; and (2) to study the effect of the sludge's chemical composition on WPC properties.

2. Material and methods

2.1. Sludge sample preparation

The raw material was obtained from three paper mills, using softwood chips from different pulping processes. The TMP sludge is from White Birch Division of Stradacona Inc. in Quebec City, the CTMP sludge is from Lac-Saint-Jean Abitibi-Bowater in Dolbeau-Mistassini, and the Kraft sludge is from SFK Pulp in St-Félicien, all in Canada. All mills use chips from North American black spruce (*Picea Mariana*).

Mixed sludge samples were collected from the sludge presses at the dewatering facilities of the three mills at two different SS to PS ratios: SS:PS = 1:9 and 3:7. The SS:PS ratio vary across mills and within mills over time, but these are typical values. PS and SS were