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Effect of Modifying Shellac with Citric Acid on Shellac-Bagasse Biocomposite

Nanik Dwi Nurhayati[1,*], Karna Wijaya[2], Triyono[2] and Eddy Heraldy[3]

[1]Departement of Chemistry, Faculty of Teaching and Education, Sebelas Maret University, Surakarta 57126, Indonesia
[2]Departement of Chemistry, Faculty of Mathematics and Natural Science, Gadjah Mada University, Yogyakarta 55281, Indonesia
[3]Departement of Chemistry, Faculty of Mathematics and Natural Science, Sebelas Maret University, Surakarta 57126, Indonesia

*Corresponding author: E-mail: nanikdn@gmail.com

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This study was aimed at modifying local Shellac with citric acid in varied concentrations of 2, 4, 6, 8 and 10 % (w/w) to prepare Shellac-Bagasse (Sh-Bg) biocomposite and determining its physico-chemical properties. The biocomposite was made from the natural Shellac matrices and Bagasse fibers. Physico-chemical properties of non-modified Shellac and Shellac modified with citric acid including functional groups, intrinsic viscosity, density, and mechanical tensile strength were characterized using Fourier transform infrared spectrometer (FTIR), Oswald viscometer and Universal Testing Machine (UTM). The analysis results showed an optimum modification of shellac-citric acid at a concentration of 4% (w/w). FTIR analysis of the modified Shellac showed a broad absorption at 3448 cm^{-1} which indicated the presence of hydroxyl groups (-OH). The presence of C=O ester groups was indicated by the absorption appearing at 1712 cm^{-1}. The absorption at 1251-1250 cm^{-1} indicated the presence of C-O groups, while the presence of $-CH_2$ methylene groups was indicated by the absorption at 1465 cm^{-1}. The modified Shellac with its optimal intrinsic viscosity of 169.97 mL/g indicated that there was a reaction between citric acid and Shellac to form an ester, so that the polymer chains formed were longer with a low density of 0,6662-0,8168 mg/L when compared to Shellac without modification. The low density indicated that the citric acid-modified Shellac could be processed to be biocomposite. The biocomposite was made with various compositions of Shellac and Bagasse with hot press at 80 °C and under a pressure of 6 Kgf/cm^2. The optimum ratio of Shellac to Bagasse in Shellac-Bagasse (Sh-Bg) biocomposite was of 60:40 %. While, the analysis using Universal testing machine resulted a mechanical tensile strength of 0.6 MPa and an elongation at break of 0.45 %.

Keywords: Shellac, Bagasse, Biocomposite, Modification, Analysis.

INTRODUCTION

The need for biocomposites in various fields continues to increase. Unfortunately, it has not been supported by natural materials. Hence, further exploration for renewable natural resources as natural matrices becomes necessary [1,2].

The biocomposite is a composite whose one of components namely matrix and reinforcement, come from natural materials. Various types of matrices used in manufacturing biocomposites depends on the designation, such as metals, ceramics and polymeric matrices [3,4]. An innovation developed to overcome environmental problems was done by producing environmental friendly biocomposite materials. Biocomposites with natural matrices have developed more rapidly and become alternative bio-based materials to generate biodegradable products due to their favourable properties such as being more environmentally safe and eco-green, compared to synthetic materials. Biocomposites are applicable in a variety of applications including packaging, pharmaceutical, agroindustry, agriculture, automotive, buildings and various industries [5,6]. As the time goes, the applications of biocomposites are getting wider, but not accompanied by variations of natural polymer matrices. This phenomenon encouraged the authors to develop local Shellac obtained from the Kesambi trees PT Banyukerto Probolinggo, East Java as a natural matrix. Local shellac as a biocomposite needs to be explored to increase its economic value by improving its physical properties. Shellac as natural matrices can be applied as a biocomposite. It is biodegradable, non-toxic, adhesive, insoluble in water, petroleum derivative products (premium, lubricating oil, kerosene), and well soluble in alcohol (methanol, ethanol, *etc.*). It is also a natural polymer to produce resin, bioadesive, a natural form of plastic and a non-conductive substance (having low thermal conductivity). Natural matrix that have been developed includes chitosan, casein, soybean, cassava flour, corn flour, albumin, silica soda, collagen [7-12].

Shellac is a natural resin consisting of polyester and esters containing hydroxyl and carboxyl groups which can react with ethanol. It also has hydroxyl groups to form ester compounds used in making biocomposites. Shellac has a low density and good thermal stability that are needed in making lighter and more stable biocomposites [13-18]. The biocomposite produced contained void that could affect the bonds between the fiber and Shellac to decrease in biocomposite tensile strength [19].

Natural fibers, biopolymers, and biocomposites contribute to the development of the technology of combining fiber materials with natural matrices. Natural fibers consist of plant fibers and animal fibers. Some reinforcement materials which have been developed are coconut fiber, bamboo, ramie, jute, kenaf, and cotton. Natural fibers provide more advantages compared to synthetic fibers given that they are abundant, cheap, renewable and environmental friendly. These properties allow them to be alternative components for biocomposite materials [20-23].

The abundance of bagasse fibers with their utilization that was still limited to non-structural materials inspired the authors to increase their economic value by developing them as biocomposite materials [24-26]. This research makes natural matrix shellac biocomposite through citric acid modification to improve the physicochemical properties of shellac so that it can be used as a biocomposite with variation compositions of citric acid of 2, 4, 6, 8 and 10 % (w/w). Biocomposites are made with various compositions of shellac and bagasse. Some physico-chemical properties of biocomposite including mass, intrinsic viscosity, functional groups and mechanical tests were analyzed.

EXPERIMENTAL

This study used Shellac which was taken from PT. Banyukerto Probolinggo East Java, as matrices of bio-based composite. Bagasse fibers as its reinforcement materials were taken from PT. Tasikmadu, Karanganyar, Central Java, Indonesia. Whereas all chemicals used as analytical reagents were taken from Merck Company.

Preparation of modified Shellac: Shellac was prepared from seedlac and sieved at 100 mesh. Seedlac was extracted using ethanol (1:5), then stirred for 2 h, heated at 60 °C, filtered using Whatman 42 filter paper (125 mm) to remove impurities that were still dissolved, and then cooled. Shellac was modified with citric acid with concentrations of 2, 4, 6, 8 and 10 % (w/w) at 50°C, then stirred for 0.5 h. The intrinsic viscosity analysis was done using Ostwald viscometer with concentrations of 1, 0.5, 0.25, 0.125 and 0.0625 %. Citric acid-modified Shellac and non-modified Shellac were then analyzed by Fourier transform infrared spectroscopic analysis, while the densities were analyzed using Picnometer.

Manufacturing biocomposite from Shellac: Non-modified Shellac and Shellac modified with citric acid of 4 % were used to produce biocomposite, combined with Bagasse fibers with varied ratios of Shellac to Bagasse of 60:40, 50:50 and 40:60 %. Both of materials were mixed using stirring machine and then put into the oven to evaporate the ethanol to let the matrices completely cover the fibers. Afterwards, the materials were put onto a mold made of stainless steel until evenly distributed and then placed in a hot press at 80 °C for 10 min under a pressure of 6 Kgf/cm^2. The mold was then cooled using a cold press at room temperature for 15 min to produce a compact biocomposite called Shellac-Bagasse (Sh-Bg) biocomposite. The next process was cutting the product on a dumbel mold. Finally, the mechanical property test was done to measure the tensile strength of the products using UTM.

Detection methods: Oswald viscometer, using ethanol, and Picnometer were used to determine Shellac intrinsic viscosity and density, respectively. Fourier transform infrared (FTIR) spectroscopic analysis was conducted on a type 8400s Shimadzu spectrometer. FTIR spectra in the transmittance were recorded in the range of 4000-400 cm^{-1} at room temperature using the KBr technique spectrometer. Universal Testing Machine Shimadzu EFH-EB20-40L was used to measure the tensile strength of each sample of the three specimens, according to ASTM D638-02 [27].

RESULTS AND DISCUSSION

Shellac was modified by citric acid with varied concentrations of 2, 4, 6, 8 and 10 % (w/w). The results of density analysis are showed in Table-1. Both modified and non-modified Shellac had almost the same densities ranging from 0.7163 to 0.8168 meaning that citric acid-modified Shellac had lower density. This is the property needed in producing light biocomposite. The results of the analysis of intrinsic viscosity is shown in Table-2. As seen, the non-modified Shellac had an intrinsic viscosity of 145.8 mL/g, while the modified one with 4 % citric acid had an intrinsic viscosity of 169.97 mL/g. This shows that there has been a reaction between citric acid with Shellac to form esters, as a result the longer chains polymer and larger molecular mass compared to shellac without modification. The increase in intrinsic viscosity is proportional to the increase in molecular weight. The greater concentrations of citric acid are added causing intrinsic viscosity to decrease. The reaction (Fig. 1) that occurred can be explained by reported work [13].

TABLE-1
SHELLAC DENSITY

Citric acid	Concentration (%)				
	1	0.5	0.25	0.125	0.0625
2 %	0.7258	0.7163	0.7297	0.7367	0.7665
4 %	0.7555	0.7482	0.7598	0.7603	0.7652
6 %	0.7622	0.7588	0.7573	0.7553	0.7805
8 %	0.7852	0.7595	0.7688	0.7581	0.7629
Without modification	0.8168	0.7157	0.7662	0.7438	0.7484

TABLE-2
SHELLAC INTRINSIC VISCOSITY

Without modification (mL/g)	Add citric acid 6 % = 166.51				
	2	4	6	8	10
145.8	150.11	169.97	166.51	165.42	164.15

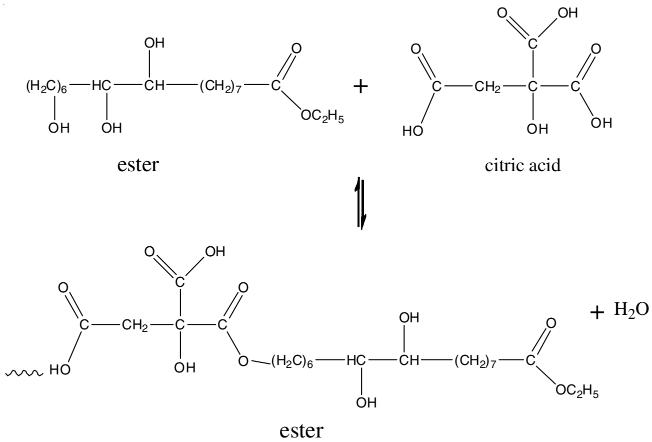

Fig. 1. Ester reaction within citric acid of 4 %

The decrease in viscosity occurred after the addition of citric acid of more than 4 % because the ester reaction did not occur in the straight chain but in the branching of -OH groups [13].

The FTIR analysis of the non-modified Shellac and the citric acid-modified Shellac showed a broad absorption on both 3411 and 3426 cm^{-1} indicating the presence of hydroxyl groups. Shellac modified with 4 % citric acid seemed to have a broad absorption of -OH indicating the free hydroxyl groups the more the -OH bonded. The absorption of C=O ester that seemed strong enough at 1716 cm^{-1} strongly indicated that citric acid modification can produce ester compounds. The strong absorption at 1251-1250 cm^{-1} indicated the presence of C-O groups. The absorption at 1465 cm^{-1} indicated the presence of $-CH_2$ methylene groups.

Shellac contains aleuritic acid consisting of carboxylic groups (-COOH) and alcoholic groups (-OH) which can react with ethanol which has –OH groups to form ester compounds used in producing biocomposites. Shellac dissolution process can be done in ethanol with citric acid through esterification reaction at a temperature of 50 °C. Farag and Leopold [16] stated that the difference of electronegativity values of carbon and oxygen is quite large so as to make the C=O bonds polar. The functional group of carboxylic acids (-COOH) at the molecular end of the aleuritic acid causes a tendency to be polar and soluble in water. The long alkyl chains cause molecules to tend to be non-polar and only their small portion dissolves in water. The spectrum of Shellac is shown in Fig. 2.

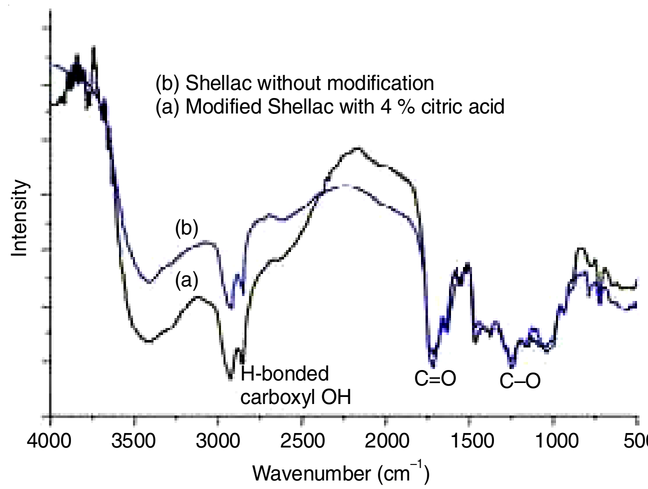

Fig. 2. FTIR spectra of non-modified Shellac and modified Shellac citric acid of 4 %

Mechanical analysis: Shellac modified with 4 % citric acid as matrices and Bagasse fibers were used to produce biocomposite with ratios of Shellac to Bagasse of 60:40, 50:50, and 40:60. Shellac-Bagasse (Sh-Bg) biocomposites produced are shown in Fig. 3.

Fig. 3. (a) Non-modified Sh-Bg biocomposite, (b) Sh-Bg biocomposite modified with citric acid with a ratio of 60:40 %, (c) Sh-Bg biocomposite modified with citric acid with a ratio of 40:60 %, (d) Sh-Bg modified with citric acid with a ratio of 50:50 %

The tensile strength of Shellac-Bagasse (Sh-Bg) biocomposite is shown in Table-3. When the biocomposite receives a load, the stress field will move to the strain field. The tensile strength testing showed that Bagasse fiber escaped from Shellac. This was due to the strength or interfacial bonds between the matrices and the fibers were not large enough.

TABLE-3
SHELLAC-BAGASSE (Sh-Bg) BIOCOMPOSITE
MECHANICAL ANALYSIS

Shellac (MPa)	Biocomposite Shellac-Bagasse (MPa)		
	40:60	50:50	60:40
0.075	0.115	0.413	0.602

Conclusion

Shellac could be investigated from seedlac. Shellac got its optimum value when modified with 4 % citric acid. The analysis of FTIR showed the presence of functional groups -OH, CH_2, ester C=O and C-O. Shellac-Bagasse biocomposite could be made with hot press at a temperature of 80 °C and under a pressure of 6 Kgf/cm^2. The analysis of mechanical properties using Universal Testing Machine showed that largest value of the biocomposite was 0.602 MPa with the elongation at break of 0.45 %.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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