Acta Scientific Agriculture (ISSN: 2581-365X)

Volume 2 Issue 5 May 2018

Research Article

Preparation of Soybean Protein-Acrylate Composite Adhesive by Mini-Emulsion Polymerization

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Received: March 01, 2018; **Published**: April 19, 2018

Abstract

An environmental-friendly soybean protein-acrylate composite adhesive was successfully prepared with the use of soy protein and acrylate by mini-emulsion polymerization. The composition, properties and adhesive performances of the composite mini-emulsion adhesive were characterized by Fourier transform infrared spectroscopy (FT-IR), water contact angle (WCA) and bonding strength. Water contact angle measurement showed that the introduction of acrylate increased the hydrophilicity of the composites. Parts of C–O and C=O groups reacted to soybean protein and finally formed carboxyl groups. Besides, bonding strengths of plywood with the amount of acrylate increasing were both higher than 0.7 MPa, which met the GB/T9846-2004 standard about the state of II plywood. Soy protein is bio adhesive, which belongs to environmental-friendly adhesive. However, soybean paste has poor water resistance and corrosion resistance, and not resistant to boiling. This paper used acrylate to modify soybean protein adhesive, and successful preparation of soy protein-acrylate composite adhesive, it could open up a new way for wood adhesives with no release of free phenol nor free formaldehyde. Moreover, could present a new research direction for modification of soybean protein adhesive.

Keywords: Miniemulsion Polymerization; Soybean Protein; Acrylate; Biomass Adhesive

Introduction

Facing the increasingly severe energy and environmental problems in the world, the development and utilization of renewable composite polymer materials have become the focus of research in many countries [1,2]. Soybean protein is the main by-product of processing agricultural products, which is a kind of renewable, biodegradable and relatively inexpensive natural plant protein [1-4]. Johnson applied for a patent on soybean protein adhesive. It was used in plywood production, wood paneling industry, and packaging materials of food. It has the advantages of low cost, easy processing, easy sizing, hot pressing, cold pressing, and no irritating odor. Compared with the formaldehyde based adhesives, soybean protein adhesive has the advantage of no release of formaldehyde, making it become one of the first to be used as environment-friendly wood adhesive. However, soybean paste has poor water resistance and corrosion resistance, which hinders the popularization and application of soybean based adhesives [1-5]. In order to overcome the disadvantages of soybean protein adhesives, a lot of modifications have been made on soybean protein adhesives in academia and industry at present [6]. The most commonly used method, and also the most suitable method for expanding the application, is to blend soy protein with other adhesives [7,8].

Acrylic emulsion is a kind of widely used polymer material with unique properties and wide variety, which has the characteristics of excellent weather resistance, water resistance and alkali resistance, and good transparency. Besides, it has good bonding strength with various other materials [1-4]. The acrylate monomer has a certain number of reaction sites, which can be crosslinked with the amino groups of soybean protein. Nowadays, there is very little research on the preparation of soybean protein by modification of acrylate emulsion [1-4].

In this paper, soybean protein and acrylate monomer were polymerized to prepare soy protein-acrylate composite adhesive used for the preparation of plywood through the method of miniemulsion polymerization [1,9]. The prepared plywood has high strength, high water resistance, no free aldehyde and free phenol release, meeting the requirements of industrial production and use, which presents a new research direction for modification of soybean protein adhesive [10-14].

Experimental Procedure

Materials

Methyl methacrylate (MMA) and butyl acrylate (BA) were of industrial grade and were purchased from Eastern Petrochemical Company. The n-hexadecane(HD) used as auxiliary emulsifier, ammonium persulfate (APS), alkylphenol ethoxylates (OP-10) and Dodecyl sulfonic acid sodium salt (SLS), used as the initiator and emulsifier were purchased from ACROS Chemical Reagent Company. Distilled water was used in this experiment. Poplar veneers, moisture content of 8%, were specification range of 400 mm x 400 mm x 1.7 mm.

Methods

Purification process of soybean protein

The extraction of soybean protein isolate was carried out by traditional method of Alkaline dissolution and acid precipitation.

Defatted soybean protein was dissolved in deionized water, then pH was adjusted to 7.5 - 8 with 2 mol/L sodium hydroxide, and then stirred at 50°C for 40 minutes. The solution was placed statically and the dissolved part was protein and monosaccharide, and the insoluble fraction was polysaccharide. Then the protein and monosaccharide were adjusted with 2 mol/L hydrochloric acid to pH 4.2 - 4.5 and stirred at 50°C for 40 minutes. The solution is placed in static filtration, dissolved part is monosaccharide, insoluble part is protein, and insoluble part is neutralized with 2 mol/L sodium hydroxide to pH, and 7 - 7.2 is isolated from soybean protein. The soybean protein isolate solution was centrifuged by 3100g at a centrifugal force at 10min, and the precipitate was partially dissolved with deionized water. At 50 DEG C, 10 minutes was stirred, 3100g centrifuged at 10 minutes, and repeated 2 times. The soybean protein isolate (SPI) solution was homogenized by high pressure homogenizer 20MPa, and the inlet temperature was 170 DEG C, and the air temperature was 80.

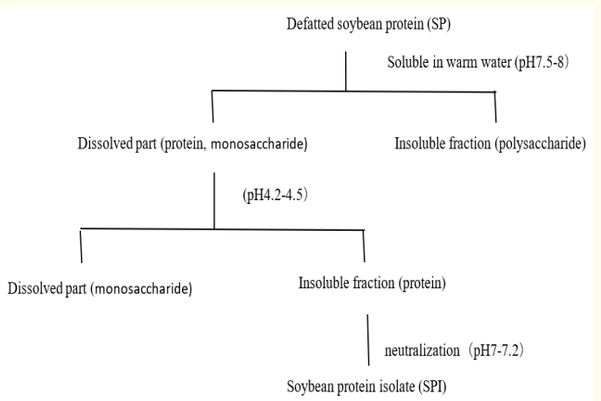

Figure 1: Flow diagram for the production of soybean protein isolate (SPI).

g/100g Soy protein powder	Defatted soybean protein (SP)	Soybean protein isolate (SPI)
Protein	48	92
Fat	0.3	0.5
Moisture [Water]	10	< 5
Fibre	3	< 1
Ash Content	7	4
Carbohydrate	31-32	-

Table 1: Composition of soybean protein powder.

Preparation of Soy Protein - Acrylate Compound Emulsion

1.2g of sodium lauryl sulfate (SLS) was dissolved in 140g of deionized water, 1.2g of n-hexadecane (HD) was dissolved in 20g of methyl methacrylate (MMA), 20g of butyl acrylate Body, the monomer solution and a certain amount of soy protein isolate (as shown in table 2 below) was added to the emulsifier solution, stirred for 30 minutes (1000 r/min) to form a monomer pre-emulsion. The pre-emulsion in a new Chi 98-3D ultrasonic cell crusher ultrasonic 300s (ice bath cooling, the instrument output power of 50%), the ultrasound resulting monomer emulsion.

The monomer miniemulsion was charged into a 500 mL four-necked reactor equipped with a condenser and a thermometer. Start stirring and purged with nitrogen for 15 minutes, heated to 55°C added 0.6gKPS, and then heated to 70°C, the reaction time began. The reaction 1-1.5h, cooled to 30°C the material was soy protein - acrylate composite fine emulsion.

Characterization

Fourier transform infrared spectroscopy (FT-IR) analysis

FTIR spectra of samples were recorded in a range of wave numbers from 4000 to 400 cm-1, using a Nicolet (Magna-IR 560) instrument.

Sample	MMA/BA (g)	SPI (g)	SLS (g)	HD (g)	APS (g)	Deionized water (g)	Viscosity (mPa.s)	Temperature (°C)
S_1	20/20	1	1.2	1.2	0.6	140	124.6	70
S_2	20/20	2	1.2	1.2	0.6	140	197.8	70
S_3	20/20	3	1.2	1.2	0.6	140	279.4	70
S_4	20/20	4	1.2	1.2	0.6	140	453.2	70
S_5	20/20	5	1.2	1.2	0.6	140	597.5	70

Table 2: Preparation process of soybean protein acrylate composite miniemulsion.

Water contact angle measurement

The water contact angle analyzer (JC2000C1, Powereach Co., Shanghai, China) at ambient temperatures with a droplet volume of 5 uL was employed to measure the contact angle (CA) of the samples. An average of the five measurements taken at different positions on each sample was applied to calculate the final WCA angle.

Preparation of Plywood and Bonding strength measurement

The three-layer plywood was prepared by poplar veneers with a width of 400 mm x 400 mm x 1.7 mm and a moisture content of 8% glued with manual glue of 200 g/m^2 soybean protein acrylate composite mini-emulsion every a single plate. The pressing temperature is 125°C hot pressing temperature, 1.1 MPa hot pressing

pressure and 1.2 min/mm hot pressing time. The prepared plywood was to submerged in 63°C water for 3h, and took out after cooling for 10 minutes at room temperature. The bonding strength were according to GB/T9846-2004 standard regulations of the state of II plywood detection method.

Results and Discussion

FT-IR spectrum

Figure 2: The infrared spectrum of soy protein acrylate mini-emulsion.

Water contact angle

Water contact angle was a measure of the degree of penetration of the material, which could characterize the wetting property of adhesive on the wood surface. The WCA was less than 90°, indicating that the surface of the material was hydrophilic. The smaller the angle is, the better wettability, figure 3 was the contact angle of soy protein-acrylate composite emulsions, which corresponded to table 2. As can be seen from figure 3, the WCAs of soybean protein acrylate composite mini-emulsion were all less than 90°, which showed that the composite mini-emulsion had good wettability to wood, and it was good for bonding with wood. Besides, it was found that the more the amount of acrylate added, the better the wettability of the composite mini-emulsion.

Figure 3: Contact angle of soy protein-acrylate composite emulsions.

Bonding strength

Table 3 showed that the good water-resistant glue, and the plywood glued strength were all greater than 0.70 MPa. Water resistance and bonding strength had reached the national standard GB/T9846-2004 II plywood requirements.

Sample	Solid mass fraction (%)	Shear strength (MPa)
S_1	32.1	0.971
S_2	31.7	0.874
S_3	31.8	0.773
S_4	31.3	0.781
S_5	30.9	0.717

Table 3: Shear strength of plywood of soybean protein acrylate composite.

Conclusion

In conclusion, a combination of polyacrylate copolymers and soy protein with different mass ratios was achieved by mini-emulsion polymerization of MMA and BA. Water contact angle measurement showed that the introduction of acrylate increased the hydrophilicity of the composites. The compatibility of soybean protein-acrylate mini-emulsion was enhanced leading to improvements in shear strength, which were all above 0.7 MPa. What's more, the water resistance of plywood was enhanced with the adding of acrylate. The successful preparation of soy protein acrylate composite adhesive could open up a new way for wood adhesives with no release of free phenol nor free formaldehyde. Moreover, could present a new research direction for modification of soybean protein adhesive.

Acknowledgments

We would like to acknowledge support from the National Natural.

National Science and Technology Support Program Project (2015BAD14B0305).

Zhejiang Provincial Natural Science Foundation of China (LZ16C160001).

Science Foundation of China (31270589), and Science and Technology.

Foundation of Jilin Province (20140204054NY), Jiangsu Provincial.

Natural Science Foundation of China (BK20131070).

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