

Modification methods of soy protein adhesive and its application

Zeyu Zhang *

Department of Material Science and Technology, Beijing Forest University, Beijing, China

* Corresponding Author Email: zhangzeyu@bjfu.edu.cn

Abstract. Soybean protein adhesive is loved by the society because of its low price, simple preparation, non-toxicity to the environment and easy decomposition. However, the soybean protein adhesive itself is easy to crack when exposed to water, the viscosity is insufficient, and there are many changes in individual users. This research will describe several methods of modifying soy protein to enhance various properties of soy protein adhesives. The first method is heat treatment, which folds the molecules of the soy protein adhesive to strengthen it. The second is a cross-linking treatment that allows soy protein to form a network with other agents to enhance its structure through chemical bonds. The third is graft copolymerization, where other agents are grafted onto the soy protein adhesive to give it some good properties. The fourth is blending, where the soy protein adhesive is mixed with other adhesives so that the new homogeneous mixture has the properties of both adhesives. And with the development of these researches, application of the modified soybean protein adhesives is further introduced.

Keywords: Soy protein adhesive, Modification, Treatment, Application.

1. Introduction

The progress of modern adhesive technology can be traced back to the Second World War. Due to the needs of the military industry, the adhesive has also changed accordingly, from the initial use of wood-based panels and daily industrial bonding to military use. Especially, the emergence of “structural adhesive” is an adhesive used on the structural parts of aircraft, and its composition types are mainly phenolic-acetal, phenolic-butyronitrile, and phenolic-chloroprene adhesives. And in 1941, the British Aero Company invented a phenolic-polyvinyl acetal resin hybrid structural adhesive, the brand name is “Redux”. This type of adhesive is mainly used for bonding the main wings of fighter jets and was put into use in July 1944. After the end of World War II, adhesives were transferred from the military to the civilian industry. Since the beginning of the 21st century, the birth of various adhesives has promoted the development of the wood industry, especially the adhesives dominated by urea-formaldehyde resins and phenolic resins, but since the preparation materials of these two kinds of adhesives come from non-renewable resources such as petroleum. According to statistics, by the end of 1997, among the total 246.6 billion tons of conventional oil reserves in the world, 110.5 billion tons had been collected, and the remaining 1,121 tons had been collected [1]. In the future, new large oilfields will hardly be discovered, and oil in deep sea areas is difficult to find due to various factors such as quality and environment. And there is always a problem with these two adhesives. The free aldehydes and free phenols they release will pose a great threat to the environment and the human body. Therefore, many countries have begun to use some natural additives to modify these adhesives.

Protein adhesives first entered the attention of many countries. According to their types, they can be divided into animal protein adhesives (gelatin, blood glue, bone glue, casein glue) and vegetable adhesives such as soybean protein glue. These adhesives are highly renewable and environmentally friendly, and these adhesives do not need to be handled as much as traditional adhesives in transportation. They were very popular in the United States at the end of the 1940s and 1960s. At this time, almost every plywood manufacturer on the west coast of the United States will use soy protein adhesives, and the usage rate accounts for more than 85% of the glue used for all plywood.

Soy protein adhesive is easy to obtain, inexpensive, and naturally pollution-free. In the beginning, soybean protein adhesive was prepared by adding soybean flour or soybean protein to gel-forming agents and additives. By directly modifying soybean protein, it tried to give it a series of chemical properties, and it was directly used as wood adhesive. However, the adhesive prepared by this method has low bonding strength, which only meets the requirements of indoor furniture and belongs to non-water-resistant adhesive. At present, most of the research is to use soy protein as a filler or modifier for synthetic resins. The starting point of this technical approach is to improve the availability of wood adhesives without sacrificing the performance of synthetic resin adhesives and reducing the release of toxic volatile substances. The content of recycled components and reduce the production cost of the adhesive.

The commonly used methods for soybean protein modification include physical modification, chemical modification and biological modification. Physical modification is to change the high-level structure and intermolecular aggregation state of proteins through physical methods such as moist heat, dry heat, freezing, mechanical action, high voltage, radiation, and high-frequency electric fields, generally not involving the primary structure of proteins. A commonly used method in physical modification is heats treatment. During heat treatment, soybean protein undergoes thermal denaturation, mainly due to changes in solubility. Under heating conditions, the original coiled and tight structure of soybean protein molecules is stretched out, only the hydrophobic groups inside the molecule are exposed to the outside, and the hydrophilic groups outside the molecule are relatively reduced, resulting in a decrease in solubility. In addition, when the protein molecules are heated, association may occur and the viscosity increases. Chemical modification is the use of chemical reagents to change the spatial conformation and physicochemical properties of protein molecules, including acid-base modification, urea modification, acylation modification, graft modification, etc. Among them, acid modification is the most widely used method, which uses acid substances to change the structure, electrostatic charge and hydrophobic groups of proteins, thereby improving the functional properties of soybean protein. The biological modification method mainly focuses on the enzymatic modification method. The principle of action is that the soybean protein is hydrolyzed by protease, and its amino acid residues and polypeptide chains are changed to cause protein molecules or connect special functional genes, and change the spatial structure and physical and chemical properties, improve surface hydrophobicity and solubility.

For this reason, this research will focus on different modification methods for soy protein adhesive, including heat treatment, epoxy treatment, tannin treatment and graphene treatment, which is expected to provide a new idea for the use of soy protein adhesive.

2. Different modification methods of soy protein adhesive

2.1. Heat treatment

The earliest treatment method of soybean protein adhesive is heat treatment. When the temperature is higher than the denaturation temperature of soybean protein, the spherical structure of soybean protein will be destroyed and the long chain will be opened, and the hydrophobic groups will be exposed. The clusters will attract each other and react differently to form some complex aggregates. For the heat treatment temperature, the experimental results show that when the main components of soybean protein are 7 S and 11 S, its thermal denaturation temperature is 68.0~79.4 °C and 88.0~99.4 °C. Under this condition, when soybean protein is heated to 120 °C, the structure can be obtained. Stable and tough adhesive [2].

2.2. Epoxy treatment

Compared with ordinary polymer adhesives, soybean protein adhesives have a larger molecular weight and because of their protein structure, they are very complex and have poor water resistance. Because soybean protein contains many active groups, its water resistance can be enhanced by cross-linking treatment. The curing of general soybean protein adhesives is a process of using the

evaporation of adhesive moisture to form crystalline regions between the adhesive molecules, and using hydrogen bonds to increase the intermolecular force. However, due to the small bond energy of hydrogen bonds, the adhesive properties of soybean protein adhesives are not stable, so epoxy compounds are used to react with active groups on soybean protein. And chemical bonds are used to replace hydrogen bonds to improve the bond energy of the connection, so as to improve the water resistance of soybean protein. In addition, epoxy compounds can reduce the crystallinity of soybean protein molecules. For example, when epoxy compound M85 reacts with soybean protein, adding 12wt% of M85 can reduce the viscosity by 49.65% and increase the strength by 236.7% [3].

Huang et al. have scientifically used trimethylolpropane, an alkaline substance, as a cross-linking agent to modify soybean protein. This adhesive has good water resistance and is easy to produce. The polymer can be polymerized with the amino group of soybean protein to form a dense solidified layer, after which the adhesive has better properties by hot pressing [4]. In addition, many people also try to treat soybean protein with acid as a cross-linking agent in addition to alkali treatment. The properties of soy protein after acid treatment were determined by Naotoshi et al. [5]. After heating for 30 min at 95 °C, various groups of soybean protein were decomposed to different degrees, which greatly improved the emulsification and hydrophobicity of soybean protein. This experiment proves that soybean protein is more active and has some good properties under acidic conditions, and epoxidized oleic acid can provide an acidic reaction environment for soybean protein, and epoxidized oleic acid has a lot of long-term properties. Carbon chain structure and carboxyl group, the former can improve the hydrophobicity of soybean protein, while the latter can react with groups such as amino hydroxyl groups of soybean protein to improve the mechanical properties of the adhesive, but the water resistance of soybean protein is not improved due to the acidic environment. Another compound, epoxy resin, can be used as a cross-linking agent to improve the water resistance of soybean protein. In addition, a mixture of epoxy resin and epoxidized oleic acid was used to modify soybean protein [6]. As shown in Figure 1, after 50% epoxidized oil, the mechanical properties and water resistance of the soy protein adhesive modified with acid and 50% epoxy resin mixture were significantly improved.

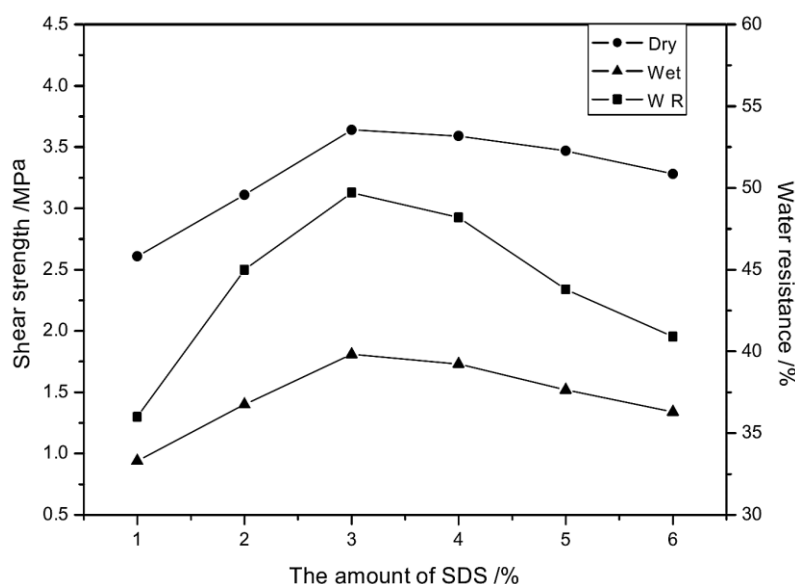


Figure 1. Effect of SDS dosage on the bonding strength of modified soybean protein [6]

2.3. Tannin treatment

Many scientists use tannin as a cross-linking agent to modify soybean protein because tannin is a very common. Biomass materials can be mass-produced at low prices, and have strong reactivity. They can react with active groups in soybean protein to replace hydrogen bonds in soybean protein to form chemical bonds, making soybean protein more stable and improving. Thus, the tannin can be used to modify soybean protein, and the water resistance of soybean protein by measuring the residual

rate of the adhesive was further analyzed [7]. The experiment proved that the residual rate of the unmodified soybean protein adhesive increased by 76.1%. The residual rate of soybean protein adhesive modified by adding 4% tannin reached 82.7%, which proves that soybean protein has a denser cross-linked structure and improved water resistance after tannin modification.

Other scholars have used condensed tannins for further processing of soy protein [8]. Compared with ordinary tannin, condensed tannin not only improves the water resistance of soybean protein adhesive, but also greatly improves the mechanical strength of soybean protein adhesive. Figure 2 show the result. Condensed tannin can cross-link with polyethyleneimine of soybean protein, and the tensile strength can be increased to 7.61 MPa. When the content of condensed tannin is 15%, it is 130.1% higher than that of unmodified soybean protein. The modified soybean protein adhesive is brittle and easy to crack, because tannins are mainly formed by the condensation of C-C single bonds of flavonoids. After mixing, the brittleness of the adhesive will increase and the toughness will decrease.

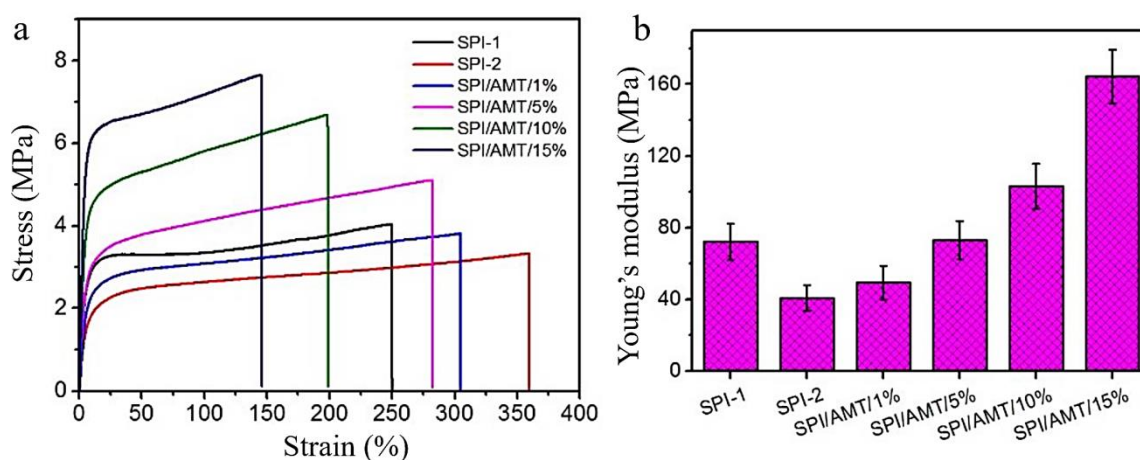


Figure 2. Stress-strain curves and Young's modulus values of the SPI composite films [8]

2.4. Graphene treatment

Because of the high brittleness of tannin-modified soybean protein adhesives, scholars have invented a method of using graphene to modify soybean protein to reduce its brittleness. Two kinds of aminated graphene oxide can be prepared [9], including electrochemical graphene oxide (EGO) and functionalized graphene oxide (FGO). Soy protein adhesives were modified to demonstrate feasibility. First, the nucleophilic reaction of succinic anhydride and diethylene acid ammonia is used to obtain FGO and the grafting of GO with diethylene is used to obtain EGO. FGO forms a dense network structure through the cross-linking reaction of cross-linking agent on soybean protein, and the hyperbranched polymer of GO makes the system of soybean protein adhesive change from brittleness to toughness. Experiments show that adding 0.4wt% EGO can increase the water resistance of plywood to 0.81 MPa. Adding 0.4wt% FGO can increase the adhesive strength of soybean protein by 180.95%, and the energy density of the adhesive can be increased due to the addition of hyperbranched polymers. Both the tensile strength and Young's modulus have been greatly improved.

2.5. Graft copolymerization

The soybean protein adhesive modified by the cross-linking reaction still has some shortcomings. Scholars have studied this and created a new modification method, that is, the grafting reaction. The main mechanism of the grafting reaction is the chemical bond on the soybean protein polymer. Open to graft other substances onto the active sites of soy protein to increase the strength of soy protein adhesives. Vinyl adhesives are usually used in the grafting reaction. American scholars Steinmetz, Krinski and others used p-hydroxyalkyl acrylate to modify soybean protein to obtain a modified adhesive with high strength [10]. The biggest difference between the grafting reaction and the cross-

linking reaction is the pretreatment. The reaction conditions of the grafting reaction pretreatment are milder and better controlled, and the properties of soybean protein will not be destroyed.

The ammonium persulfate (APS) is used as an initiator to graft soy protein with methacrylic acid to increase the viscosity of soy protein [11]. Figure 3 shows the change in viscosity. The APS can provide an acidic environment for the reaction. The dissociation range of soybean protein is in different pH. At this time, reagents are added to break the disulfide bond of soybean protein, and methacrylic acid is grafted on soybean protein, to form a new adhesive system. The results show that the viscosity of the grafted product would gradually increase when the mass fraction of the solution increased from 0.5% to 4.5%.

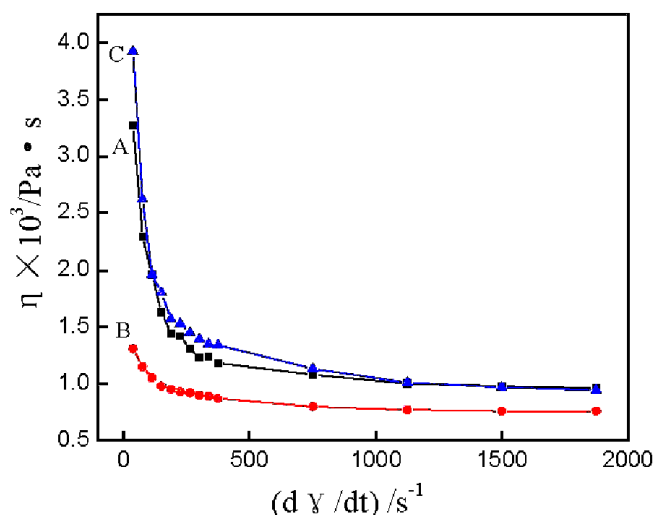


Figure 3. The rheological curve of the grafted product solution of soybean protein isolate under different salt concentrations [11]

However, the shear strength of the soy protein adhesive treated with methacrylic acid did not increase too much. Tang et al. treated soy protein adhesive with the hydrophobic monomer glycidyl methacrylate (GMA) to enhance its hydrophobicity [12]. They used ammonium persulfate-ammonium bisulfite (ASP- NaHSO_3) as an initiator to carry out the chemical reaction in the form of free radical polymerization. The shear strength of soy protein adhesive has a great relationship with its hydrophobic and hydrophilic groups. The hydrophobic group can improve the annual and water resistance of the adhesive, while the hydrophilic group can improve the bond strength between wood and adhesive. GMA, as a monomer with double shoulder and epoxy group, can provide these two groups for soybean protein adhesive at the same time, ASP- NaHSO_3 can be used as an initiator and can undergo redox reaction with soybean protein adhesive GMA was grafted on soy protein adhesive. According to the experimental results, when the amount of SMA reaches 3.39 g, the increase in shear strength reaches the maximum value. And when the amount of SMA reaches 4.52 g, the water resistance reaches the maximum value. Figure 4 shows these conclusions.

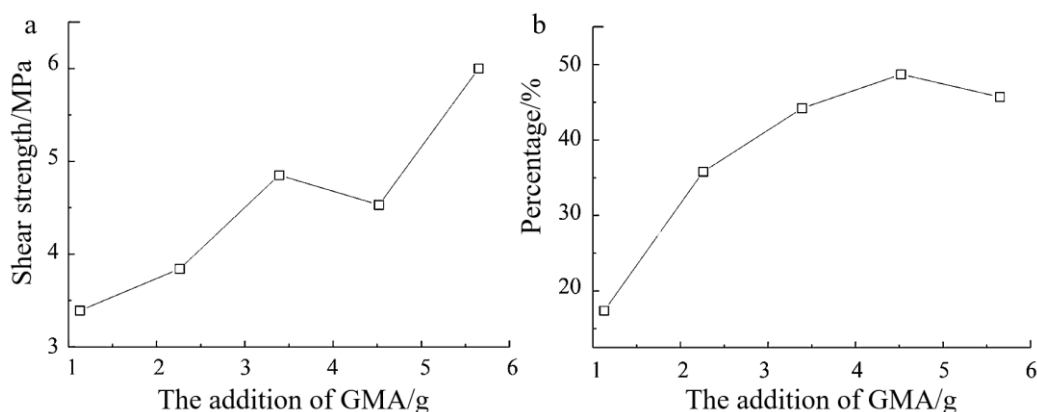


Figure 4. The effect of addition of GMA on shear strength and water-resistant ability [12]

These scholars also studied the change of this reaction on the shear strength of soybean protein adhesives at different temperatures. Reacting for three hours at 70 °C can maximize the shear strength of soybean protein adhesives. As shown in Figure 5, At 70 °C, the molecules of soybean protein begin to activate but do not decompose, and the properties of soybean protein do not change and it is easy to react with other reagents.

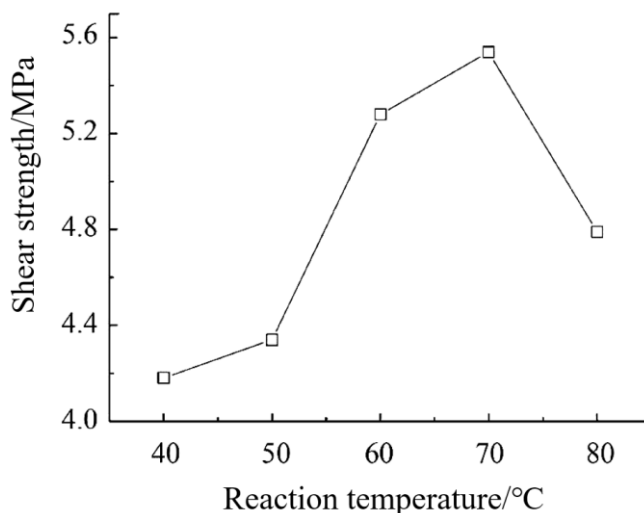


Figure 5. The effect of reaction temperature on shear strength [12]

At present, modified soybean protein isolate (SPI) is used in various fields. After graft modification of SPI, its emulsification, water absorption and other properties have been greatly improved, and the amino acid residues on SPI have been greatly improved. The base and polypeptide chain will undergo spatial changes to form different structures, and SPI can form different macromolecular structures with different molecules, such as SPI and gelatin composite membranes. At the same time, SPI can also be applied to different plastics industries such as Alcalase protease and Protamex complex protease.

In addition to graft copolymerization and cross-linking reactions, soy protein adhesives can be blended to improve its performance. Zeng et al. used the blending of soybean protein adhesive and white latex to prepare a blended adhesive for wood gluing [13]. Because the amino acid in protein has a poor blending effect with white latex, the phenolic resin was used as a cross-linking agent to obtain a homogeneous blend. It was determined experimentally that the mass ratio of urea-modified SPI to PVAc latex was 10:1, the blending time was 1 h, the cross-linking time was 1.5h, and the viscosity was 2090mPa·s. The dry and wet shear strengths between the bonded plywood were 1.97 MPa and 1.02 MPa. Compared with ordinary soy protein adhesives, these two strengths have been significantly improved.

3. Applications

Various modified substances of SPI are also widely used in the medical industry. SPI can be used as a dressing film for medical wounds [14], because in the mixed film of polysaccharide and protein, protein can provide a large number of binding sites, which is conducive to the adhesion of film material to cells. This material is used in wound healing and other aspects. There are very broad prospects. Because the protein polysaccharide structure is a biomass material, it is easy to decompose when it encounters water. And its water resistance is average, so a series of chemical reactions are often used to add some proteins and polysaccharides that are not easily hydrolyzed during production. Scholar Silva uses Chitosan and SPI made a hybrid film which greatly enhanced its properties [15]. At the same time, Song et al. grafted SPI with hydroxyethyl cellulose (HECO and 2-acrylamido-2-methylpropane sulfide (AMPS)) to obtain an example complex [16], which can be used as a drug carrier, and it has different responses to different pH values, and can accurately release the drug.

SPI is also used in people's lives. Because SPI has strong water absorption, moisturizing and antioxidant properties, it is often used as a surfactant. At the same time, SPI is rich in glutamic acid and amino acid complexes [17], which can promote the growth and development of human cells and repair damaged cells in the human body. SPI can also be used in food additives. It is biodegradable and non-toxic, and will not cause damage to people's bodies. Because it contains a large amount of amino acids and carotenoids, these nutrients are decomposed by SPI in the human body. It can be absorbed by people, it will reduce the incidence of liver and brain to improve liver function [18].

4. Conclusions

Soy protein adhesives have been studied to enhance their chemical and physical properties through many modification methods, including heat treatment, epoxy treatment, tannin treatment and graphene treatment. Therefore, these modification methods have been analyzed in this research, and the effect of modification is also further systematically discussed. With the progress of these researches, soy protein adhesives can be better used in different fields, which makes the environmental protection of soy protein adhesives, such as reducing fossil fuel emissions and pollution.

References

- [1] World Petroleum Industry, 1998.
- [2] Renkema J M S, Van T. Heat-induced gel formation by soy proteins at neutral pH[J]. Journal of Agricultural and Food Chemistry, 2002, 50(6): 1569-1573.
- [3] Luo Jing. Cross-linking architecture regulation and reinforcement mechanism of soy protein-based adhesive[D]. Beijing Forest University, 2018.
- [4] Huang J. Development and characterization of new form aldehyde-free soy flour-based adhesives for making interior plywood[D]. America (USA): Oregon State University, 2007.
- [5] Naotoshi M., Tetsuyuki S. A., Kunihiko K.. Conformational changes and functional properties of acid-modified soy protein[J]. Agricultural and Biological Chemistry, 1985, 45(5): 1251-1256.
- [6] Zhu Chao. Preparation and performance of soy protein materials with epoxy compounds modification[D]. Hubei University, 2017.
- [7] Zhang Xiaowei, Zhao Jianfeng, Lu Mingliang, Zhan Xianxu, Luo Jing. Study on tannin modified soy protein adhesive[J]. Chinese Science Citation Database, 2020, 35(05): 1-4.
- [8] Wang Liuliu. Study on preparation and performance of condensed tannin modified soy protein adhesive[D]. Beijing Forest University, 2021.
- [9] Sun Gang. Study on amination of graphene and its enhancement of soy protein adhesive[D]. Beijing Forest University, 2020.
- [10] Steinmetz L, Krinski T, et al. Modified Protein adhesive Binder and Process for producing[P]. US: 4687826, 1987-02-18.
- [11] Sun Chao. Studies on Graft Modification of Soybean Protein Isolate and Their Solution behaviors[D]. Jiangnan University, 2005.
- [12] Tang Weibo, Zhou Hua, Zhou Cui, Yang Cheng, Bai Huiyu, Liu Xiaoya. Synthesize and Characterize of Grafted Soybean Protein Adhesives[J]. Soybean Science, 2008, 27(06):1031-1036.
- [13] Zeng Nian, Xie Jianjun, Liu Junxia. Preparation and properties of blending adhesives for PVAc latex/modified soy protein isolate[J]. Chinese Science Citation Database, 2014,33(12): 3368-3373.
- [14] M G Jeschke, G Sandman, T Schubert et al. Wound Repair Regulation, 2005, 13(3): 324-331.
- [15] S S Silva, B J Goodfellow, J Benesch et al. Morphology and miscibility of chitosan/soy protein blended membranes[J]. Carbohydr. Polym., 2007. 70(1): 25-31.
- [16] Song Xiaoqing, Yang Cheng, Liu Xiaoya, Xu Fangping. Study on polyion complexes comprising hydroxyethylcellulose/poly(AMPS) graft copolymer and soybean protein isolate[J]. Jiangnan University, 2009, 4(21): 486-490.

- [17] M Maillot, N Darmon, M Darmon et al. Nutrient-dense food groups have high energy costs: an econometric approach to nutrient profiling[J]. J. Nutr., 2007, 137(7): 1815-1820.
- [18] S Proot, V Biourge, E Teske et al. Soy protein isolate versus meat-based low-protein diet for dogs with congenital portosystemic shunts[J]. J. Vet. Intern. Med., 2009, 23(4): 794-800.