Industrial Crops and Products 50 (2013) 219–226

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Contact angle and surface energy analysis of soy materials subjected to potassium permanganate and autoclave treatment

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ARTICLE INFO

Article history:
Received 23 January 2013
Received in revised form 5 June 2013
Accepted 16 June 2013

Keywords:
Soy flour
Autoclave treatment
Potassium permanganate treatment
Contact angle analysis
Surface energy
Composites

ABSTRACT

Initial water contact angle, apparent rate of water absorption and dispersive and polar surface energy were investigated for compacts of soy flour, two reference materials, soy protein isolate (protein reference material) and soy hulls (carbohydrate reference material), and the residue obtained after alkaline treatment of soy flour (insoluble soy). Untreated soy flour compacts had an initial water contact angle (57°) similar to soy protein isolate compacts (64°) but significantly lower than insoluble soy compacts (74°) and soy hulls compacts (85°). Potassium permanganate oxidation treatment increased the initial water contact angle of all soy materials compacts except for soy hulls compacts. The apparent rate of water absorption after potassium permanganate treatment, decreased for all types of soy compacts except for insoluble soy compacts. Autoclave treatment did not affect the initial water contact angle of soy flour and soy hulls compacts but increased significantly for soy protein isolates and insoluble soy compacts. The effect of autoclave treatment was reflected by the apparent rate of water absorption where significant increase was measured according to the type of soy material. The total surface energy and the dispersive and polar components, estimated from water and diiodomethane contact angle, indicated similar dispersive surface energy for soy flour, soy protein isolate and insoluble soy compacts (30 mN/m) but higher for soy hulls (36 mN/m). Significant differences of the polar surface energy component of treated materials compared to compacts of the untreated materials were measured, 18.4 mN/m (soy flour), 13.6 mN/m (soy protein isolate), 8.2 mN/m (insoluble soy) and 2.7 mN/m (soy hulls). The potassium permanganate oxidation treatment reduced significantly the polar surface energy component of soy materials compacts except soy hulls which increased. In contrast, autoclave treatment did not affect the polar surface component of soy flour but increased for all other soy materials compacts. The most appropriate soy material, based on the polar surface energy characteristics, for compatibility with hydrophobic polymeric materials, appear to be soy hulls, insoluble soy and soy protein isolate subjected to potassium permanganate treatment.

1. Introduction

The interest in lightweight materials for automotive and construction applications has significantly increased over the past years. The petroleum supply has become less secure resulting in price volatility. In addition, environmental concerns are becoming more pronounced. The increase in weight for improved safety and comfort can be reduced by employing lightweight composite materials. Composite materials for automotive interior parts commonly contain minerals or glass materials which possess high density (compared to agricultural fillers) and result in somewhat heavy composite materials. Agricultural fillers represent a promising alternative that can deliver similar performance materials for reduced weight.

Agricultural fillers can be taken from by-products or waste products during the harvesting and the processing of agricultural resources such as corn, wheat, rice, hemp, palm, soybean, cotton and other plants cultivated predominantly for their seeds and fruits. Soybeans are the number one (53%, 2009) oil seed crop and protein meal (66%, 2009) in the world (Soy Stats® and The American Soybean Association, 2011). The production of soybeans in 2009 represented nearly 400 million metric tons with at least 40% of the production in North America (Soy Stats® and The American Soybean Association, 2011). Intense research on chemical and thermal treatments of natural materials has been on-going for the development of advanced materials. For example, oxidation by potassium permanganate is a well-established treatment in the paper industry for lignin removal but which can also affects

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http://dx.doi.org/10.1016/j.indcrop.2013.06.035

cellulose (Garves, 1997). Recently, potassium permanganate treatment of biomass has shown positive effects for the mechanical properties of biomass containing composite materials. Improved stability of jute polypropylene composites was observed when jute fiber was treated with potassium permanganate (Khan et al., 2012; Zaman et al., 2010). In food and feed products, heat treatment of soy flour or soy meal can decrease the activity of protease inhibitors which increase their nutritional value but may reduce the amino acid bioavailability and their functional attributes (Gonzalez-Vega et al., 2011; Radha and Prakash, 2009). Autoclave treatment duration of soy meal was shown to reduce the total lysine and reactive lysine content (Fontaine et al., 2007) and was associated with lower digestibility when fed to growing pigs while the color change of autoclaved soy meal was indicative of the occurrence of Maillard reactions (Gonzalez-Vega et al., 2011). Significant differences in surface hydrophobicity and the poor emulsion stability of soy flour subjected to autoclave at 121 °C and 15 psi were also reported (Radha and Prakash, 2009).

When developing composites from agricultural fillers and polyolefins, the major challenge remains their incompatibility due to differences in surface properties. Fillers derived from agricultural resources are hydrophilic in nature because of their composition (cellulose, hemicellulose, lignin, protein) and their water content. Polyolefins on the other hand, are mainly derived from petroleum and are hydrophobic. As a result of such differences, the two materials are difficult to mix and have little interaction resulting in poor mechanical properties (Christophe et al., 2006; Dekker, 1999; Pietak et al., 2007). Surface modification and the addition of coupling agents have been used to improve the interaction between the surface of the two materials (Bledzki and Gassan, 1999; Dekker, 1999; Jacob et al., 2005; Saheb and Jog, 1999). Surface modifications that alter the properties of the materials can be chemical or physical and can target the filler or the polymer matrix (Angles et al., 1999; Ashori and Nourbakhsh, 2009; Bledzki and Gassan, 1999; Domka, 1994; Saheb and Jog, 1999; Zhang et al., 2006). Combinations of two or more treatments are also possible (Dekker, 1999; Li et al., 2007; Rothon, 2003).

The surface characteristics of inert solid materials with smooth surfaces, such as films, sheets, plastics and composites, are well established and obtained by contact angle analysis and surface energy study (Dankovich and Gray, 2011; Novák et al., 2007; Owens and Wendt, 1969; Tian et al., 2010). In contrast, powder-like materials, such as milled agricultural materials, need special attention because of their interaction with liquids, their particles size and shape and their heterogeneous surface characteristics. Several studies, by Buckton and his colleagues, on methods for contact angle and surface energy analysis of powder-like materials have been published mainly for pharmaceutical applications (Buckton and Newton, 1986; Buckton, 1990, 1992). Sample preparation, initially developed for powder materials (Buckton, 1990), has recently been reported by Roman-Gutierrez and his colleagues for wheat flour and its constituents (Roman-Gutierrez et al., 2003). Sample preparation consists of a preliminary stage of compaction at high pressure and equilibration of the materials under controlled humidity conditions. Roman-Gutierrez and his colleagues showed that wheat flour and its constituents possess significantly different initial water contact angle characteristics. The initial water contact angle for two types of wheat flour, hard and soft wheat, was 68° while the initial water contact angle for the two major wheat flour constituents was 85° for gluten (protein rich fraction) and between 38 and 41° for starch and pentosans (Roman-Gutierrez et al., 2003). Montaño-Leyva et al. used a similar method for the analysis of the contact angle of wheat gluten powders and wheat straw fibers subjected to different grinding conditions. Contact angle measurements were obtained for pellets prepared by compaction at 140 MPa pressure and a camera equipped goniometer (Montano-Leyva et al., 2013). Their study concludes that increased hydrophobicity was obtained by successive grinding which could improve the interface between the dispersed phase and matrix.

The total free surface energy can generate information on specific forces. Owens and Wendt developed a method for the estimation of surface free energy of polymers based on the theories of Young's equation and Fowkes (Owens and Wendt, 1969). Surface free energy analysis for natural materials is based on the Wilhelmy method for wood plates (Shen et al., 1998) or the receding and advancing contact angle method for cellulose films (Dankovich and Gray, 2011). The two major contributing forces were identified as the dispersive and hydrogen (polar) forces. The surface free energy of polypropylene is around 30 mN/m mainly contributing to dispersive forces (Diversified Enterprises, 2009). The grafting of maleic anhydride onto polypropylene will modify primarily the polar component of its surface free energy (Angles et al., 1999; Novák et al., 2007). Agricultural materials have significant polar surface energy component due to their high carbohydrate content (Bledzki et al., 2002).

The motivation for this study was to evaluate and compare the effects of autoclave and potassium permanganate treatment on the surface properties of soy flour with the ultimate goal of matching its surface properties to those of polypropylene for the development of quality composite materials. Four types of soy materials, soy flour, soy protein isolate (protein reference constituent), soy hulls (carbohydrate reference constituent) and insoluble soy (by-product) were selected to better understand the contribution of proteins and carbohydrates, the two major constituents of soy flour. To our knowledge, this is the first study reporting the surface properties of soy flour and its constituents. The potential of contact angle analysis as a screening tool for the relative assessment of the effect of potassium permanganate and autoclave treatment on soy flour will also be discussed.

2. Materials and methods

2.1. Materials

Bunge Inc. (Hamilton, Canada) supplied defatted soy meal and soy hulls (SH) and Archer Daniels Midland (ADM) Company (Decatur, USA) supplied soy protein isolate (SPI) ProFam 974.

2.2. Preparation of soy materials

2.2.1. Soy flour processing

The soy flour processing with the corresponding intermediate products is schematically shown in Fig. 1 and was described previously in detail (Guettler et al., 2013). Briefly summarized, the soy meal was milled (particle size <0.08 mm) to produce soy flour (SF) which was combined with Milli-Q water and pH adjusted with NaOH to 9.0. After heating at 50 °C for one hour the aqueous soy flour mixture was centrifuged (Sorvall WX 100 with A-621 rotor, Thermo Scientific, USA) and the solid residue (insoluble fraction (IS)) was dried. The supernatant, containing mostly proteins, sugars and minerals, was adjusted to pH 4 with H_2SO_4 (95–98%, GR ACS, Fisher Scientific, Canada) and centrifuged at 10 000 rpm. Soy protein isolate (SPI) is the resulting precipitate. The so called "soluble sugar extract" (SSE) was the remaining liquid solution, containing mostly sugars and minerals.

After their treatments, the soy materials were milled and dried as previously described (Guettler et al., 2013).

2.2.2. Autoclave treatment

The autoclave treatment was described previously (Guettler et al., 2013). The soy material was exposed to direct steam at 125 °C