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MODIFICATION OF LAC INSECT SECRETION WITH CITRIC ACID AS NATURAL MATRIX IN PREPARATION OF BIOCOMPOSITE

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Abstract

The objective of this research was to know the effect of addition citric acid on intrinsic viscosity, functional groups, and thermal properties of lac insects secretion, and also to know the mechanical properties of biocomposite from citric acid modified lac insects secretion as natural matrix and reinforcement ramie fiber.

Lac insects secretion was dissolved in ethanol with a ratio of 1: 2 to generate the natural matrix of lac insects secretion. Then natural matrix of lac insects secretion was modified by the addition of citric acid, concentration 5%, 10%, 15%, 20% and 25% m/m. Biocomposites were prepared from fiber ramie and modificated lac insect secretion by citric acid with a comparison matrix of 40% and 60% random fiber. Biocomposites manufacturing process with temperature at 90° C and a pressure of 90 kgf/cm^2. The viscosity of lac insect secretion was measured by a viscometer. The functional group of lac insects secretion was characterized by FTIR and the thermal properties of its was characterized by DTA-TGA. The mechanical properties of biocomposites were measured by tensile tester.

The addition of citric acid effected on intrinsic viscosity of lac insect secretion. The addition of 5% citric acid produced maximum intrinsic viscosity. Spectra of FTIR showed that the reaction occured between lac insect secretion in ethanol and citric acid. The optimum viscosity can raise the melting point of the natural matrix. The tensile strength, strain, and Young’s modulus of biocomposite from ramie fiber and modificated lac insect secretion was 5.129 MPa, 0.301%, and 1759.450 MPa, respectively.

Key words: biocomposites, citric acid, lac insects secretion, natural matrix, ramie fiber.

INTRODUCTION

Biopolymer has been developed as natural matrix for composites, such as starch, soybean, and chitosan (Lanzilotta, *et al*., 2002; Wollerdorfer and Bader, Lodha and Netravali, 2002; Curvelo, *et al*., 2001; Cyras, *et al*., 2001). This is done because persistence of plastics in the environment, the shortage of landfill space, the depletion of petroleum resources, concerns over emissions during incineration, and entrapment by and ingestion of packaging plastics by fish, fowl, and animals have spurred efforts to develop biodegradable/biobased plastics (Mohanty, *et al*., 2005; Mujiyono, *et al*., 2010a). Production of biodegradable biobased material is now widely expected to contribute to the solution of the problem, since biodegradable biobased material would enter the material cycles in the environment.

Composites consist of two or more distinct constituents or phases, which when married together result in a material with entirely different properties from those of the individual components. Typically, a man made composite would consist of a reinforcement phase of stiff, strong material, frequently fibrous in nature, embedded in a continuous matrix phase.

Biocomposites have been the subject of international research since at least the mid-1990s and a number of practical applications are now emerging, including interior lining for automotive components, packaging materials, insulation, acoustic absorption panel, building materials, and housings for notebook computers. Commercial interest in manufacturing these products is driven by the derivation of the polymers from renewable sources as well as by their specific properties including biodegradability (Hashim *et al*., 2006, Plackett and Vazquez, 2004; Mujiyono, *et.al*., 2010a)

Biocomposites are composite materials comprising one or more phases derived from a biological origin (Fowler *et al,* 2006). Biocomposite with natural matrix developed more rapidly because they are more environmentally safer. The natural matrix was used in this experiment was obtained from Kesambi tree lac from secretion of lac insect. The lac is resinous compound which has special properties: biodegradable, non-toxic and provides immense employment opportunities (Mujiyono, *et al*., 2010a). Naturally, the soft-bodied lac insects produced a resinous secretion which protects them from adverse environment. The major constituent of lac is the resin and other constituent of lac is the resin and other constituents present were: dye, wax, sugar, proteins, soluble salts, sand, woody matter, insect body debris. (Mujiyono, *et al*., 2010b). Shellac is also produced from lac insect (*laccifier lacca*) that has an attractive material and economically important species (Sharma, *et al*., 2005). The secretion of lac insect on Albazia tree (ISA) as a candidate feasible biobased matrix for biocomposite with the main constituent aleuritic acid (Mujiyono, *et al*., 2010a). ISA disbursement method with aleuritic acid chemical structure can be done by using the solvent ethanol (Mujiyono, *et al*., 2010a).

Reference study showed that the lac is secretion of lac insect. It is renewable, biodegradable versatile and has good bonding strength, non toxic resin, which leads great potency of lac as natural matrix for biocomposite. A feasibility of the matlac as natural polymeric matrix composite or green matlac composite reinforced by ramie-woven fiber has relatively the same tensile strength to the composite of polyester (Mujiyono, *et al*., 2010a; Mujiyono, *et al*., 2010c). The matlac matrix is well compatible with ramie, indicated by contact angle of about 30^0 (Mujiyono, *et al*., 2010c). The biocomposite potents to be a novel material from renewable resources. Plain weave hybrid ramie–cotton fabrics were used as reinforcement in polyester matrix composites. The tensile strength of the composites was determined as a function of the volume fraction and orientation of the ramie fibers. Values of tensile strength of up to 338% greater than that of the matrix were obtained which shows the potential of the ramie fiber as reinforcement in lignocellulosic fiber composites. (Paiva Ju´nior, *et al*., 2004)

Investigations were conducted to modification secretion of lac insect by esterification using citric acid. The objective of this research was to know the effect of addition citric acid on intrinsic viscosity, functional groups, and thermal properties of lac insects secretion, and also to know the mechanical properties of biocomposite from citric acid modified lac insects secretion as natural matrix and reinforcement ramie fiber.

MATERIALS AND METHODS

Materials

Natural matrix of biocomposite was prepared from secretion of lac insect that separated from Kesambi plant and collected. Ethanol p.a. from Aldrich Lab, Yogyakarta, Indonesia was used as lac solvent with composition 1:2. Secretion of lac insect is reacted with citric acid concentration 5, 10, 15, 20, and 25% m/m.

Equipment

Yield of reaction product was determined with gravimetry technique by using balance. Intrinsic viscosity of insect secretion with and without modification was measured by using viscometer Ostwald in Organic Chemistry Lab, Yogyakarta State University, Yogyakarta. Infrared spectra were recorded on KBr pellets by using a Shimadzu FTIR spectrophotometer in Indonesia Islam University, Yogyakarta. Thermal properties of reaction product after modification were determined by using DTA-TGA analyzer in Leather Technology Academy, Yogyakarta. X-Ray diffractogram of modificated insect secretion was determined by using XRD diffractometer in Engineering Faculty, Gadjah Mada University ,Yogyakarta.

Procedures

Sample Preparation

Natural matrix was prepared by solving secretion of lac insect into ethanol p.a. at a room temperature with mass ratio of 1:2 for 6 hours. Natural matrix was herein after referred as matlac (matric lac). Meanwhile, modificated matrix was prepared through esterification reaction between secretion of lac insect with citric acid. Reaction was conducted at 50^0C with agitation during 2 hours. Afterward, modificated matrix was ready to be characterized. Biocomposites were prepared from fiber ramie and modificated lac insect secretion by citric acid with a comparison matrix of 40% and 60% random fiber. Biocomposites manufacturing process with temperature at 90° C and a pressure of 90 kgf/cm^2.

Characterization

Matrix from secretion of lac insect is characterized yield by gravimetry technique. The viscosity of lac insect secretion before and after modification by using citric acid was measured by a viscometer. The functional group of lac insects secretion was characterized by FTIR and the thermal properties of its was characterized by DTA-TGA. The crystallinity of lac insect secretion was characterized by XRD diffractometer.The mechanical properties of biocomposites were measured by tensile tester.

RESULT AND DISCUSSION

Yield of Matrix Matlac from Modificated Secretion of Lac

Modifications carried out by adding citric acid into a liquid secretion shellac (matrix matlac of secretion of lac insect that are dissolved in ethanol with a ratio of 1:2) with modifier concentration 5, 10, 15, 20, and 25% m/m. The process of dissolving shellac in ethanol performed at room temperature to obtain a homogeneous liquid secretion of lac insect, further into the liquid matrix of SKL matlac modifier is added through esterification reaction at a temperature of 50^0C and stirring for 2 hours. The reaction product obtained weighed next to obtain the data yield from each product as shown in Table 1.

Table 1. *Yield* of modificated secretion of lac insect

No	Matrix matlac of secretion of lac insect with adding	*Yield* of matrix (%) at adding *modifier*				
		5%	10%	15%	20%	25%
1	Citric acid	98.45	99.65	89.09	100.00	98.89

Based on the data from Table 1. indicated that the product matrix of secretion of lac insect has a very high yield between 89.09% to 100%. The addition of citric acid 20% into the matrix matlac of secretion of lac insect can produce 100% of the reaction product.

Intrinsic Viscosity of Modificated Natural Matrix Matlac from Secretion of Lac Insect

Matlac matrix of a modified secretion of lac insect was analyzed intrinsic viscosity using Ostwald viscometer. Intrinsic viscosity for matlac matrix of secretion of lac insect before modification was 72.93 cP. Table 2. showed intrinsic viscosity data of modified matlac matrix. The *intrinsic viscosity* is a measure of the intrinsic ability of a polymer to increase viscosity in a given fluid. It is defined as the limit of the reduced viscosity as the polymer concentration approaches zero.

Table 2. Intrinsic viscosity of modificated matrix from secretion of lac insect

No	Matrix matlac of secretion of lac insect with adding	Intrinsic viscosity (mL/g) at adding *modifier*				
		5%	10%	15%	20%	25%
1	Citric acid	74.684	48.535	55.250	51.767	43.067

Based on the intrinsic viscosity in Table 2. it can be seen that the addition of citric acid 5% can increase the intrinsic viscosity of the matrix matlac. The addition of 5% concentration can be produced much longer molecular chain matrix or the highest intrinsic viscosity. However, the addition of as much as 25% of citric acid produces a matrix with the lowest intrinsic viscosity. This indicated that the optimum concentration for modification matlac of secretion of lac insect was the addition of citric acid by 5%. The high intrinsic viscosity means matlac matrix with the addition of 5% of citric acid has the highest molecular weight. The high molecular mass matlac matrix indicated the molecular chain length. The reaction can occurred between –OH in the long chain molecule of citric acid with –COOH of lac insect secretion, is shown Figure 1.

The long-chain molecules that can affect the thermal stability and the transition temperature of the matrix. The intrinsic viscosity of a polymer is a function of many parameters, including polymer molecular weight and molecular weight distribution, polymer/solvent interactions, temperature, shear rate, branching, and copolymer composition. The molecular weight average obtained from viscosity measurements is the viscosity average molecular weight, Mv, whose value lies between Mn and Mw, but closer to Mw.

Requirements of a polymer matrix composites can be summarized from several references (Schwartz, 1984; Feldman, 1989; Kavelin, 2005). First, the matrix must be able to withstand and protect the fiber. Thus the fiber matrix must be able to wrap properly and does not cause excessive internal strain between the fiber and the matrix. Second, the matrix must always be able to keep the fiber in place so it does not disintegrate. Third, the matrix must be able to distribute the load to the fibers. This means that the matrix must have a good bond to the fiber. The increasing chain length of matrix is expected to have thermal properties similar to hemp fiber composed of cellulose threads that have high thermal stability. Furthermore, the increasing length of the molecular chain of matrix can certainly improve the mechanical properties of the resulting biocomposites.

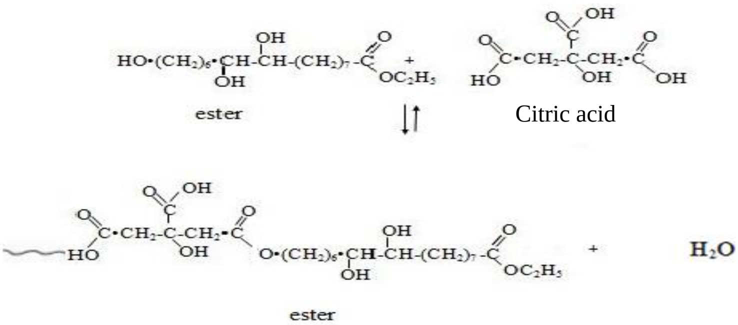


Figure 1. Chemical structure of modificated matrix by citric acid 5%

Modification of natural matrix by citric acid with concentration higher than 5% caused decreasing in intrinsic viscosity of matrix without modification. The increasing in concentration of citric acid caused the decreasing of intrinsic viscosity, except in addition citric acid 10%. The decreasing of viscosity can be caused the reaction of ester formation at branch in molecule, is shown Figure 2.

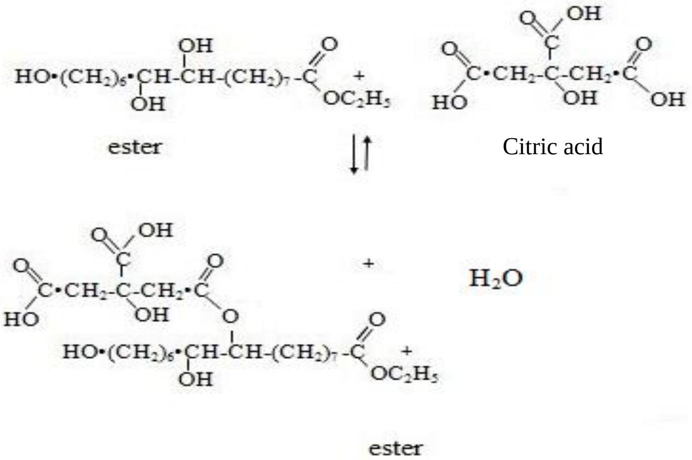


Figure 2. Chemical structure of modificated matrix by using citric acid with concentration higher 5%

Functional Groups of Matrix Matlac from Secretion of Lac Insect)

Secretion of lac insect is composed of biobased material aleuritic acid is polar because it has a carbonyl functional group (C = O) (Mujiyono, *et. al*., 2010a). According to Bodner (2004), the electronegativity difference between carbon and oxygen is large enough to make the C = O tends polar. Carboxylic acid functional group (-COOH) at the end of the molecule has a tendency aleuric acidic nature of polar and soluble in water. Long alkyl chains, causing the molecules tend nonpolar and only the water-soluble fraction. Therefore, the method of disbursement aleuritic acid with the chemical structure of a matrix Matlac can be performed using ethanol solvent.

Matrix matlac without modification and after modified with citric acid is shown in Figure 3. Based on FTIR spectra can be seen that the matrix before and after modified matlac showed absorption bands at specific wave numbers are almost the same. This shows that the functional groups of matrix before and after the modified similar qualitatively.

Matrix Matlac before the modified showed absorption bands more sharply than matlac matrix after modification. After modification with citric acid 5% showed more broad absorption band especially at wave numbers indicating alcoholic functional groups-OH,-CH methylene group, an aromatic ring. The addition of citric acid into matlac matrix showed more absorption bands widened again mainly on the wave number indicates the -OH and C = O ester groups and the presence of a new absorption band at -1500 cm^{-1} region. Furthermore, the addition of as much as 5% of citric acid appeared two absorption bands around 1700 and 1720 cm^{-1} indicating the presence of C = O hydrogen bond and C = O free. The existence of both types of the C = O can amplify low intrinsic viscosity of the data matrix with the addition of citric acid to matlac. Increasing the hydrogen bond index (the hydrogen bonds) in the matrix matlac would have reduced viscosity.

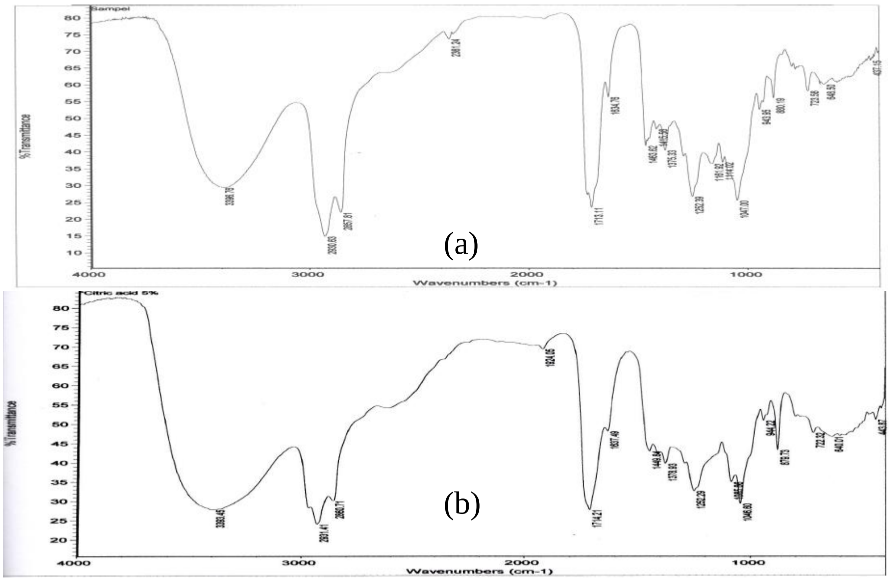


Figure 3. Spectra FTIR of matrix matlac from secretion of lac insect (a). before modification, (b). after modification with citric acid 5%

Based on FTIR spectra can be stated that there wasn't difference in FTIR spectrum between matrix matlac from secretion of lac insect before modification with after modification significantly. Those spectrum showed –OH acoholic and ester functional groups. The addition of citric acid in the matrix matlac of secretion of lac insect caused a reaction between aleuritic acid with citric acid. The wide absorption band at a wave number indicated the-OH and C = O groups. The presence of -OH and C = O to form hydrogen bonds to strengthen the intrinsic viscosity of the data, the lower the molecular chain length of the matrix matlac. Interpretation of functional groups for the matrix matlac before and after modified with citric acid can be seen in Table 3. The functional groups are often generated by the chemical reaction of citric acid with hydroxyl group in aleuritic acid of matrix.

Tabel 3. Interpretation of functional groups for the matrix matlac

Wave number of secretion of lac insect	Wave number of matrix with adding citrc acid 5%	Functional Group
3396.76	3393.45	-OH
2930.63	2931.41	C-H
2857.81	2860.71	C-H
1713.11	1714.21	C=O ester
1634.76	1637.49	C=O ester
1463.62	1449.84	$-CH_2-$
1415.56		$-CH_2-$
1375.33	1378.93	$-CH_3-$
1252.39	1252.29	C-O ester
1161.92	1085.66	C-O ester
1114.02	1046.60	C-O ester
1047.00		C-O ester

All the FTIR peaks showed functional group characteristic of matrix matlac of secretion of lac insect before and after modification with citric acid, i.e. –OH, C=O, and C-O group, appear in all spectra. Closer inspection revealed two unique peaks in the spectrum of Matlac after modification with citric acid 5% m/m, one appearing around 1714.21 cm^{-1}, arising from the stretching vibration of –C=O ester, and one at 3393.45 cm^{-1}, arising from the stretching vibration of -OH alcoholic group. Two peaks in FTIR spectrum of lac insect after modification were wider than theirs before modification. Both therefore due to the existence of-OH and –C=O hydrogen bonding caused by chemical reaction when treated with citric acid.

FTIR analysis also allowed verification of ester bond formation in matrix before and after modification. All material before and after modification can be used as matrix in preparation biocomposite, because those materials had the same characteristic functional group, i.e. –OH and C=O, respectively (Chin-San Wu, 2007).

Thermal Properties of Matrix Matlac from Secretion of Lac Insect

The results of the analysis of thermal properties by using DTA-TGA is shown in Figure 4. Figure 4. DTA-TGA thermogram for matrix without and with modification through the addition of citric acid 5%. Based on Figure 4. DTA thermogram showed that the thermogram pattern for matlac from secretion of lac insect without and with the addition of phthalic anhydride have almost the same pattern, ie a sharp endothermic peak at around 100^0C.

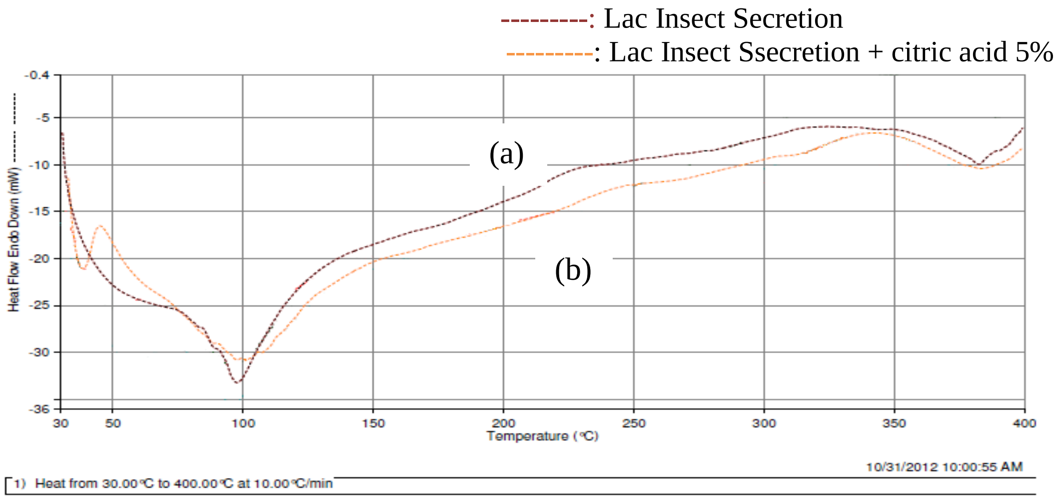
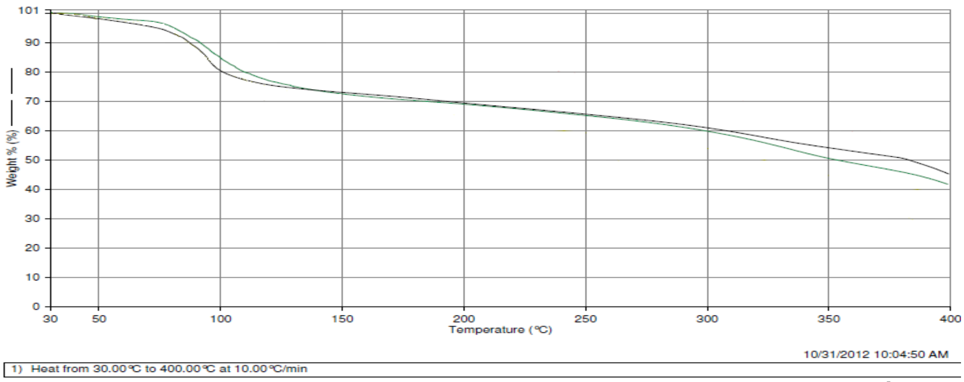


Figure 4. DTA-TGA Thermogram for matrix matlac of secretion of lac insect (a). without modification and (b). addition of citric acid 5%

Based on thermogram DTA, all matrix had glass transition. This showed that all matrix had amorphous region. 86.71°C dan 80.76°C Glass transition is an character of amorphous region. Glass transition temperature, Tg values characterized pure polymers, polymer blends, copolymers, as well as matrices in polymer-based composites. Tg as function of composition reflect miscibility (or lack of it) and determine all properties. There is no glass transition temperature Tg; there is a glass transition region. The change from the glassy state into a liquid or a rubbery state is gradual. Tg values are reported by analogy with the melting temperature Tm values, so as to represent a region by a single number.

While Tm values do not depend on the direction of the change (freezing a liquid, melting a solid) or on the change rate, the location of the glass transition region depends on both factors (Brostow, 2008). Endothermic peak indicated the melting temperature of the matrix matlac without and with modification. Melting point of lac insect secretion without modification was 97.44^0C, but melting point of lac insect secretion after modification was 100^0C. Matlac matrix with the addition of citric acid has shown any degradation temperatures up to 400^0C temperature.



_______: Lac Insect Secretion + citric acid
_______: Lac Insect Secretion

Figure 5. TGA thermogram for matrix matlac of secretion of lac insect without modification and addition of citric acid 5%

Based on TGA thermogram in Figure 5., that all matrix products from secretion of lac insect without and with modification showed almost the same pattern. The increasing of temperature can cause decreasing mass percent of matrix. This showed that increasing of temperature can cause depolymerization reactions or decomposition in matrix. Based on the pattern of the thermogram can be stated that with increasing temperature the mass matrix decreased or increased mass loss with increasing temperature. Matlac matrix of citric by the addition of citric acid 5% has higher than martiks matlac without modification, especially at higher temperatur than 150^0C.

Matlac matrix of phthalic anhydride by the addition of 5% showed the mass loss below 5% at a temperature of 100^0C, while the other matlac matrix of SKL and also the addition of 25% of phthalic anhydride has suffered a loss of mass of about 15-25 % at a temperature of 100^0C. The difference in temperature required for thermal decomposition was probably due to modificated matrix having a more prohibitive effect movement of the polymer segments at higher mass percent (Chin-San Wu, 2007). At each temperature range, matlac matrix with the addition of phthalic anhydride showed the mass loss of 5% lower than the matrix without and with modification using phthalic anhydride 25%.

The Diffraction Patern of Matrix Matlac from Secretion of Lac Insect

X-ray diffraction was used to examine the crystalline structures of matrix before and after modification. Crystallinity is a factor that can affect the mechanical properties of the material. Materials with high crystallinity will have mechanical properties such as stress at break higher as well. However, there are many other factors that can affect the mechanical properties of a material, such as chain length, branching, crosslinking, and molecular mass. The longer the chain, toughness and strength increased crystallinity. This is due to the increase in chain interactions such as Van der Waals bonding. Chains become stronger hold on its position in the matrix deformation and fragmentation, both high voltage and high temperature. Branching will increase the strength and toughness of the polymer. Crosslinks that many will increase the strength and toughness of the polymer. Similarly, the molecular mass can increase the mechanical strength of the polymer.

Modification did not alter crystallinity peak at 10 and 20^0 of the base material, except modificated matrix by using citric acid 5% had disappeared crystallinity peak at 10^0, changed to amorphous. The peak at $2\theta = 18^0$, may be due to the formation of an ester carbonyl functional group, as described in the discussion of FTIR analysis (Chin-San Wu, 2007).

All XRD diffractogram of matrix similar to those reported by Chin-San Wu (2007). Based on XRD diffractogram, further crystallinity of matrix matlac is measured as showing by Table 4. Matrix matlac of secretion of lac insect without adding modifier (before modification) had the highest crystallinity and matrix matlac with adding citric acid 25% had the lowest crystallinity.

Table 4. Crystallinity of matrix matlac without and with adding citric acid

No	Matrix Matlac	Crystallinity (%)
1	Secretion of Lac Insect	72.59
2	Secretion of Lac Insect + citric acid 5%	66.88
3	Secretion of Lac Insect + citric acid 25%	42.86

Based on the calculation of crystallinity (Table 4.), modifications to the matrix matlac of lac insect ecretion with citric acid can lower crystallinity of course this can decrease the mechanical properties of the matrix. However, because many factors can affect the mechanical properties, only one molecular mass. Thus, because based on the measurement of flow time and the calculation of the intrinsic viscosity, the addition of citric acid (Table 2.) can increase the intrinsic viscosity which means it can increase molecular mass matrices, it is possible that the addition of citric acid can enhance the mechanical properties of the matrix.

The Mechanical Properties of Biocomposite

The process of making these biocomposites, using hemp fibers are cut into pieces 2 cm and arranged randomly in the alumunium mold with a ratio of 40% and 60% fiber matrix. According to Daniel Andrew Porwanto. (2011), short fiber composites in the correct orientation will result in greater strength when compared to continuous fiber, in addition to mixing and direction of fiber has several advantages, if the fiber orientation more random, the mechanical properties at 1 direction will be weakened, if the direction of each fiber spread, its power will spread in all directions, the strength will increase. Biocomposites with a ratio of 40% and 60% (matrix : ramie fiber) is the optimum ratio've done on previous research by Mujiyono (2010).

Biocomposites process is done by means of hot press with heating at a temperature of 90 °C for 15 minutes. After the heating process, carried out a pressure of 90 kgf/cm^2 for 15 minutes, then cooled with a pressure of 90 kgf/cm^2 within 10 minutes. The results of the process of making biocomposites as in Figure 6.

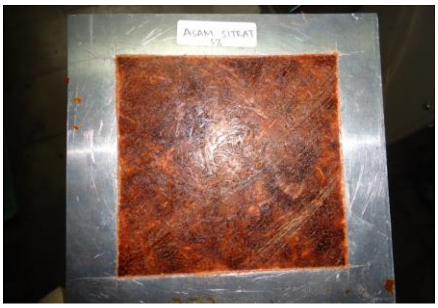


Figure 6. Preparation of biocomposites in mold

The results of these biocomposites conducted tests on mechanical properties such as tensile strength with a tensile test ASTM D 638-02 Type IV. Table 5. shows the results of the analysis of tensile strength biocomposites from natural matrix secretion of matrix natural lacquer lice infestation secretion shellac with 5% citric acid modifications are reinforced with flax fibers.

Table 5. Mechanical properties of biocomposites of lac insect secretion with 5% citric acid and ramie fiber

Biocomposite	Stress (MPa)	Strain (%)	Young’s Modulus
Sample 1	4.821	0.363	1326.579
Sample 2	4.838	0.233	2079.118
Sample 3	5.725	0.306	1872.652
Average	5.129	0.301	1759.450

Based on Table 5. tensile strength of biocomposites from natural matrix secretion shellac with 5% citric acid modifications are reinforced with flax fibers was equal to 5.129 MPa. The research that has been done before by Mujiyono in 2010, the most optimum biocomposites comparison is 40% natural matrix secretion shellac and 60% hemp fibers with tensile strength of 87 MPa. This result is much higher than the tensile strength of biocomposites with matrix modified with 5% citric acid. This is because the flax fibers used in research Mujiyono been woven, so the mixture between the fiber matrix with more flat and can minimize the cavity between those.

Biocomposite results with 5% citric acid modification in the natural matrix secretion shellac ticks as in Figure 6. that there are air bubbles and different colors due to the mixing process between the matrix and the fibers uneven. Voids or air bubbles can not be avoided during the manufacturing process. Composite strength associated with voids is inversely proportional: the more void the increasingly fragile composite and composite void if a little stronger. Voids can also affect the bond between the fiber and the matrix, ie the gap in the fiber is less than perfect form which can cause the matrix will not be able to fill the empty space in the mold. When the composite receives a load, the voltage area will be moved to the void that will reduce the strength of the composite. In the composite tensile test will result in the escape of fibers from the matrix. This is due to the strength or interfacial bonding between the matrix and the fibers are less bulky (Schwartz, 1984: 2:27).

CONCLUSIONS

Matrix matlac of secretion of lac insect can be modified by the addition of citric acid by the presence of functional groups -OH, CH methylene, ester C = O, and C-O. Matrix matlac of secretion of lac insect modified had very high yield between 89.09% to 100%. The addition of citric acid produced matlac matrix with a high of 74.684 mL/g viscosity and the higher thermal stability as well. Matlac matrix modification by the addition of citric acid has DTA and TGA thermogram pattern is almost the same. The addition of citric acid can decrease crystallinity of the secretion of matrix matlac.

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