

Development of Green Resin Using Solid Waste Protein Soybean Curd “Tofu” Production

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Abstract

One of the most concerns associated with many commercially available composites is that they used of non-degradable resins and fibers that primarily made using non-degradable, petroleum-based chemicals as feed stock. These conditions will create a serious problem in term of waste disposal after end of their life. Unlike petroleum, plant based protein and starches are yearly renewable. These resins are increasingly developed for various applications as replacements for non-degradable petroleum based resins. In addition, these resins may be easily composted after their life. In this study, Soybean Pulp Hemi-cellulose (SPH) was modified by cross-linking it with glutaraldehyde (GA). The modified SPH resins were characterized for its surface morphology, tensile and mass losses or biodegradability properties. The effect of GA on the surface morphology, tensile and biodegradability of the SPH resins were discussed. The SPH resins showed improved surface morphology and ductility. However, the increasing the GA content reduces the Young's modulus of the SPH resins. The SPH resins exhibited fracture stress point and Young's modulus maximum of and 3.02 MN/m², respectively, and biodegradability of 40.42% after 30 days placed on the open air. These properties seem to be sufficient for developing green composites from the SPH resins reinforced with natural fiber for indoor structural applications.

Keywords: Green Resin, Soybean Pulp Hemi-cellulose (SPH), Mechanical Properties, Biodegradation.

Introduction

Fiber reinforced composite materials have replaced metals in many applications. Initially developed for the aerospace applications because of their light weight and the ability to manipulate the properties in various directions as desired, composites technology has matured in the past few decades. Currently they are being used in a multitude of applications from automotive parts to circuit boards and from sporting goods to household appliances. At present they are also being used in civil and structural applications including buildings and bridges. One of the major concerns associated with most commercially available composites is that they use non-degradable fibers and resins that are primarily made using petroleum as feed stock. In most cases, non-degradability is required. However, their non-degradability has also created a serious problem in terms of waste disposal. Since composites are fabricated by combining two dissimilar materials they are difficult to be recycled or reused. While a small

fraction of the composites is incinerated to recover the energy value or crushed into powder and used as filler, most composites end up in landfills, at the end of their useful life, making that land unusable for several decades at the least. Both incineration and landfill disposal are environmentally unsound, wasteful and expensive. Further, at the current rate of consumption of the oil, by some estimates, the world reserves are expected only for the next 50 years or less [1].

In response to the concerns mentioned above there have been efforts to develop non-petroleum based composites that are environment friendly and fully sustainable, using plant based fibers and resins. Biodegradable resins produced from renewable resources such as plants, animal and microbes through biochemical reactions offer a convenient and environment friendly solution to the problem of plastic waste. Various biodegradable resins such as starch, wheat gluten, whey protein, and soy protein have been explored for application in making composites [2-6]. Compare with others, soy protein offers several advantages over synthetic resins [7]. First, the soy protein purification process is benign and environment friendly. Second, these proteins can form ductile and viscous polymers that can be used as resins. Third, the cost of raw materials is low. Fourth,

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soybean is an annual crop and is abundantly available worldwide. In the 1930s, Henry Ford pioneered the use of soy protein for plastic and fibers [8]. Ford used soy plastic for various car parts such as gear shift knobs, horn buttons and window frames in an effort to produce an all agricultural car. However, these efforts are stop it because of World War II. At present, because of the increased environment awareness and stringent environmental laws, most manufactures are looking towards greener and more environment friendly alternatives for conventional polymers and composites [9].

Soybean products are available commercially as defatted soy flour (SF), soy protein isolate (SPI), and soy protein concentrate (SPC). Chemically, SF, which requires less purification, contains about 55% protein and 32% carbohydrate, SPC contains 70% protein and 18% carbohydrate, while SPI contains 90% protein and 4% carbohydrate. Soy protein consists of various polar and reactive amino acids such as cystine, arginin, lysine, and hystidine which can be used for cross-linking it and improving the tensile and thermal properties. Several researchers [10-12] have shown that glutaraldehyde (GA) react with the amine groups in protein, particularly in an alkaline pH, to form intermolecular cross-links. Although GA can readily react with the amine groups, there has been no agreement on the reaction of protein with GA. Different mechanisms have been proposed for explaining the reaction between GA and proteins. Blass *et al.* [12] have shown that monomeric GA binds reversibly to proteins. Habeeb and Hiramoto [11] reported that GA reacted extensively with α -amino group of glycine and the α - and ϵ -amino groups of lysine, while it only partially reacted with α -amino groups of histidine and tyrosine. Chabba and Netravalli [13] cross-linked SPC using GA to form suitable resin system. As a result of the cross-linking, the strength of the SPC resin increased significantly while the moisture absorption decreased.

In the mean time, large quantities of solid wastes, named Soybean Pulp Hemi-cellulose (SPH) were discarded during protein soybean curd "tofu" production. In Indonesia, about 1.2 million tons/year SPH were produced and discarded as organic wastes. Only few amounts of SPH wastes were utilized as feed supplement. Investigation showed that fresh SPH contain 75-

80% of water content, but dried SPH consist of carbohydrates as hemi-cellulose 50-55%, protein

25-30% and lipid 10-15% so that this could be reasonably recovered and utilized by isolating the protein from the SPH to produce fully sustainable and biodegradable green resins.

Based on the above descriptions, modified of soy protein from the SPH using GA as cross-linking agent and glycerin as a plasticizer, to produce fully biodegradable and sustainable resin, mechanical and biodegradation properties of these resins will be carried out.

Experimental Methods

Soybean protein hemi-cellulose (SPH) from the solid waste "tofu" production around Jember was modified with GA. GA was used as cross-linking agent to obtain better mechanical and physical properties [12]. To process SPH to be resin, SPH powder was mixed with distilled water in ratio of 1:8 and 15% glycerin (by SPH weight) was added as plasticizer. The mixture was homogenized by using a magnetic stirrer for 30 minutes. After homogenizing, the pH of the mixture was adjusted to 11 using 0.2 m/liter NaOH solution. To obtain modified soybean protein hemi-cellulose (MSPH), 30%, 40% and 50% of GA (by weight of SPH) was added. The mixture of MSPH was then pre-cured for 30 minutes at 70°C, poured on Teflon coated sheets and dried at room temperature. The final MSPH resin curing was done for the pre-cured, the dried MSPH resin sheets in a hot press at 120°C for 30 minutes.

Surface morphology of MSPH resins were characterized by using *Dino Lite* Optical Microscope. Tensile properties of MSPH resin sheets were characterized in accordance with ASTM D 638. Conditioned resin sheets were cut into rectangular specimens of 20 mm x 180 mm x 10 mm dimensions. Three thickness measurements were carried out along the length of each specimen and the average of these values was used for calculating the fracture stress and Young's modulus. The tests were performed on tensile tester, model TM 113 Universal 30 KN. In the mean time, biodegradability of the SPH resins was evaluated by characterizing the mass changes after placed in the open air during 30 days. The mass changes of the SPH resins were calculated using equation (1) below.

$$dD = \left(\frac{m_i - m_f}{m_i} \right) \times 100\% \quad (1)$$

dD = Degree of degradation.

m_i = Mass of SPH resin before composting.

m_f = Mass of SPH resin after composting.

Results and Discussion

Figure 1 shows typical Optical Microscope photomicrographs of the surface morphology of the SPH resin containing 15% glycerin and (a) 30% GA, (b) 40% GA, and (c) 50% GA. As shown in the photomicrograph, the SPH resin with 50% GA showed lower roughness at the surface morphology as compared to the SPH resin with 30% GA. The improved of the surface morphology of SPH resins is attributed to the cross-linking between GA and SPH. It was, however, difficult to assess the average degree of cross-linking because of the complexity of the chemistry. The cross-linking was judged based on the improved tensile strength and moisture absorption after the GA modification as well as the significant increase in the viscosity immediately following the addition of GA to the SPH solution.

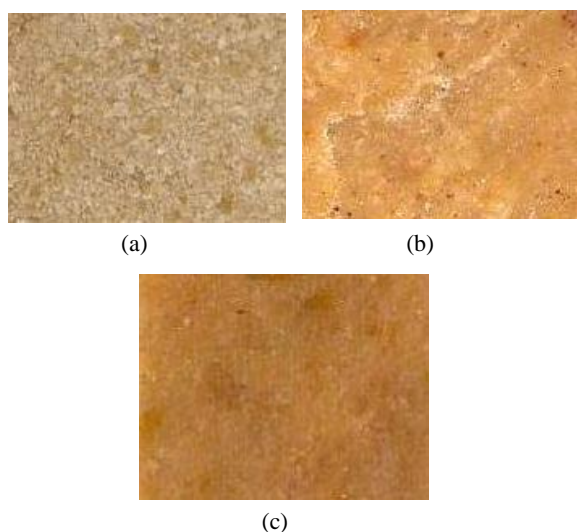


Figure 1. Photomicrograph showing the surface morphology of MSPH resin containing (a) 15% glycerin and 30% GA; (b) 15% glycerin and 40% GA; and (c). 15% glycerin and 50% GA.

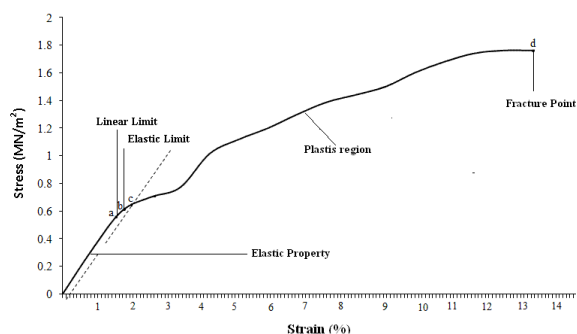


Figure 2. Typical stress versus strain plot for the MSPH resins with 15% glycerin and 30%, 40% and 50% GA .

Figure 2 shows the typical stress versus strain plot for the SPH resins containing 15% glycerin obtained from the Universal tensile tester model 113 30 KN.

This result was agreed with the theoretical predictions. As shown in the Figure 2 above, for small values of the strain, the stress-strain graph is a straight line; the stress σ is proportional to the strain ϵ . In general, this is called the linear region for material. Beyond the linear limit **a**, the stress is no longer linearly proportional to the strain. However, from **a** to the elastic limit or yield point **b**, the SPH resins still returns to its original dimensions when the applied force F is removed. The deformation up to **b** is said to be elastic. When the applied force is further increased, the strain increases rapidly. In this region, if the applied force is removed, the object does not return completely to its original dimensions; it retains a permanent deformation. The point **c** on the stress-strain graph is the ultimate tension strength σ_u of the MSPH resins. Beyond this point fracture occurs at point **d**. From **b** to **d** the MSPH resins is said to undergo plastic deformation. In general, if the ultimate tension strength and fracture points **c** and **d** are close together, the material is brittle; if they are far apart the material is said to be ductile.

Figure 3 shows stress associated with a given strain for the MSPH resin containing 15 % of glycerin and 30%, 40% and 50% GA. It is clear from Figure 3 that increasing GA content from 30% to 50% leads to increase in the fracture stress and the fracture strain points from 1.281 MN/m² to 2.401 MN/m² and 10.0 % to 18.3 % , respectively. It should be noted from Figure 3 that increasing the GA contents on the SPH resins leads to increase in distance between ultimate tension strength point **c** and fracture stress point **d**. This means that increasing the GA contents on the SPH resins to cause increasing ductility of the SPH resins.

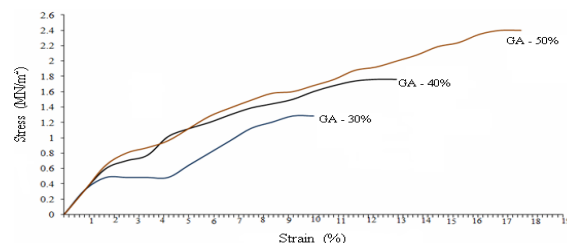


Figure 3. Stress versus strain plots for modified SPH resin with containing 15% of glycerin and 30%, 40%, and 50% of glutaraldehyde (GA).

Tensile properties such as tension strength (σ), strain and Young's modulus (E) of SPH resins are summarized in Table 1. It is evident from these data that increasing the GA content from 30% to 50% increases UTS of the SPH resin from 1.30 MN/m² to 2.09 MN/m², however, Young's modulus of the SPH resin decreases from 3.02 MN/m² to 2.82 MN/m². These confirms that the GA is an good cross-linking although in the special case further increasing GA content does not improve the tensile property.

Table 1. Values of tension strength (σ), strain (ϵ), and Young's Modulus (E) of SPH resins

Amount of GA in the sample (%)	σ (MN/m ²)	ϵ (%)	E (MN/m ²)
30	1.30	0.43	3.02
40	1.68	0.53	2.85
50	2.09	0.74	2.82

Table 2 summarizes the effect of the GA mass loss or degree of degradation of the SPH resins after 30 days placed on the open air. It is evident from Table 2 that increasing the GA content reduces the mass loss of SPH resins. The SPH resin with containing 30% GA was lost 40.42% of mass after 30 days placed in the open air.

Table 2. Mass loss (degrees of degradation) of SPH resins after composting

Amount of GA in the sample (%)	Initial Mass (gram)	Final Mass (gram)	Degrees of Degradation (%)
30	4.7	2.8	40.42
40	4.7	3.1	34.04
50	4.7	4.1	12.77

Very limited information, however, is available on the biodegradability of green resins in soil or other environments. Takagi and Ochi [14] examined weight loss of biodegradable resin as a function of composting time. They found that the weight loss rate was very slow in the initial period of up to 15 days but accelerated after that. The weight loss of the biodegradable resin after 30 days composting was found 15%. One important point to be noted is the use of the biodegradable resins in making green composites has considerable advantages in enhancing their biodegradability.

Conclusions

It has been successfully developed resin from modified SPH with GA to give better mechanical properties. As the petroleum supplies dwindle and get costlier, plant based biodegradable resin will become cost effective. It is also expected that the SPH resin may be used

in development of fully biodegradable composites with good mechanical properties so it can be use in many applications, likes for packaging and panels for indoor and outdoor applications, secondary structural applications in automotive and housing.

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