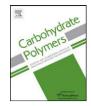
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Effects of extractives on some properties of bagasse/high density polypropylene composite

Shabnam Sheshmani*

Department of Chemistry, Shahr-e-Rey Branch, Islamic Azad University, P.O. Box 18155-144, Tehran, Iran

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ABSTRACT

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Keywords: Lignocellulosic filler Extractives Water uptake Compatibility In this study, the effects of two variable parameters, namely the extractives and filler loading level, on the physical properties of composites were examined. Composites based on high density polyethylene (HDPE), bagasse flour (BF) as filler were made by injection molding. In order to increase the interphase adhesion, maleic anhydride grafted polyethylene (MAPE) was added as a coupling agent to all the composites studied. Three different solvents, ethanol-benzene, 1% NaOH and hot-water, were used to remove extractives. Physical properties, namely, water absorption (WA) and thickness swelling (TS) were investigated for a long period. At same filler loading, composites made with extracted bagasse had higher WA and TS values. In addition, the TS of samples showed a similar pattern to the water uptake data. The difference in WA between extracted and unextracted composites is due to blocking of –OH groups by extractives. The results also showed that as the BF content was increased, significant increase in WA and TS occurred. Statistical analysis confirmed that the effects of both variables and their interactions on the WA and TS properties were significant at 1% confidence level.

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1. Introduction

In recent years, lignocellulosic materials are used as filler or reinforcement for wood plastic composites (WPCs) in various applications such as building and automotive industries (Sheshmani, Ashori, & Farhani, 2012). Their biodegradability, renewability, low cost, UV resistance, and machining properties are some of the advantages of these composites compared to plastic. However, one of the disadvantages of WPCs is its hydrophilic nature compared to pure polymers. The hydrophilic nature of natural fibers contributed by the hydroxyl groups cause increased water absorption by WPCs (Shinoj, Panigrahi, & Visvanathan, 2010). The absorption of water, through the formation of hydrogen bonding, takes place in the cell wall of lignocellulosic materials, and it subsequently swells the cell wall. This phenomenon is reflected in changes in the dimensions of the composites (Kiani, Ashori, & Mozaffari, 2011). The application of WPCs in the automotive, construction, marine, and consumer goods necessitates exposure to water or high-moisture environments. Water absorption may adversely affect the physical properties of composites and also the fiber matrix interactions and may result in changes in the bulk properties, such as the dimensional stability and mechanical and electrical properties (Sheshmani et al., 2012). However, there are treatment technologies to improve the hydrophobicity of lignocellulosic fibers. Treatments used to

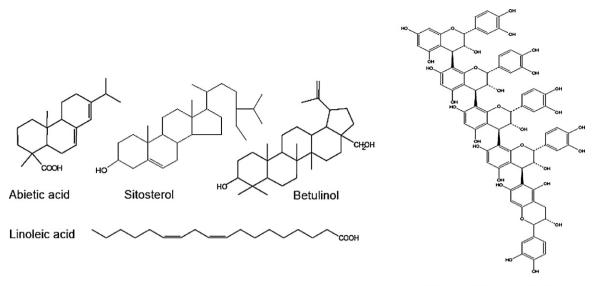
E-mail address: shabnam_sheshmani@yahoo.com

improve fiber–matrix adhesion include chemical modification of the lignocellulosic biomass (anhydrides, epoxies, isocyanates, etc.), grafting of polymers onto the lignocellulosic biomass, and use of compatibilizers and coupling agents (Ashori, Sheshmani, & Farhani, 2013).

All species of wood and non-wood plant tissues contain small to moderate quantities of chemical substances in addition to the macromolecules of cellulose, hemicelluloses, and lignin. To distinguish them from the major cell wall components, these additional materials are known as the extractive (nonstructural) components, or simply "extractives". Extractives content in most temperate and tropical wood species are 4-10% and 20% of the dry weight, respectively. Although extractives contribute merely a few percent to the entire wood composition, they have significant influence on its properties, such as mechanical strength or color and the quality of wood, which can be affected by the amount and type of these extractives (Sjöström, 1993). Chemically, extractives consist of those components that are soluble in neutral solvents, either organic solvents, or water (TAPPI, 2002). A wide range of different substances is included under the extractive heading: flavonoids, lignans, stilbenes, tannins, inorganic salts, fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, terpenes, starch, glycosides, saponins and essential oils (Fig. 1). Extractives occupy certain morphological sites in the wood structure. No single organic solvent is capable of removing all extractives, however mixtures of solvents have been most commonly used method over the past 50 years. The ethanol-benzene extractable content consists of waxes,

^{*} Tel.: +98 21 5522 9200; fax: +98 21 5522 9297.

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Condensed tannin (5 x catechin)

Fig. 1. Some extractives components of lignocellulosic materials.

fats, resins, phytosterols, low-molecular-weight carbohydrates, salts, and even some water-soluble substances. Hot aqueous alkali extracts low-molecular-weight carbohydrates consisting mainly of hemicellulose and degraded cellulose. Hot water also removes a part of non-lignocellulosic components of wood, such as inorganic compounds, tannins, gums, sugars, and coloring matter present in wood and pulp (Sheshmani et al., 2012).

As mentioned earlier, extractives are hydrophobic substances with low molecular weights. In the preparation of WPCs, natural fiber is thoroughly mixed with a thermoplastic at high temperatures, e.g. $170 \,^{\circ}$ C. At such high temperatures, extractives may tend to migrate to the wood flour surface, thus accumulating in the wood-plastic interphase (Shebani, van Reenena, & Meincken, 2009).

The main objective of this study is to investigate the effects of the extractives on some physical properties of bagasse/high density polyethylene (HDPE) composites. In order to gain a full understanding of these effects, hot water (HW), ethanol-benzene (EB) and 1% alkali solution (AL) extractives, respectively, were removed from bagasse before the preparation of the WPCs. The physical properties, namely, water uptake and dimensional stability of WPCs produced with extracted bagasse were determined and compared to the properties of composites with unextracted samples. In addition, the influences of filler loading level and different mixing formulations on water resistance and dimensional stability of the composites were studied.

2. Materials and methods

2.1. Materials

Lignocellulosic material: bagasse stalks, a by-product from the sugar industry, were obtained from Khuzestan Cultivation and Industry Co., Iran. The bagasse stalks were depithed and cut to 2–3 cm in length by hand. They were then washed, air-dried and screened through a series of screens to remove dirt. The depithed bagasse stalks were ground with a Thomas-Wiley miller to fine powder of 40-mesh size, and then oven-dried and stored in sealed plastic bags before processing.

Polymer matrix: virgin high density polyethylene (HDPE), with trade name of HD5620EA, an injection molding grade was supplied by Arak Petrochemical Co. (Iran), in the form of pellets. Some

Table 1 Physical and mochanic

Physical and mechanical properties of used HDPE.

Properties	Test method	Unit	Value
MFI @ 190 °C, 2.16 kg	ASTM D1238	g/10 min	20
Density	ASTM D1505	g/cm ³	0.956
Vicat softening point	ASTM D1525	°C	124
Tensile strength	ASTM D638	MPa	22
Tensile modulus	ASTM D638	MPa	900
Elongation at break	ASTM D638	%	700
Flexural modulus	ASTM D790	MPa	1000
Hardness shore D	ASTM D2240	-	66
Notched impact strength	ASTM D256	kJ/m ²	4

important physical and mechanical properties of the used polymer are presented in Table 1.

Coupling agent: maleic anhydride grafted polyethylene (MAPE), in the form of powder (grade PPG-101) with a density of 0.92 g/cm^3 and a melting flow index of 5 g/10 min, was obtained from Kimia Javid Sepahan Co., Iran.

2.2. Extractives determination

The extractives of the samples were determined gravimetrically following the appropriate TAPPI Test Methods (2002). The screened samples were extracted with BE (T 204 cm-97), hot 1% AL solubility (T 212 om-98) and HW solubility (T 207 cm-99), individually. In addition, cellulose (T 203 cm-99) and Klason lignin (T 222 om-02) were determined (Table 2). Four replicates were done for each experiment.

Table 2
Chemical composition of used bagasse.

Chemical	Value (%)
Cellulose	54.5
Hemicelluloses	17.1
Lignin	19.7
Extractives	
Hot-water	9.0
1% NaOH	7.6
Ethanol-benzene	13.1
Ash	1.5

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