International Journal of Adhesion & Adhesives 62 (2015) 1–6

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

Rheological behavior and bonding performance of an alkaline soy protein suspension

Alejandro Bacigalupe [a], Andrea K. Poliszuk [b], Patricia Eisenberg [c], Mariano M. Escobar [a,*]

[a] Centro de Caucho, Instituto Nacional de Tecnología Industrial (INTI), Avenida General Paz 5445, B1650WAB San Martín, Buenos Aires, Argentina
[b] Centro de Procesos Superficiales, Instituto Nacional de Tecnología Industrial (INTI), Avenida General Paz 5445, B1650WAB San Martín, Buenos Aires, Argentina
[c] Centro de Plásticos, Instituto Nacional de Tecnología Industrial (INTI), Avenida General Paz 5445, B1650WAB San Martín, Buenos Aires, Argentina

ARTICLE INFO

Article history:
Accepted 10 June 2015
Available online 18 June 2015

Keywords:
Wood adhesives
Biodegradable adhesive
Rheology

ABSTRACT

The goal of this work is to study the rheological properties of based-modified soy protein concentrate (SPC) adhesives and the relationship between viscoelastic properties and bonding performance. Chemical modification of SPC with sodium hydroxide was made to evaluate the effect of alkali on the viscoelastic proper ties. Viscosity and solubility depends directly on the 3D structure and the isoelectric point (pI) of the protein. Results show that viscosity is strongly pH dependent due to the protein unfolding. Solubility profiles exhibit the typical U-shaped curve, being higher on either side of the isoelectric point. Fourier transformed infrared analysis was used to analyze Amide I (1720–1600 cm^{-1}) and Amide III (1400–1200 cm^{-1}) band patterns which reflect the different secondary structures in proteins. The intensity of the band at 1250 cm^{-1} increases with respect to that at 1235 cm^{-1} for higher pH values. This could be associated with the destruction, at least partially, of the β-sheet structure. Bonding performance was measured in dry conditions and the wetting properties were analyzed by scanning electron microscopy. The bonding performance improves when the SPC is stabilized at pH 12 due to the protein unfolding, revealing a strong interaction between the secondary structure and the wood surface. As part of an ongoing project it was concluded that alkali modification is a suitable procedure to modify a protein suspension, improving application conditions and mechanical properties of bioadhesives of a semistructural type.

1. Introduction

Petroleum-based adhesives like urea–formaldehyde (UF) are widely used in plywood, composite wood panels and furniture because of high adhesion strength and low cost. This adhesive has replaced historic based protein products such as casein or blood [1], which were displaced from the market.

However, highly toxic formaldehyde is emitted during the production and post-production processes. It is important to note that formaldehyde was declared a carcinogen by the World Health Organization (WHO) in 2004. Besides, the future shortage of petrochemical-based products supposes a rise in the relative price and lack of availability, leading to an increase in the development of green products from inexpensive and renewable resources. A potential solution to this problem is the use of soy based products which are renewable, non-toxic and environment friendly materials [2]. Soybean is an abundant raw material in the South American region commonly used for the production of oil and starch with different protein amount. Argentina is the third largest producer of soybeans after the United States and Brazil due to the favorable weather conditions of the region [3]. Soybean meal can be processed to concentrate, and furthermore, isolate the protein and obtain a more concentrated product. Soy protein concentrate (SPC) contains approximately 60% of protein. Although soy protein isolate (SPI) contains nearly 90% of the protein, it has been decided to work with the SPC as it is cheaper than SPI but maintains an acceptable bonding performance. Nishinari et al. studied the main components of soybean proteins [4]. They studied a mixture of various proteins, and the main ingredients are classified into four protein categories according to their sedimentation coefficients 2S, 7S, 11S and 15S. Among these four, 7S (β-conglycinin) and 11S (glycinin) represent more than 80 wt%, and the ratio 7S/11S has been reported to be about 0.5–1.3 depending on the varieties [5]. 11S globulin is a hexamer, made up of five different subunits, each of which consists of an acidic subunit A (acidic isoelectric point) and a basic subunit B (basic isoelectric point), linked by a disulfide bond.

* Corresponding author. Tel.: +54 11 4724 6200.
E-mail addresses: abac@inti.gob.ar (A. Bacigalupe), ankapoli@inti.gob.ar (A.K. Poliszuk), patsy@inti.gob.ar (P. Eisenberg), mescobar@inti.gob.ar (M.M. Escobar).

http://dx.doi.org/10.1016/j.ijadhadh.2015.06.004
0143-7496/

Bonding strength of protein plant adhesives must be improved to achieve the performance of conventional wood adhesives. Proteins are formed by a combination of different amino acids. Each amino acid contains functional groups attached to the polypeptide backbone of the biopolymer. The denaturation of the protein by chemical modification exposes the functional groups; such as OH, COOH, NH_2, and SH; being available to interact with the wood and improve the bonding strength [6].

Several researchers have employed different physical and chemical methods to improve the bond strength and water resistance of the soybean protein. Their studies report on the successful use of heat treatment and addition of different denaturation agents, e.g. alkali, urea, guanidine hydrochloride; and different anionic and cationic surfactants, as a means to unfold the protein structure and make it more available for interaction and reaction. Zhong et al. reported that proteins are completely denatured after treatment with a 6 M solution of guanidine hydrochloride. The same authors also reported that the maximum strength for wood joints was achieved with 1 M guanidine hydrochloride solution. More recently, Santoni et al. [7] modified soy protein in acid (pH 3) and basic (pH 10) media to evaluate the solubility and the mechanical properties as a wood adhesive. From Fourier transformed infrared (FTIR) analysis, they found that variations in the acidity level did not change the conformation of all proteins, as evidenced by the invariance in the position of the amide I band at 1630 cm^{-1}. In addition, IR spectra evidenced the effect of pH on the protein structure; an increase in pH increases the unfolding of the protein. Nordqvist et al. [8] compared the bonding performance of soy protein isolate and wheat gluten when a sodium hydroxide solution (0.1 M) was used as a denaturation agent. Recently, the same author expanded the characterization to acidic media [9] and evaluated adhesion measurements at the nanoscale using atomic force microscopy.

Rheology has become an important and useful technique to study the properties of viscoelastic materials. This method allows analyzing the internal structure of the adhesive that will be affected by chemical phenomena, such as interactions due to weak intermolecular forces; and physical phenomena, such as entanglement and coiling of the polymer chains. The study of the internal structure of viscoelastic materials allows us to understand the behavior during processing conditions, i.e. such as mixing and applying. Furthermore, viscosity is an essential adhesive's property affecting the wetting parameter and, therefore, modifying their performance. The operating viscosity limits of soybean glues are very large ranging from 500 to 75,000 cP depending upon the application and the nature of the materials to be glued. A viscosity of 500–5000 cP is needed for gluing materials which are highly absorbing such as paper, soft board and dried wood aggregates, 5000–25,000 cP for most wood laminating purposes (both cold or hot press) and over 50,000 cP for mastic consistency wood laminating operations [10]. A less viscous adhesive is preferable as it is easier to produce and to apply.

The main goal of this work was to study the rheological properties of base-modified soy protein concentrate suspensions and simultaneously explore the relationship between viscoelastic properties and bonding performance. This work is part of a wider research plan aimed to modify vegetable proteins by means of additives to improve their water resistance, thus to obtain high performance adhesives of a semistructural type.

Rheological studies were carried out with different pH values to analyze suspensions' microstructure and FTIR analysis was made to study the denaturation process. Solubility profiles of the SPC in water were made to determine the relationship between viscosity and the isoelectric point. Bonding performance was measured in dry conditions meanwhile the wetting properties were analyzed by scanning electron microscopy (SEM) to study the relationship between viscoelastic properties and bonding performance.

Table 1
Designation code of the samples.

Sample	pH
SPC-8	8
SPC-9	9
SPC-10	10
SPC-11	11
SPC-12	12
SPC-13	13

2. Experimental

2.1. Materials

Soy protein concentrate (SPC) Alpha DK was kindly donated by Tecnoalimenti S.A. Sodium hydroxide (NaOH) was purchased from Merck. The TEGO Foamex 1488 was used as antifoam, provided by Clariant Argentina S.A.

2.2. Preparation of SPC adhesives

All samples were formulated by dispersing 20 g of SPC in 154 g of de-ionized water in an industrial stirrer at 300 RPM for two hours. Degree of denaturation was achieved by adding different amounts of NaOH to adjust the pH ranging from 8 to 13. A few drops of a diluted antifoam solution were added and then a vacuum was applied for air elimination before analysis or application. Table 1 summarized the identification of each sample.

2.3. Characterization

Viscosity was measured at 25 °C over a shear rate range of 10–250 s^{-1} using a rotational test on an oscillatory rheometer (Physica MCR301, Anton Paar GmbH) equipped with concentric-cone geometry (CC27). Viscoelastic properties were evaluated through an amplitude sweep test at 10 s^{-1} over a strain range of 0.01–100% using an oscillatory test equipped with cone–plate geometry (CP50) at 25 °C. The viscosity of each suspension was measured 6 h after preparation. In order to obtain a representative value, the test was replicated five times for each sample and the average values are reported.

Solubility profiles of the protein were determined over the pH range 8–13. SPC samples were suspended in de-ionized water at 1 g/100 g protein concentration and stirred for 1 h at room temperature, readjusting the pH if necessary. The dispersions were then centrifuged at 4600 RPM for 30 min at room temperature. Crude protein content in the supernatant was determined using a spectrophotometer (Shimadzu UV-1800) by the Biuret method. This procedure was repeated three times with each sample and the average values are reported. Solubility was expressed as the percentage of original protein present in the supernatant and the solubility of SPC at pH 7 was determined as standard.

The effect of protein modification was studied through FTIR (ATR) using a Thermo Scientific Nicolet 6700 spectrometer. Each spectrum was collected by accumulating 64 scans at a resolution of 6 cm^{-1}. Samples were freeze dried before FTIR analysis.

A tensile testing machine (INSTRON 4467) with a cross-head speed of 2.54 mm/min was used to evaluate the bonding strength. The test was replicated 10 times for each sample. The adhesive was manually applied on two pieces of hardwood (*Balfourodendron riedelianum*), over an area of 5.0×5.0 cm^2. They were then heat