Carbohydrate Polymers 94 (2013) 416–419

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

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ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form
20 December 2012
Accepted 13 January 2013
Available online 29 January 2013

Keywords:
Lignocellulosic filler
Extractives
Water uptake
Compatibility

ABSTRACT

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 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,

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0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.01.067

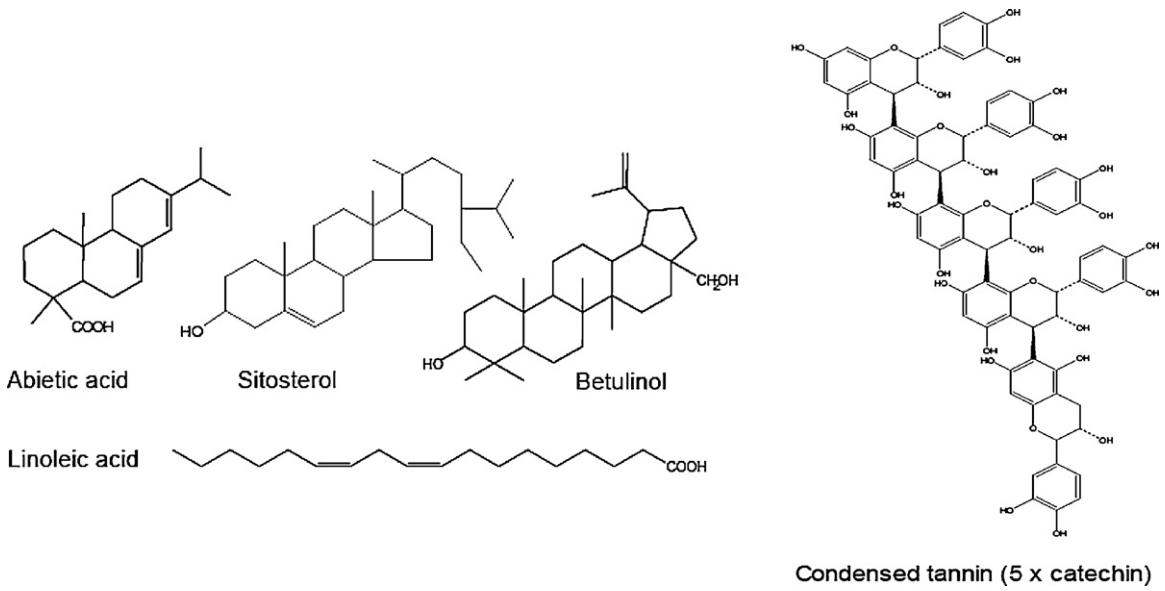

Fig. 1. Some extractives components of lignocellulosic materials.

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

Table 1
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

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

Table 3
Formulations of the used experimental composites.

Codes	EX wt.%	UN wt.%	MAPE wt.%	HDPE wt.%
A1	10	–	3	90
A2	20	–	3	80
A3	30	–	3	70
A4	40	–	3	60
A5	50	–	3	55
A6	60	–	3	50
B1	–	10	3	90
B2	–	20	3	80
B3	–	30	3	70
B4	–	40	3	60
B5	–	40	3	55
B6	–	60	3	50

EX: extracted bagasse; UN: unextracted bagasse.

2.3. Preparation of composites

Formulations of the treatments used for the respective mixes prepared are given in Table 3. Composites were produced in a two-stage process. In the first stage, HDPE and MAPE were mixed with extracted (EX) and un-extracted (UN) bagasse powder (depending on formulations) using a co-rotating twin-screw extruder. The barrel had five heated zones, which were set at 165, 170, 175, 180 and 185 °C, respectively. Screw speed was 60 rpm and the pressure at the die was 1500 MPa. The product was recovered by guiding the molten extrudate into a cold water stranding bath. The cooled strands were pelletized using a pilot scale grinder (Collin model), dried and stored in sealed plastic bags. In the second stage, test specimens were injection molded at 190 °C to produce standard ASTM specimens. Molding conditions were: press temperature 190 °C and pressure during heating 4 MPa. Size replications were prepared for each treatment.

2.4. Physical testing

Physical properties in terms of thickness swelling (TS) and water absorption (WA) were tested in accordance with ASTM D570. Before testing, the weight, and dimensions of each specimen were measured. Conditioned samples of each composite type were either soaked in distilled water at 23 ± 1 °C for 80 days. Samples were removed at certain periods of time, wiped with tissue paper to remove the excess water on the surface and immediately measured again. Each value obtained represented the average of 6 samples.

2.5. Statistical analysis

The experimental design consisted of two variable factors (namely extractives and filler content) and their interaction. Data for each treatment was statistically studied by analysis of variance (ANOVA). When the ANOVA indicated a significant difference among factors and levels, a comparison of the means was done employing Duncan's multiple range test (DMRT) to identify the groups that were significantly different from others at 99% confidence levels.

3. Results and discussion

3.1. Water uptake

One of the important properties to be evaluated for WPCs is WA, since it can limit their use. The high WA of the composites may be an indicative of difficulties during processing, such as incomplete curing of the thermoset matrix, or of the presence of voids or cracks or even poor matrix/fiber adhesion (Hamzeh, Ashori, & Mirzaei, 2011). Fig. 2 shows the percentages of the water uptake

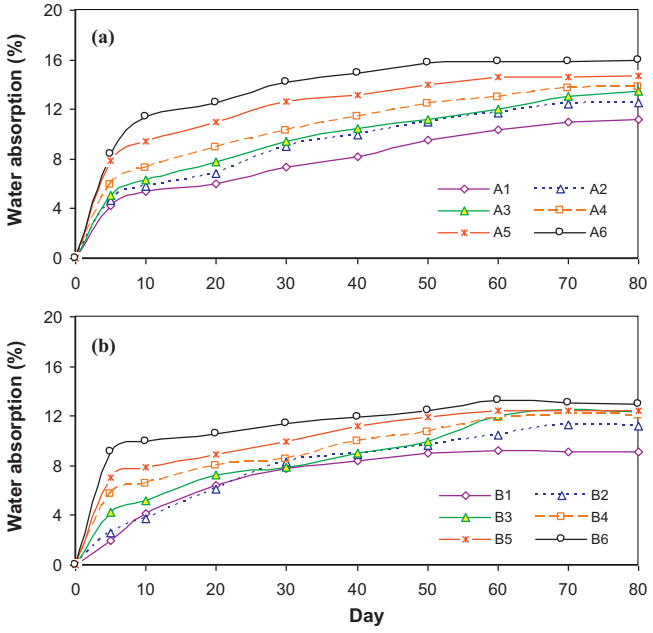

Fig. 2. Long-term water absorption of the (a) extracted and (b) un-extracted bagasse filled composites.

for the composites at different periods of immersion, which vary depending upon the filler type and filler loading level. The WA of the pure HDPE, however, was very low (<1%) due to its hydrophobic nature. In general, polymers do slightly absorb moisture, indicating that moisture is absorbed by the cellulosic material in the composite. It was clearly observed that there is a sharp increase in WA when the FB content in the mix is more than 30% by weight. There are at least three possible reasons for this phenomenon. One is that the lower bonding strength between the FB and matrix led to a tendency for more springback of water immersion. Another possible reason is that like other woody materials, the FB has high hemicelluloses content (17.1%) resulting in a high WA rate. This then affects the WA could be considered an important reason for the reduced dimensional stability of boards. The third possible reason could be attributed to low bulk density of FB which causes more void space in the board (Xu, Wu, Lei, Yao, & Zhang, 2008).

It is also clear from Fig. 2 that water uptake of all composites increased with increase of immersion time, reaching a certain value at saturation point where no more water was absorbed and the composites water content remained constant. According to Das et al. (2000), initially, water saturates the cell wall (via porous tubular and lumens) of the fibers, and next water occupies void spaces.

The hygroscopic properties of wood can be affected by the extractives. Nzokou and Kamdem (2004) believe that extracted wood generally absorbs more water and swells more than unextracted wood, which is due to the increased availability of moisture sites previously occupied by extractives and increased diffusion coefficient. Wood contains numerous free hydroxyl groups present in the cellulosic cell wall materials, which are responsible for interaction with water molecules by hydrogen bonding. The absorption of water by different fiber-based composites is largely dependent on the availability of free hydroxyl groups on the surface of the wood flour. On unextracted samples, some of these hydroxyl groups are blocked, as a result of which the absorption of water gets restricted (Kim, Harper, & Taylor, 2009). Fig. 2b clearly shows that the WA of unextracted composites is less than extractive-free samples. As mentioned earlier, extractives may have acted similar to wax, which is normally used to control WA. It could result

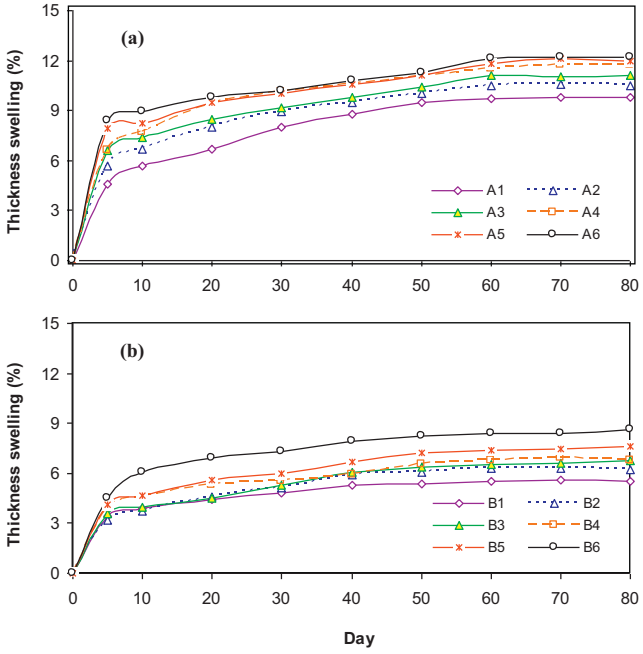

Fig. 3. Long-term thickness swelling of the (a) extracted and (b) un-extracted bagasse filled composites.

in a significant decrease in the degree of moisture absorption of the composite. Since the lumens of bagasse flour were filled with extractives, the penetration of water by the capillary action into the deeper parts of composite was prevented. This may suggest that the WA has occurred in the surface layer.

3.2. Thickness swelling

Fig. 3 shows the values of the TS for the composites, which vary depending upon the filler types and filler loading levels. Results indicate that as the amount of BF increases, the TS of the samples increases significantly. Average TS of the samples ranged from 4.6 to 12.2% and 3.2 to 8.6% for extracted and unextracted samples, respectively. In general, the TS of the WPC samples showed a similar pattern to the water uptake data. It is obvious that extractive-free samples cause considerable higher values of TS, compared to the unextracted composites. At the end of the test, the maximum TS of extracted wood WPC samples were greater than that of samples made with unextracted bagasse. In addition, there is significant difference in TS between the two (extracted and unextracted) filler types, and filler contents, as can be seen from Fig. 3a and b. Kim et al. (2009) reported that the TS of WPCs made with extracted wood is also higher than unextracted wood.

The hygroscopic properties of wood can be affected by extractives (Nzokou & Kamdem, 2004). Extracted BF generally sorbs more water and swells more than unextracted BF from increased availability of moisture sites previously occupied by extractives and increased diffusion coefficient (Kim, Harper, & Taylor, 2008). The increased water sorption and TS characteristics of extracted WPCs as well as BF in this study are consistent with previous results with wood (Kim et al., 2009; Steckel, Clemons, & Thoemen, 2007). In addition, the swelling of the wood component in WPCs affects the composite's microstructure by expanding cracks, debonding wood–plastic interfaces, and thereby providing more pathways for water penetration (Steckel et al., 2007). The low moisture sorption and TS characteristics of WPCs made with unextracted bagasse are likely the result of the low water sorption and low volumetric swelling of the wood component.

4. Conclusions

The main conclusions drawn from this study are as follows:

- The majority of water absorption occurred during the first 5 days. After that, the percentage of changes is negligible.
- The WPCs with extracted wood flour absorbed water more than those made with unextracted wood. The difference in water uptake between extracted and unextracted composites is due to blocking of the free hydroxyl groups by extractives.
- The rate of water uptake correlated with percentage weight of BF, higher filler loadings in composites exhibited higher rate of absorption.
- Both WA and TS properties of specimens increased with an increase in the BF content and the maximum values were obtained at 60% by weight. It is due to the hydrogen bonding of the water molecules to the free hydroxyl groups present in the cellulosic cell wall materials and the diffusion of water molecules into the filler/matrix interface.

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