

## Investigation and characterization of insect secretion on Albazia tree as biobased material alternative for matrix composite

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### ABSTRACT

The people of Ciamis regency, West Java district, Indonesia have been using biobased material to patch the tin roof, to join rod of machete and rod of hoe. They call it with the term "ant's house". This paper reports the investigation and characterization of the material as an alternative material for biobased composite matrix. Investigations were carried out in the traditional market Ciganjeng, Padaheurang, and Banjarsari subdistrict, Ciamis regency, West Java District, to obtain samples of the biobased material and collect information related to the main sources location. The sample was characterized by FTIR to predict functional group and SEM-EDAX to count mass of its chemical structure. Polarity and visualization of samples were done to prove the chemical structure prediction of the material. The results of the investigation and characterization showed that the sample is lac secretion of insect that live on Albazia tree, so it is not the "ant's house". The main source location of the material is mountain area of Karangnangka village, Banjarsari subdistrict, Ciamis regency of West Java district. The chemical structure of the biobased materials is aleuritic acid. The next paper will report engineering aspect of matrix composite from this biobased material alternative.

**Key words:** Biobased material alternative, aleuritic acid, matrix composite.

### INTRODUCTION

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 or biobased plastics<sup>1</sup>. 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. Commercial interest in manufacturing these products is driven by the derivation of the biobased material from renewable sources as well as by their specific properties including biodegradability<sup>2</sup>.

Wastes from plastics have become a worldwide environmental problem, not only in developed countries but also in developing countries. 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<sup>3</sup>.

In Indonesia, precisely in the area of Ciamis regency, West Java District, some people have been using biobased material to patch the roof, to join rod of machete and rod of hoe. They call it with the term "ant's house". Analysis of these facts provides three important informations related to alternative biobased materials. First, biobased material has good adhesive properties of being able to joint the hoe stem and a machete rod. Second,

the polymer has a sufficient availability with ease indicators obtained in traditional markets, Jabar Ciamis district. Third, the polymer is derived from the renewable sources because they call it with the term "ant's house". Therefore, the investigation and characterization of the biobased material is needed to know the main sources and its chemical structure composition.

Investigations were conducted in the traditional markets Ciganjeng and Padaheurang, Ciamis, West Java to obtain samples of biobased materials. While the collection of information related to the location of main sources of the biobased material were carried out through interviews with people around. The objective of this research was investigation and characterization of insect secretion on albazia tree as biobased material alternative for matrix composite.

## MATERIALS AND METHODS

The sample comes from biobased material used by the people Ciamis regency, district of West Java, Indonesia as an adhesive material. Investigation and characterization were conducted to ensure the main source of the sample and determine the chemical structure of it, respectively, in order to find an alternative biobased material. Therefore, the sample can be engineered into a natural matrix composite.

### Investigation for Ensuring Main Source of The Sample

Investigation through collecting and finding out informations related to the main source of sample was conducted in 3 traditional markets: Ciganjeng and Padaheurang traditional market at Padaheurang subdistrict and Banjarsari traditional market at Banjarsari subdistrict, Ciamis regency, district of West Java, Indonesia.

### Characterization for Determining the Samples' Chemical Structures

The Fourier Transform Infrared (FTIR) Test was conducted at room temperature of 20°C and humidity of 60% by FTIR Shimadzu Seri 8400S with beam splitter of KBr wrapped Germanium plat. By FTIR, functional groups of sample could be known in order to predict its chemical structure.

### Elements Mass Measurement of Sample

The sample was coated with gold by sputtering process and then analyzed using a JEOL SEM-EDAX Model J6360LA. Elements mass of sample were measured with EDAX processing in order to predict its chemical structure.

### Polarity Test of Sample

Polarity test of sample was done to prove polarity of the chemical structure prediction through mixing it with water (polar material), alcohol (semi-polar material) and gasoline, kerosene, acetone (non polar materials)

### Visualization of Sample

Test Visualization of investigation results by photographs was done to validate biobased material and renewable resource of the sample.

## RESULT AND DISCUSSION

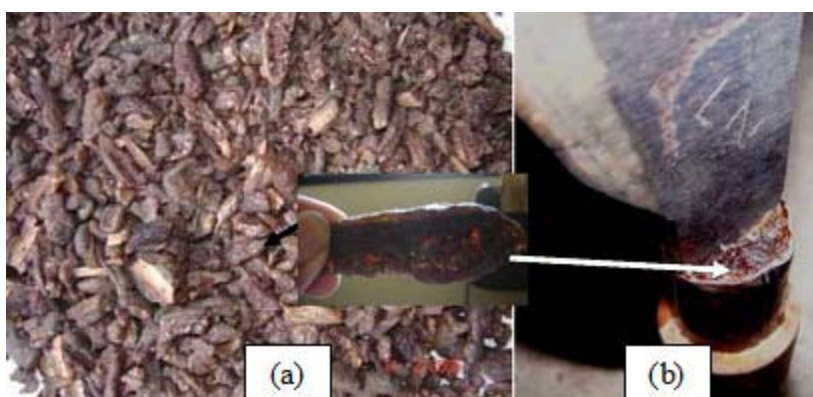
Initial investigation showed the fact that some people in Ciamis, have been using the sample (Figure 1a) as an adhesive material such as for patching a leaky tin roof, bonding hoe with its rod, machete with its stems as shown Figure 1b. The sample which is usually called "Imah sireum" or "house ants" can be obtained in traditional markets, such as Ciganjeng, Padaheurang, and Banjarsari traditional market at Ciamis district. Figure 1. Biobased material and its utilization (a) Sample of biobased material alternative (b) Sample for bonding machete and its stem

Further investigation was performed to determine the main source of biobased material with a trace of remote and rural mountain areas of village of Karangnangka, subdistrict of Banjarsari, Ciamis regency, West Java. The investigation results showed that the sample comes from the secretion of insects that live in Albazia trees (*Albazia falcataria* sp.) as shown in Figure 2. To simplify the writing, hereinafter, this biobased material will be written ISA (Insect Secretion on Albazian tree) sample. The insects cause tree branches to be dried (Fig 2 c-d) but do not die the trees (Fig 2a-b). This is evidenced by the discovery of ISA on the not-dying large trees eventhough their twigs which are used as the colony becomes dry.

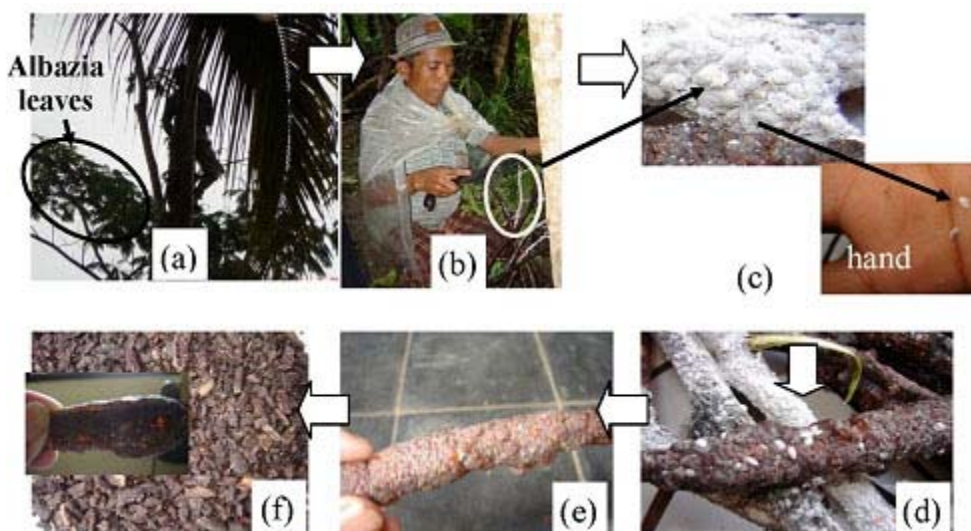
**Characterization of ISA by FTIR**

Initial characterization of ISA was done by FTIR to know the functional groups content in it that built its chemical structure. Peaks of infrared (IR) spectrum absorption in ISA existed only at specific wave due to vibration of inter-molecular bonds, as shown by Figure 3. Identification of each peak was conducted by entering them to wave range indicated identity of each atomic bond as shown by Table 1. These atomic bonds built functional groups which form chemical structure of sample.

Wave number of  $1726\text{ cm}^{-1}$  and  $3429\text{ cm}^{-1}$  showed energy absorption of carbonyl C=O and hydroxyl O-H functional group, respectively, that enable to form carboxylate (-COOH). O-H functional group for carboxylate was usually detected at  $2500\text{-}3400\text{ cm}^{-1}$  [4], but for this sample, it appeared at  $3429\text{ cm}^{-1}$  due to the OH overtones of alcohol that is about  $3500\text{ cm}^{-1}$ . This was supported by the absorption of energy that produced the wave numbers of  $1245$ ,  $1168$ ,  $1010$  and  $937\text{ cm}^{-1}$  which indicated that there were 4 CO



**Fig. 1: Biobased material and its utilization (a) Sample of biobased material alternative (b) Sample for bonding machete and its stem**



**Fig. 2: Investigation results of insect secretion which has been used as adhesive bonding (a) Insect secretion deattachment from Albazia tree (b) Albazia twigs with insects (c) Insects live on Albazia twigs (d) Insects and their secretion which were on a twig (e) Insect secretion which was on a twig (f) Insect secretion which was scrapped from twigs**

functional groups, and allowed binding to OH group. In this sample the wave numbers of 721  $\text{cm}^{-1}$  was also found that indicated more than 4 Carbon chain built the chemical structure of sample, because the  $\text{CH}_2$  rocking with wave numbers 720-730  $\text{cm}^{-1}$

occurred in the chain C is greater than 4 [4].

C=O functional group at this sample did not come from aldehyde due to the absence of C-H at about 3000  $\text{cm}^{-1}$  even though C-H aliphatic in

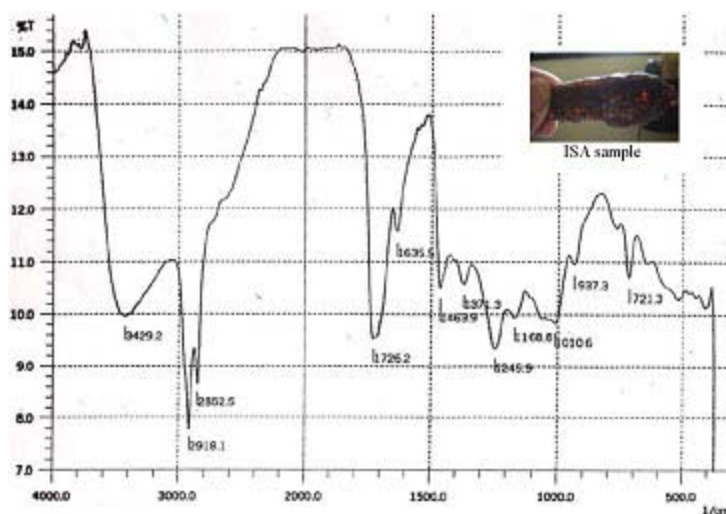


Fig. 3: Peaks of infrared (IR) spectrum absorption in ISA existed only at specific wave due to vibration of inter-molecular bonds

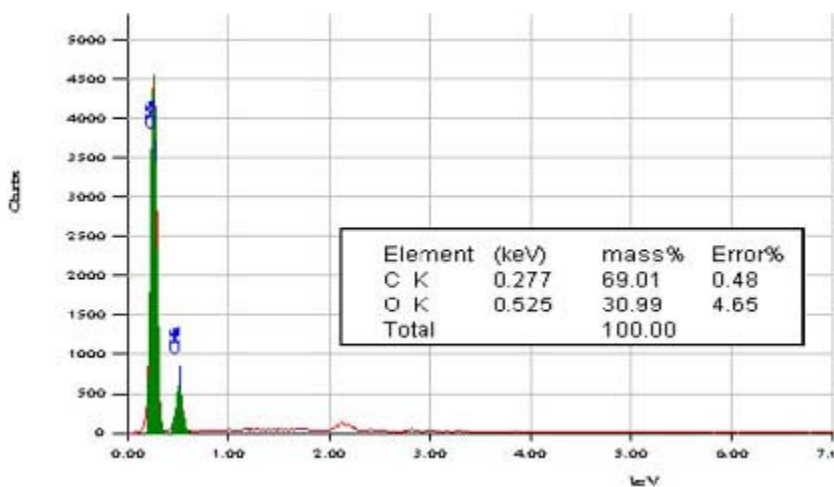


Fig. 4: SEM-EDAX of ISA biobased material

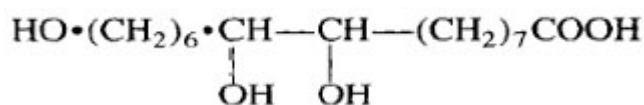


Fig. 5: Chemical structure of aleuretic acid

methylene (-CH<sub>2</sub>) was detected at 2918 cm<sup>-1</sup> (asymmetric) and 2858 cm<sup>-1</sup> (symmetric). This is in line with [5] who stated that the CH stretching in a single methylene usually occurs around 2853 cm<sup>-1</sup> (symmetric) and 2926 cm<sup>-1</sup> (asymmetric). The sample did not have 2 small bands: 2962 and 2872 cm<sup>-1</sup> so that there was not methyl group (-CH<sub>3</sub>). It did not also have the aromatic C-H due to no indication of very strong wave numbers in at 3100-3000 cm<sup>-1</sup> [4]. This is also in line with Hardjono [5]

who stated that the C-H stretching aromatic and alkene occurs above 3000 cm<sup>-1</sup>, whereas the C-H alkane under 3000 cm<sup>-1</sup>. The Sample also have CH<sub>2</sub> scissoring with wave number indication of 1463 cm<sup>-1</sup> because CH<sub>2</sub> scissoring usually occurs in the wave numbers 1465 cm<sup>-1</sup> [4].

Based on data analysis of the FTIR results, the functional groups contained in the sample are presented in Table 2.

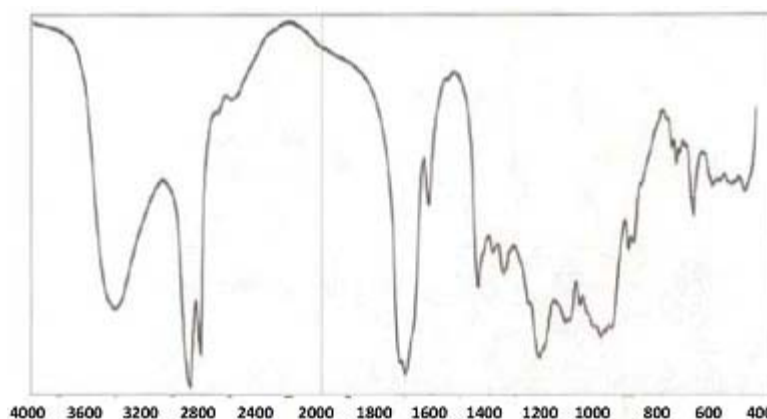


Fig. 6: IR spectrum absorption peaks at shellac



Fig. 7(a): ISA changed to liquid phase in methanol and ethanol which are semipolar solvent (b) ISA remained at solid phase due to its low solubility in water



Fig. 8: ISA did not dissolve in non polar solvent (a) ISA remained in solid phase due to its no solubility in gasoline and kerosene (b) ISA remained in solid phase due to its no solubility in acetone



### Atom Weight of ISA Biobased Material

The results of SEM-EDAX to the sample, C and O atoms with mass ratio 69% for C and 31% for O were detected, as shown in Figure 4. Actual sample atoms consisted of H, C and O, however, H

atoms are too light to be able to detect so that the atomic weight of C and O only which had been recorded. Base on the periodic table, the mass of C and O atom are respectively 12 and 16 while the total mass ratio of C and O atoms that make up the

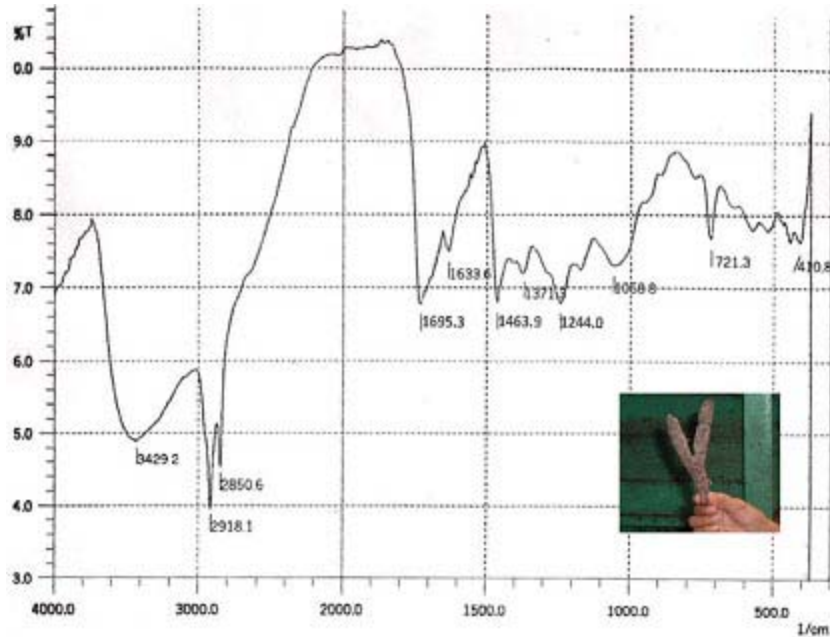


Fig. 9: IR absorption peaks at specific wave of LSK sample.

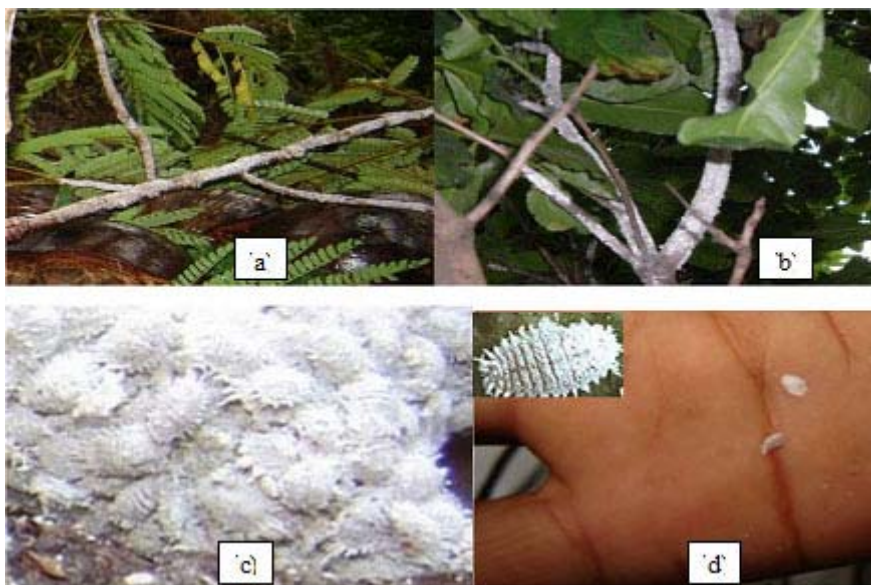


Fig. 10(a): lac insect live on Albizia tree (b) lac insect live on Kesambi tree (c) Immature lac insect (d) mature lac insect

ISA is 69:31. These data can predict the amount of C and O atoms with the argument that the multiplication of the amount of atom C with its mass compared to that of O atoms equals the total mass ratio of C and O atoms in the sample.

$$12 \text{ C} : 16 \text{ O} = 69 : 31 \rightarrow \text{C} = 2,94 \times \text{O} \rightarrow \text{C H} \approx 3 \times \text{O}$$

The number of C atoms that built ISA is about 3 times more than O atoms, so that it can be used roughly as a chemical structure prediction. If the O atoms amounts 5, the C atom amounts 15, however the SEM-EDAX data has an error tolerance of about 4%, consequently, it is still possible for the C atoms to get amount of 14 or 16. These results are helpful in predicting the chemical structure of ISA biobased material by eliminate chemical

structures that have a ratio of C and O atoms greater than 3:1.

Langenheim<sup>5</sup> classify natural polymers from renewable sources into several groups of resins (eg, resin), gum (eg gum arabic), Mucilage (for example gelatin), waxes (eg, night), fat (oil) and latex. Natural biobased material belonging to the group of resins has a chemical composition of terpenoids, or phenol, gum and Mucilage is composed by polysacharida, wax composed by esteryfied fatty acids, fats or oils composed of fatty acids and glycerol, while the latex is a complex compound of terpenoids, phenols, proteins, etc.

Terpenoid is a complex compound with isopentane as a basic constituent with methyl group



**Fig. 11: (a) Lac insect secretion on Albazia tree (b) Lac insect secretion at Kesambi tree (c) Lac insect secretion on Albazia tree which was granulated to pass mesh 10 (d) Lac insect secretion on Kesambi tree which was granulated to pass mesh 10**

(-CH<sub>3</sub>), while a phenol has an aromatic benzene group. ISA sample are not resin because they do not have methyl group (-CH<sub>3</sub>) and benzene. Polysaccharida is saccharida polymer composed of the glyceraldehyde with aldehyde group (-CHO) as one of its functional groups. ISA sample are not gum and mucilage gum because they are built functional groups rather than aldehyde. While wax has a fatty acid compound that is composed by one of methyl functional groups (-CH<sub>3</sub>) and esters. ISA sample is not part of wax and latex. Groups of


biobased material with carboxylic groups can compose many type of carboxylic acids.

One of the carboxylic acid belongs to C atom about three times the O atom and present all the functional groups detected in the sample is an aleuretic acid as shown in Figure 5. This acid has functional groups (-OH), (-CH<sub>2</sub>), (-COOH) and the chemical bonds (C-C), (C-H) and (C-O) which are all detected in the sample. So the preliminary conclusion is ISA sample is composed of aleuretic acid.

**Table 1: Identification of IR Spectrum peaks in ISA at specific wave**

Wave number of specific peak(cm <sup>-1</sup> )	Wave range (cm <sup>-1</sup> )	Atomic bond	Type of Vibration
3429	3600-3200	O-H	Stretching band
2918 dan 2852	3100-2800	C-H	Stretching bands
1726	1740-1640	C=O	Stretching band
1635	1650-1600	C-C	Stretching band
1463 dan 1371	1480-1300	C-H	Bending bands
1245,1168,1010,937	1300-900	C-O	Stretching bands

**Table 2: The functional groups and chemical bonds which were detected in the sample**

Functional groups	Chemical formula	Chemical structure prediction
Hidroxy	-OH	
Methylene	-CH <sub>2</sub>	
Carboxilate	-COOH	
Carbo-Carbon	C-C	Carbon chain:
Hydrocarbon	C-H	more than 4

**Table 3: IR absorption peaks identification at specific wave of LSK sample**

Absorption peaks wave of the sample (cm <sup>-1</sup> )	Wave range (cm <sup>-1</sup> )	Atomic bond	Spectrum type
3429	3600-3200	O-H	Stretching band
2918 dan 2850	3100-2800	C-H	Stretching bands
1695	1740-1640	C=O	Stretching band
1633	1650-1600	C-C	Stretching band
1463 dan 1371	1480-1300	C-H	Bending bands
1244,1050,1010	1300-900	C-O	Stretching bands



### Examination of ISA Chemical Structure

According to Brydson<sup>6</sup>, aleuretic acid is the main constituent of shellac. Therefore, the validation of the prediction that aleuretic acid is the main constituent of ISA polymer can be proved by comparing FTIR results of ISA polymer as shown Figure 2 to FTIR of shellac from Gatty Conservation Institute<sup>7</sup> as shown Figure 6. Detection wave ranges ( $\text{cm}^{-1}$ ) in Figure 6 were 3600-3200 (O-H stretching band), 3100-2800 (C-H stretching band), 1740-1640 (C=O stretching band), 1650-1600 (C-C stretching band), 1480-1300 (C-H bending bands), 1300-900 (C-O stretching bands). Both of the FTIR result in similar absorption. It indicates that both samples composed of the same functional groups.

### Polarity of ISA Biobased Material

Second examination to prove that the main content of ISA sample is aleuretic acid was done by dissolving method in which polar substances dissolve in polar solvents and insoluble in non-polar. A -COOH functional group is polar, but the long alkyl chain in the aleuretic acid causes this material to be semi-polar. The great amount of hydroxyl group content causes the sample to be soluble in alcohol (Figure 7a). Solubility in water is very low because it has a long alkyl chain that is 16 as shown in the Figure 7b. Bodner [9] revealed that the carboxylic acid solubility has decreasing levels in the water along with increasing amounts of alkyl chain. Long alkyl chain is non-polar, however, the -COOH group at the end of the molecule is polar so that the carboxylic acid will dissolve in water even though only slightly and the water color changed to be reddish but ISA remains in solid phase.

Hypothesis that chemical structure of the sample was proven right by the unsolubility in non-polar hydrocarbons such as gasoline and kerosene as shown by Figure 8a. This sample does not include ketones, due to no evidence of solubility in acetone as shown by Figure 8b. This related to the presence of wave number of around  $1700 \text{ cm}^{-1}$  which is C = O carbonyl group which allows ketone group (RCOR).

### Proving of ISA Chemical Structure prediction by Comparing to Raw Material of Shellac

If ISA and shellac biobased material

composed of the same chemical structure, then logically ISA and shellac basic material biobased material also composed of the same chemical structure. Therefore, studies related to the shellac basic are necessary. According to Singh<sup>10</sup>, the lac treatment process comprises of stick lac, seedlac and shellac. Stick lac is lac which still attached to the parent branch. Seedlac is the further process of the lac stick into granules which passed mesh<sup>10</sup> so as not to clot and prevent the breeding of pests in the storage room. While shellac is the end product of the lac processing. According to Chauhan<sup>11</sup>, lac is resin shaped secretion produced by the soft body lac louse to protect the unfavorable environment and attached to the parent branch. In summary, it can be concluded that the shellac comes from the lac bug secretions in the form of resin. Shellac is made from raw materials originating from lac louse secretion, whereas ISA sample has chemical structure similarity with shellac. Therefore, ISA sample functional group should be equal to that of lac secretion as basic materials makers of shellac. To prove this conclusion, characterization and investigation of lac secretion that has been produced in Indonesia is needed. The results of investigation showed that the insect that produce secretion for shellac basic materials have been cultivated at Kesambi tree by PT. Banyukerto, Probolinggo under PT. National Plantation II (PTPN II) of East Java<sup>12</sup>. To simplify the writing, the lac secretion of Kesambi tree is hereinafter referred to as LSK.

LSK characterization by FTIR can reveal that the compilers of its functional groups are the same as that of ISA, ie (-OH), (-CH<sub>2</sub>), (-COOH) and (C-C), (C-H) and (C-O) as shown by Figure 9 and Table 3. ISA and LSK have the same chemical structure. LSK is the secretion of lac insect that live in trees Kesambi, and ISA sample is a secretion of lac insect that

### The visually similarity examination of ISA and LSK

Conclusion that the ISA is the secretion of lac insect live on Albazia tree, has been supported by visual comparison between LSK and ISA samples related to types of insect, secretion attached to twigs and seedlac products. Basically both insect that appear in the Figure 10 are the same. Insect which are found on the Albazia tree is

immature fleas that are still in their colony as shown in the Figure 10c. When getting mature, these insect will run and leave the colony as shown in the Figure 10d.

Secretion insect attached to the Albazia and Kesambi trees have form and color in common, as seen in the Figure 11a and 11b. The similarity of the two secretions was also supported by the same visible apparition when the grains are made to pass mesh 10 as shown by Figure 11c. and Figure 11d.

#### Implication of Research Results

Lac insect can live on Albazia tree without treatment and do not cause the death of the parent tree. This conclusion is supported by the fact that the lac insect secretion were used by community obtained from Albazia trees grown and live wildly in a rural mountain area of Karangnangka village, Banjarsari subdistrict, Ciamis regency, West Java District, Indonesia. The results of the investigation and characterization may have implications for the potency for cultivation of lac insect at Albazia trees. Albazia trees have in nature easy planting and maintenance, relatively short age, and versatile wood so that many people who planted them both in the yards and other vacant lands. If lac insect cultivation ways can be developed on Albazia tree, then the added advantage can be gained as lac insect secretion attached on it branches. These branches will dry, but the Albazia trees do not die so that timber harvest can still be done.

#### CONCLUSIONS

Based on data and discussions of ISA sample, including: functional groups, the similarity in the wave range of energy absorption between the ISA sample, shellac and LSK, the solubility in polar solvents and the insolubility in non-polar solvents, the similar insect visualization, insect secretion visualization both before and after granulated, the conclusion can be drawn as the following:

- Insect which live on Albazia trees are lac insect.
- ISA sample that has been used by the surrounding community as an ingredient for adhesive is the secretion of lac insect that live on Albazia trees.
- The term "imah sireum" or "ants house" used by Ciamis community refers to this biobased material is not appropriate. So, ISA sample is not "ant's house" but lac secretion and one of alternative biobased materials for matrix composite application development.
- Lac insect can live on Albazia tree without treatment and do not cause the death of the parent tree.

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