

MODIFICATION OF LAC INSECT SECRETION BY USING ADIPIC ACID AS MATRIX IN PREPARATION OF BIOCOMPOSITE

Eli Rohaeti^{1,*} Mujiyono² Rochmadi³

¹ Faculty of Mathematics and Natural Sciences, Yogyakarta State University, Indonesia

² Faculty of Engineering, Yogyakarta State University, Indonesia

³ Faculty of Engineering, Gadjah Mada University, Indonesia

For correspondence: eli_rohaeti@uny.ac.id; rohaetieli64@gmail.com

Abstract— Secretion of lac insect was used as matrix lac (matlac). Matrix phase was changed from solid to liquid by using an ethanol p.a. as a solvent by mass ratio of matlac-solvent in composition 1:2, so the matrix distributed homogeny. Matlac was modified by adipic acid with concentration 5, 10, 15, 20, and 25%, respectively. Polymerization was conducted at 50^oC with agitation during 2 hours. Matrix matlac of insect secretion after modification was characterized in some properties e.g ;the intrinsic viscosity by Ostwald viscosimeter, functional group by FTIR spectrophotometer, and thermal properties by Differential Thermal – Thermogravimetric Analyzer. Mechanical properties of biocomposite from modified natural matrix of lac insects with reinforcement ramie fibers were characterized by tensile tester based on standard ASTM type IV. The result of this research showed that modified matrix has very high yield between 98.62% to 99.24%. The addition of 5% adipic acid 5 can produce matlac matrix with high viscosity of 77.08 cP. Addition 5% of adipic acid into matrix of lac insects didn't change the functional group qualitatively but can decrease the thermal stability of matlac. Strength at break of biocomposite was 14.299 MPa, elongation at break was 1.02%, and modulus Young was 1391.877 MPa.

Keywords: *adipic acid, biocomposite, matlac matrix, secretion of lac insect on Kesambi tree*

I. INTRODUCTION

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 [1]. Materials from renewable resources are being sought to replace not only reinforcement element but also the matrix phase of composite materials, thereby alleviating some of the sustainability issues associated with using synthetics in composites [2]. Natural fibers that can be used to manufacture biocomposites include banana fibers [3], coco fiber [4], sugar cane fibers [5], and fiber flax [6, 7].

Biopolymer has been developed as natural matrix for composites, such as starch, soybean, vegetable oil, and chitosan [8-14]. 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 plastics [15, 16]. Production of biodegradable material is now widely expected to contribute to the solution of the problem, since biodegradable material would enter the material cycles in the environment.

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 automotive components and housings for notebook computers [17, 18]. 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 [16, 19, 20].

Biocomposite with natural matrix developed more rapidly because they are more environmentally safer. The natural matrix in this experiment was obtained from secretion of lac insect on Kesambi tree (Shellac). Shellac flea *Laccifer lacca* Kerr is a phytophagous insect, which lives on Kesambi tree (*Schleichera oleosa* Merr) [21]. During its life cycle, shellac flea secretes liquid known as LAK and has

many uses, such as varnish/polish, food cover, drug capsule, cassette ribbon, etc. In 2005, Perum Perhutani produced 60.547 kg LAK pellets, but has not fulfilled market demand. The lac is resinous compound which has special properties: biodegradable, non-toxic, and provides immense employment opportunities [16]. 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. Other constituents present were: dye, wax, sugar, proteins, soluble salts, sand, woody matter, insect body debris [23]. Shellac is also produced from lac insect (*Laccifer lacca*) that has an attractive material and economically important species [22]. The secretion of lac insect on Albizia tree (ISA) as a candidate feasible biobased matrix for biocomposite with the main constituent aleuritic acid [16]. ISA disbursement method with aleuritic acid chemical structure can be done by using the solvent ethanol [23].

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 [6, 7]. The matlac matrix is well compatible with ramie, indicated by contact angle of about 30° [6]. The biocomposite potents to be a novel material from renewable resources. Biopolymer has been developed as natural matrix for composites, such as starch, soybean, and chitosan [9-14, 24].

Investigations were conducted to modification secretion of lac insect by esterification using adipic acid. The objective of this research was to modify and characterize of insect secretion on Kesambi tree as biobased material alternative for matrix composite, and also to prepare and study mechanical properties of biocomposite from modified matlac by adipic acid and ramie fiber.

II. METHODS

A. Materials

Natural matrix 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, the concentration of 5, 10, 15, 20, and 25% m/m.

B. Instrumentation

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. The mechanical properties of biocomposite from modified natural matrix of lac insect secretion and ramie fiber were determined by using tensile tester in Faculty of Engineering, Yogyakarta State University.

C. Modification of matrix and Preparation of Biocomposite

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 referred as matlac (matric lac). Meanwhile, modified matrix was prepared through esterification reaction between secretion of lac insect with adipic acid. Reaction was conducted at 50°C with agitation during 2 hours. Afterward, modified matrix was ready to be characterized and be used as matrix in preparation of biocomposite. Biocomposites were prepared from fiber ramie and modified lac insect secretion by adipic acid with a comparison matrix of 40% and random fiber of 60%. Biocomposites manufacturing process was conducted at a temperature of 90°C and a pressure of 90 kgf/cm^2 . Biocomposites were prepared by a 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.

D. Characterization of Matrix and Biocomposite

Matrix from secretion of lac insect before and after modification by using adipic acid is characterized i.e. yield by gravimetry technique, intrinsic viscosity by measuring flow time, functional group by using FTIR technique, and thermal properties by using DTA-TGA technique. The mechanical properties of biocomposite were characterized by using tensile tester based on standard ASTM type IV.

III. RESULT AND DISCUSSION

A. Yield of Matrix matlac from Modified Secretion of Lac

Based on the data from Table 1 indicates that the product matrix of secretion of lac insect has a very high yield between 98.62% to 99.24%. The addition of adipic acid 25% into the matrix matlac of secretion of lac insect can produce the highest yield of the reaction product.

Table 1. Yield of Modified Secretion of Lac Insect by Adipic Acid

| Matrix matlac of secretion of lac insect with adding | Yield of matrix (%) at adding modifier | | | | |
|--|--|-------|-------|-------|-------|
| | 5% | 10% | 15% | 20% | 25% |
| Adipic Acid | 98.62 | 99.06 | 98.82 | 99.03 | 99.24 |

B. Intrinsic Viscosity of Modified Natural Matrix

Intrinsic viscosity for matlac matrix of secretion of lac insect before modification was 72.93 cP. Table 2 shows intrinsic viscosity data of modified natural matrix of lac insect secretion. Based on the intrinsic viscosity in Table 2. It can be seen that the addition of 5% adipic acid can increase the intrinsic viscosity of the matrix matlac. The increasing of intrinsic viscosity, it will be followed by the increase in molecular weight [25]. So the interaction that occurs between 5% adipic acid and natural matrix of secretion of shellac occur in a straight chain (linear) esters are described as Fig. 2. The intrinsic viscosity of a polymer solution depends on the shape and size of the polymer. For linear polymer molecules, the increasing in the intrinsic viscosity is due to the intermolecular hydrogen bonds of carboxyl group contained in adipic acid so that the addition of 5% adipic acid can produce the maximum intrinsic viscosity.

Table 2. Intrinsic Viscosity of Modified Matrix from Secretion of Llac Insect

| Matrix matlac of secretion of lac insect by adding | Intrinsic viscosity (cP) at adding modifier | | | | |
|--|---|-------|-------|-------|-------|
| | 5% | 10% | 15% | 20% | 25% |
| Adipic acid | 77.08 | 64.90 | 72.46 | 29.66 | 36.26 |

However, the addition of 20% adipic acid produces a matrix with the lowest intrinsic viscosity. This indicates that the optimum concentration for modification matlac of secretion of lac insect was the addition of adipic acid as much as 5%. The high intrinsic viscosity means matlac matrix with the addition of 5% of adipic acid has the highest molecular weight. The high molecular mass of matlac matrix indicates the molecular chain length. The long-chain molecules that can affect the thermal stability and the transition temperature of the matrix.

Requirements of a polymer matrix can be summarized from several references [26, 27, 28]. First, the matrix must be able to withstand and protect the fiber. Thus the 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.

C. Functional Groups of Matrix Matlac

Secretion of lac insect is composed of biobased material is aleuritic acid. This aleuritic acid is polar because it has a carbonyl functional group (C = O) (Mujiyono *et al.*, 2010a; Mujiyono, *et al.*, 2010d). The electronegativity difference between carbon and oxygen is large enough to make the C = O tends polar [29]. Carboxylic acid functional group (-COOH) at the end of the molecule has a tendency aleuritic acidic nature of polar and soluble in water. Long alkyl chains cause 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. FTIR spectra of matrix without modification and

after modification with adipic acid are shown in Fig. 1. Based on FTIR spectra can be seen absorption bands for those materials at specific wave numbers are almost the same. These shows that the functional groups of matrix before and after modification are similar qualitatively.

After modification with 5% adipic acid shows more broad absorption band especially at wave numbers indicating alcoholic functional groups-OH,-CH methylene group, and C=O ester.

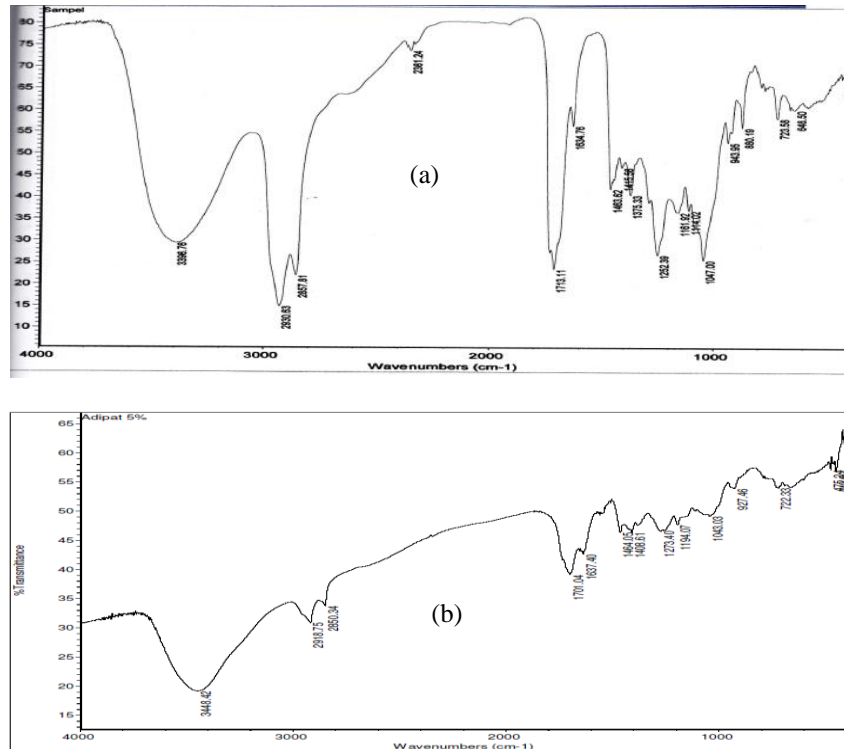


Fig 1. Spectra FTIR Matlac (a). before Modification, (b). after Modification with 5% Adipic Acid

The presence of -OH and C = O to form hydrogen bonds to strengthen the intrinsic viscosity of the data. Interpretation of functional groups for the matrix matlac before and after modification with adipic acid can be seen in Table 3. Absorption bands at certain wave numbers of natural matrix without modification and natural matrix with modification by 5% of adipic acid are almost the same. Thus, the chemical structure of natural matrix without modification and natural matrix after modification is a similar qualitatively. It proves that the natural matrix without modification and after modification show -OH groups, -COO ester, and there are no changes in functional groups. Shellac is consisted of aliphatic hydroxy and esters with carbon chain lengths of 13-15 [30].

Board peak of the spectrum for natural matrix after modification indicates the occurrence of hydrogen bonds between ester, resulting from reaction among aleuritic acid, ethanol, and adipic acid. Less extensive hydrogen bonding, will appear much sharper peak -OH. If the peak appears to be wider, it means -OH bonded hydrogen. The presence of hydrogen bonds may be composed of a polymer chains united straight. The sharper functional groups -OH in the natural matrix without modification indicates that the -OH is not attached hydrogen bonding. Uptake more -OH functional groups widened in the natural matrix with addition of adipic acid 5% indicates a hydrogen bond, so it can be stated that the addition of 5% of adipic acid on a natural matrix causes a reaction between an aleuritic acid with adipic acid to form a linear chain. These results are in accordance with previous research that has been done by Mujiyono in [6], in the study showed an -OH group at a wavelength of $3600-3200\text{ cm}^{-1}$ and CH at a wavelength of $3100-2800\text{ cm}^{-1}$ and the absorption band at $1820 - 1600\text{ cm}^{-1}$ indicate the presence of a carbonyl group C = O ester reinforced with the emergence of C-O ester absorption at wave number 1300 to 1000 cm^{-1} . Figure 2. showed chemical structure for modified matrix of secretion of lac insect by using adipic acid.

Table 3. Interpretation of Functional Groups for The Matrix Matlac

| Wave number of secretion of lac insect | Wave number of matrix with adding adipic acid 5% | Functional Group |
|--|--|------------------|
| 3396,76 | 3448,42 | -OH |
| 2930,63 | 2918,75 | -CH |
| 2857,81 | 2850,34 | |
| 1713,11 | 1701,04 | |
| 1634,76 | 1637,40 | C=O |
| 1463,62 | 1464,05 | -CH ₂ |
| - | 1408,61 | |
| 1252,39 | 1273,40 | C-O |
| 1161,92 | 1194,07 | |
| 1114,02 | - | |
| 1047,02 | 1043,03 | |
| ~ 900 | ~ 900 | Fingerprint |

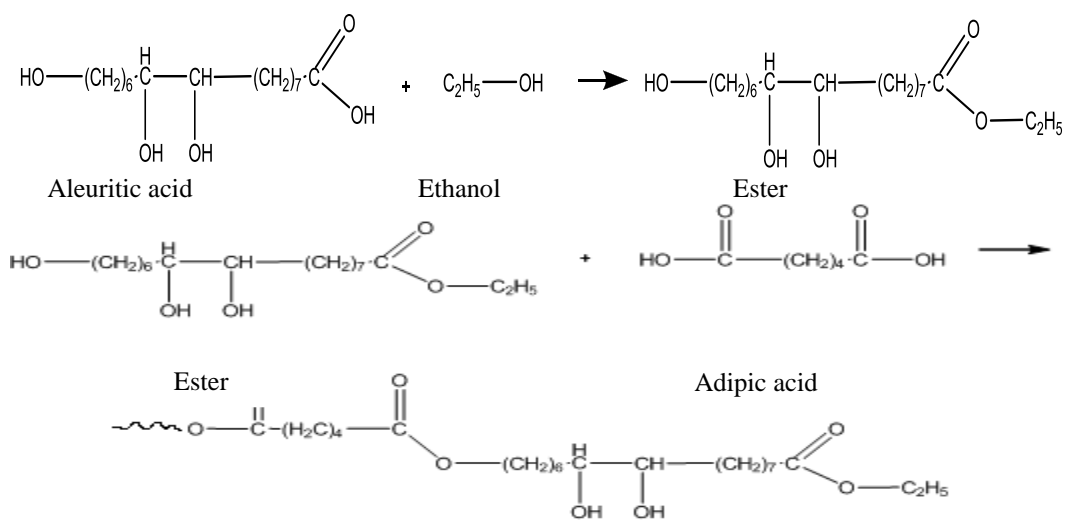
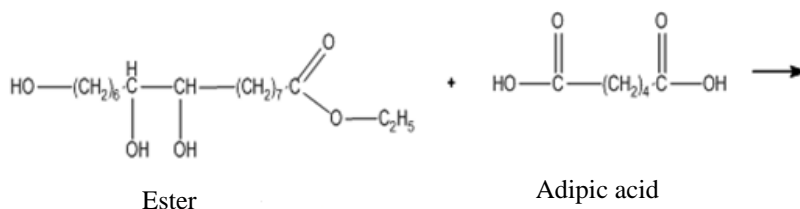


Fig 2. Chemical Structure of Modified Matrix

Natural matrices of secretion of lac insect with adding adipic acid 10% , 15% , 20% , and 25% have a viscosity that is lower than the natural matrix of secretion of lac insect without modification. Based on Table 2. indicates that more concentration of adipic acid, value of the intrinsic viscosity decreases. It shows the initial interaction between adipic acid and natural matrix secretion shellac does not occur in a straight chain of ester [30] but in -OH branching (Fig. 3).



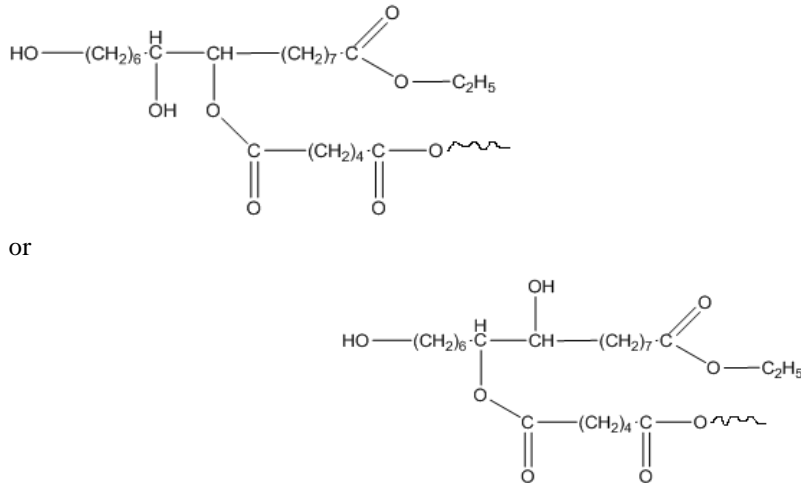
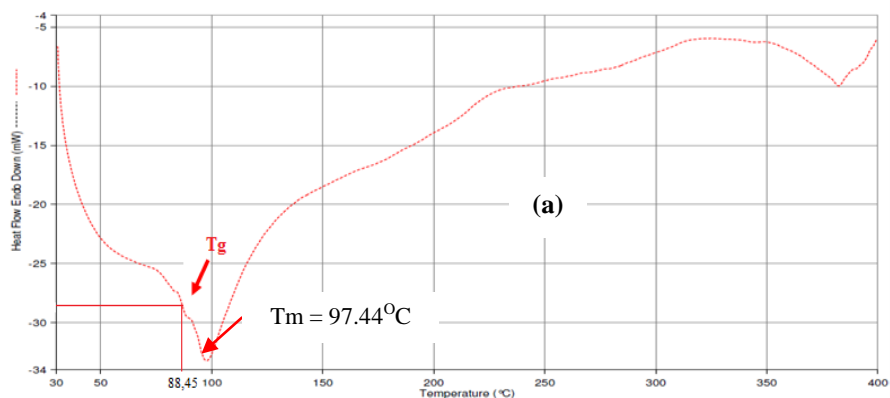


Fig 3. Reaction between Natural Matrix with Adipic Acid in Chain Branching

D. Thermal Properties of Matrix Matlac

The results of the analysis of thermal properties by using DTA-TGA is shown in Figure 4 and 5. Based on Figure 4, showed that the thermogram pattern for matlac from secretion of lac insect without and with the addition of adipic acid has almost the same pattern. In the Figure 4.(b), the glass transition temperature (T_g) of the matrix is not detected, it is possible the glass transition temperature (T_g) occurs after the temperature 400°C . The glass transition temperature (T_g) in natural matrix by adding adipic acid 5% is higher than the glass transition temperature (T_g) of the matrix natural without modification. This is supported by the value of higher intrinsic viscosity, analysis of functional groups by FTIR which showed absorption -OH functional groups and the melting temperature (T_m) are higher than the natural matrix without modification, so the structure is more rigid.

The change of the melting point of the matrix natural of secretion of lac insect without modification and natural matrix with the addition of adipic acid can be caused by the interaction between adipic acid and secretion of shellac, so it takes a higher temperature to melt the natural matrix of secretion of lac insect with the addition adipic acid.



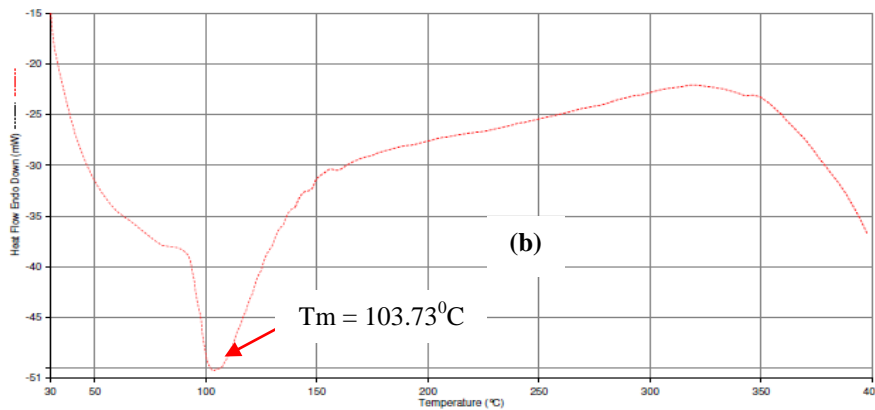


Fig 4. DTA Thermogram for Matrix Matlac (a). without Modification, (b). Addition 5% Adipic Acid

Endothermic peak indicates the melting temperature of the matrix matlac without and with modification. Based on the DTA thermogram in Fig. 3., natural matrix of secretion of shellac without modification has a T_g of 88.45°C . The glass transition temperature is the temperature at which the phase changes occur glassy or rigid (rigid) into a rubbery phase [31]. The existence of a glass transition temperature of the natural matrix without modifications shows that this material has amorphous and crystalline regions [32]. At temperatures 97.44°C shows endothermic peak which is the melting point of the natural matrix. However, natural matrix with addition of 5% adipic acid shows the endothermic peak at a temperature 103.73°C . It shows the initial interaction between adipic acid and natural matrix does not occur in a straight chain of ester but in -OH branching (Fig. 3).

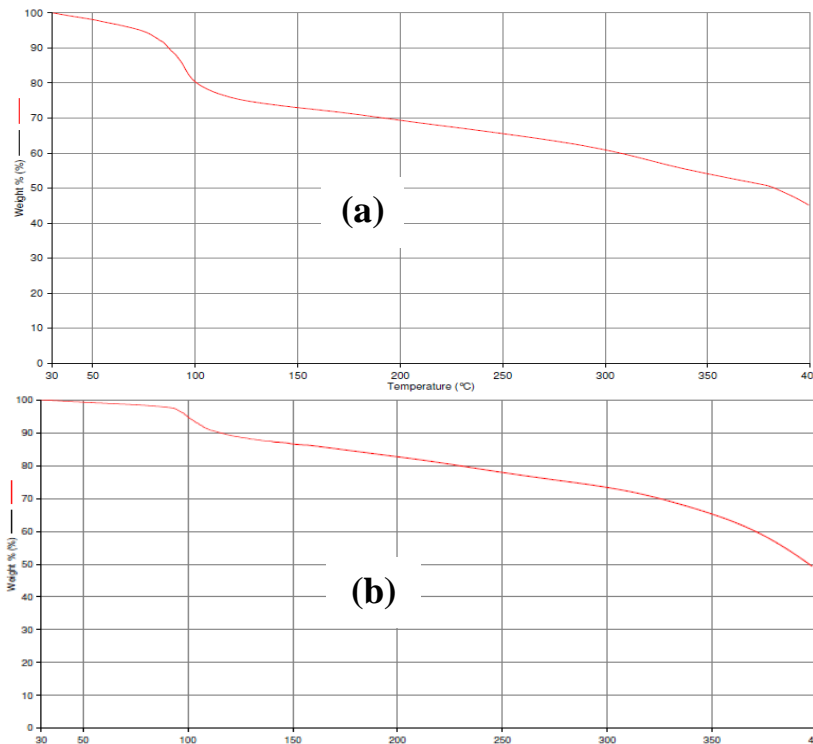


Fig 5. TGA Thermogram for Matrix Matlac (a). without Modification, (b). Addition 5% Adipic Acid

Based on TGA thermogram in Fig. 5 showed that all matrix products from secretion of lac insect without and with modification showed almost the same pattern. Based on the pattern of the thermogram can be stated that increasing of temperature causes the decreasing of mass matrix or the increasing of mass loss. Matlac matrix by the addition of 5% adipic acid has the highest thermal stability. The natural matrix without modification and natural matrix with the addition of adipic acid 5% show the change in mass in

TGA analysis. At each temperature range, the natural matrix with the addition of 5% adipic acid has a more thermal stability. At the initial temperature 50⁰C, mass of natural matrix without modification of 98.107% and the mass of the modified natural matrix of 99.556 % . At a temperature of 75⁰C - 400⁰C sample mass decreases. The mass of the natural matrix without modification at a temperature of 75⁰C has decreased to 94.716 % , while the natural matrix with the addition of adipic acid 5% of 98.222 % . At a temperature of 400⁰C, sample mass for natural matrix without modification as much as 45.338 % and 49.111 % for natural with the addition of adipic acid 5 %.

Matlac matrix by the addition of 5% adipic acid showed the mass loss below 5% at a temperature of 100⁰C, while the other matlac matrix and also the addition of 5% of adipic acid has suffered a loss of mass about 20 % at that temperature. At each temperature range, matlac matrix with the addition of adipic acid shows the mass loss of 2 - 12% lower than the matrix without modification.

E. 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 aluminium mold with a ratio of 40% and 60% fiber matrix. According to Daniel Andri Porwanti and Lizda Zohar [33] 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 in [6, 7].

Table 4. shows tensile strength for biocomposites from natural matrix with 5% of adipic acid and ramie fibers. Based on Table 4. tensile strength of biocomposites from natural matrix with 5% of adipic acid are reinforced with ramie fibers is equal to 14.229 MPa. The research that has been done by Mujiyono in [6], the most optimum biocomposites comparison is 40% of natural matrix and 60% of hemp fibers with tensile strength of 87 MPa. That result is much higher than the tensile strength of biocomposites from modified matrix by 5% of adipic acid. This is because the flax fibers used in research Mujiyono [6, 7] been woven, so the mixture between the fiber and matrix more flat and can minimize the cavity between those.

Table 4. Mechanical Properties of Biocomposites

| Biocomposite | Stress (MPa) | Strain (%) | Young's Modulus (MPa) |
|--------------|--------------|------------|-----------------------|
| Average | 14.299 | 1.02% | 1391.877 |

Decrease in stress was also caused by the interaction of the matrix with fiber is weak when given load, causing biocomposites become less potent against a given load. If the interaction between the matrix with fiber a strong, the load imposed on the matrix can occur both on the transfer with fiber to make biocomposites become strong against the load. Besides the fiber is too short causing less strong bonding between the fibers. Long fibers are stronger than short fibers, long fibers can stream or load voltage from the voltage point toward another fiber [33, 34]. It is also found that, modulus of biocomposite from modified matrix by adipic acid and ramie fiber is high. It can be caused by high crosslink density. The compressive strength and modulus are due to the high crosslink density [35, 36].

ACKNOWLEDGMENT

In this opportunity, we would thank to State Minister for Education and Culture which gave fund to this research according to the decree of State Minister for Education and Culture, Indonesian Government and Perhutani Unit II, West Java, Indonesia for providing secretion of lac insect.

REFERENCES

- [1] M. H. S. Ginting, "Pembuatan Komposit dari Karung Plastik Bekas dan Polietilena dengan Pelembut Heksan", *Jurnal Teknologi Proses* 5(2):129-13, 2006.
- [2] P.A Fowler, J.M. Hughes, and R.M. Elias, "Biocomposites : technology, environmental credentials and market forces", *Journal of the Science of Food and Agriculture*, 86(1), 1781-1789, 2006.
- [3] R. Kartini, H. Darmasetiawan, A. K. K. Sudirman, "Pembuatan dan Karakterisasi Komposit Polimer Berpenguat Serat Rami", *Jurnal Sains Materi Indonesia* 2(3):30-38, 2002.
- [4] J. Oroh, F. P. Sappu, R. Lumintang, "Analisis Sifat Mekanik Komposit dari Serat Sabut Kelap", *Artikel Ilmiah*. Manado: Universitas Sam Ratulangi, 2013.
- [5] M. B. N. Rahman and B. P. Kamiel, "Pengaruh Fraksi Volume Serat terhadap Sifat-Sifat Tarik Komposit Diperkuat *Unidirectional* Serat Tebu dengan Matriks Poliester", *Jurnal Ilmiah Semesta Teknik*, 14(2):133-138, 2011.

- [6] Mujiyono, Jamasri, S. B. R. Heru, J.P. Gentur S., “Mechanical Properties of Ramie Fibers Reinforced Biobased Material Alternative as Natural Matrix Biocomposite”, *International Journal of Materials Science*, 5 (6), 811–824, 2010.
- [7] Mujiyono, Jamasri, S. B. R. Heru, J.P. Gentur S., “Rekayasa Biokomposit dari Sekresi Kutu Lak dan Serat Rami”, *Seminar Nasional Hasil-hasil Penelitian Teknologi, MIPA dan Pendidikan Vokasi*. Yogyakarta: pp. 421-434, 2010.
- [8] M. B. Agustin, B. Ahmmad, E. R. P. De Leon, J. L. Buenaobra, J. R. Salazar and F. Hirose, “Starch-based Biocomposite Films Reinforced with Cellulose Nanocrystals from Garlic Stalks”, *Polymer Composites*, 34(8), 1325 – 1332, 2014..
- [9] A.A.S Curvelo, A. J. F. Carvalho, J. A. M. Agnelli, ”Thermoplastic starch cellulosic fibers composites: preliminary results”, *Carbohyd. Polym.*, 45 (2), 183–8, 2001.
- [10] V. P. Cyras, S. Iannace, J. M. Kenny, and A. Vázquez, ”Relationship between processing conditions and properties of a biodegradable composite based on PCL/ starch and sisal fibers”, *Polym. Compos.*, 22 (1), 104–10, 2001.
- [11] C. Lanzillotta, A. Pipino, A. and D. Lips, ”New functional biopolymer natural fiber composites from agricultural resources”, *In Proceedings of the Annual Technical Conference – Society of Plastics Engineers*, San Francisco, California, 2, 2185–9, 2002.
- [12] R. Rudianto, “Pengaruh Fraksi Volume Serat Rami Terhadap Kekuatan Bending Biokomposit Bermatriks Pati Sagu”, *Jurnal Teknik Mesin*, 1(1):8-12, 2012.
- [13] M. Wollerdorfer and H. Bader, ”Influence of natural fibres on the mechanical properties of biodegradable polymers”, *Ind. Crop. Prod.*, 8, 2, 105–12, 1998.
- [14] P. Lodha and A. N. Netravali, ”Characterization of interfacial and mechanical properties of ‘green’ composites with soy protein isolate and ramie fiber”, *J. Mater. Sci.*, 37 (17), 3657–65, 2002.
- [15] A. K. Mohanty, M. Misra, L. T. Dzral, S. E. B. R. Harte, and G. Hinrichsen, “Natural Fibers, Biopolymers And Biocomposite: An Introduction”, Chapter 1 in *Natural Fibers, Biopolymers, and biocomposite*, edited by Mohanty, A.K., Misra, M., Dzral, L.T., CRC Press, Taylor and Francis Group, 6000 Broken Sound Parkway NW, USA, 2005.
- [16] Mujiyono, Jamasri, S. B. R. Heru, J.P. Gentur S., “Insect secretion on Albazia tree as biobased material alternative for matrix composite”, *Material Science and Research India*, 7(1), 77-87, 2010.
- [17] R.Adistya, “Sifat Mekanik Biokomposit Serat Rami (*Boehmeria Nivea L.*) dengan Matriks Propilen”, *Skripsi*, 2013.
- [18] K. G. Kavelin, “Investigation of Natural Fiber Composites heterogeneity with respect to automotive structure”, *Thesis for degree of doctor at Delfi University of Tecnology*, Netherland, 2005.
- [19] M. Y. Hashim, M. N. Roslam, A. M. Amin, A.M.A. Zaidi, and S. Ariffin, “Mercerization Treatment Parameter Effect on Natural Fiber Reinforced Polymer Matrix Composite : A Brief Review”, *International Scholarly and Scientific Research & Innovation*, 6(8), 8-24, 2012.
- [20] D. Plackett and A. Vazquez, “Natural polymer source”, Chapter 7 in *Green Composites. Polymer composites and the environment* edited by Caroline Baillie, Woodhead Publishing Limited, Abington Cambridge, UK, 2004.
- [21] I. Taskirawati, F. G. Suratmo, D. Darusman, and N. F. Haneda, “Peluang Investasi Usaha Budidaya Kutu Lak (*Laccifer lacca Kerr*): Studi Kasus di KPH Probolinggo Perum Perhutani Unit II Jawa Timur”, *Jurnal Perennial*, 4(1):23-27, 2008.
- [22] K. K. Sharma, A. K., Jaiswal, and K. K. Kumar, “Role of lac culture in biodiversity conservation: issues at stake and conservation strategy”, *Review article, Current Science*, 894 91(7), 894-898, 2006.
- [23] Mujiyono, Jamasri, S. B. R. Heru, J.P. Gentur S.,” Investigation and characterization of insect secretion on Albazia tree as biobased material alternative for matrix composite”, *Material Science and Research India*, 7(1), 37-48, 2010.
- [24] R. L. Quirino, T. F. Garrison, and M. R. Kessler, “Matrices from Vegetable Oils, Cashews Nut Shell Liquid, and other Relevant Systems for Biocomposite Applications”, *Green Chem.* 16(1), 1700 – 1715, 2014.
- [25] Prima Astuti Handayani, “Polimerisasi Akrilamid dengan Metode Mixed-Solvent Precipitation dalam Pelarut Etanol-Air”, *Jurnal Sains dan Teknologi Universitas Negeri Semarang*, 8(1): 69-78, 2010.
- [26] S. S. Munawar, K. Umemura, S. Kawai, “Characterization of The Morphological, Physical, Mechanical Properties of Seven Nonwood Plant Fiber Bundles”, *J.Wood Science*, 53, 108-113, 2006.
- [27] M. M. Schwartz, *Composite Materials Handbook*, McGraw-Hill Book Company, New York, USA, 1984.
- [28] Vasiliev, V.V, Morozov, E.V., “Mechanic and Analysis of Composite Materials. Elsevier Science Ltd”, *The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK*, 2001.
- [29] G. M. Bodner, “The Carbonyl Group”, *College of Science Chemical Education Devision Group, Purdue University, West Lafayette, Indiana, USA*. 2004.
- [30] S. Pakan, “Pelapis Pangan Alami Asal Lak: Kondisi Saat Ini dan Potensi Pengembangan di Propinsi Nusa Tenggara Timur”, *Jurnal Teknol. & Industri Pangan* 18(2), 2007.
- [31] Zulfikar Rachman Aji, “Studi Pengaruh Kondisi Pengujian Tarik Pada Film Plastik BOPP (*Biaxial Oriented Polypropylene*)”, *Skripsi. Universitas Indonesia: Departemen Teknik Metalurgi dan Material FT*, 2008.
- [32] W. Brostow, R. Chiu, I. M. Kalogeras, and A. V. Dova, “Prediction of glass transition temperatures: Binary Blends and Copolymers”, *Materials Letters*, 62, 3152-3155, 2008.
- [33] Daniel Andri Porwanto & Lizda Zohar, “Karakterisasi Komposit Berpenguat Serat Bambu dan Serat Gelas sebagai Alternatif Bahan Baku Industri”, *Artikel Ilmiah. Surabaya: ITS*, 2011.
- [34] I. P. Lokana, N. G. P. Suardana, I. M. G. N. Karonika, “Pengaruh Panjang Serat pada Temperatur Uji yang Berbeda Terhadap Kekuatan Tarik Komposit Polyester Serat Tapis Kelapa”, *Jurnal Ilmiah Teknik Mesin*, 4(2):166-172, 2010.
- [35] N. M. Ahmed, M. E., and A. A. Ward, “Characterization of A Polymer Composite from Treated Kaolin and Unsaturated Polyester Based on PET Waste”, *Polymer Composites*, 34(8), 1223 – 1234, 2013.
- [36] N. M. Ahmed and S. H. El-Sabbagh, “The Influence of Doped-Kaolin on the Properties of Styrene-Butadiene Rubber Composites”, *International Journal of Advanced Research*, 3(5), 1-19, 2015.

