

Preparation and characterization of non-isocyanate polyurethane resins derived from tannin of *Acacia mangium* bark for the modification of ramie fibers

Manggar Arum Aristri^{1, 2}, Muhammad Adly Rahandi Lubis^{2, 3}, Rita Kartika Sari^{1*},
Lubos Kristak⁴, Apri Heri Iswanto⁵, Efri Mardawati^{3, 6}, Lee Seng Hua⁷

¹IPB University, Faculty of Forestry and Environment, Department of Forest Product, Jl. Raya Dramaga Kampus IPB Dramaga Bogor, ID-16680 West Java, Indonesia

²Research Center for Biomass and Bioproducts, National Research and Innovation Agency, Cibinong Science Center, West Java, ID-16911, Indonesia

³Research Collaboration Center for Biomass and Biorefinery Between BRIN and Universitas Padjadjaran, Jatinangor, West Java, ID-40600, Indonesia

⁴Technical University in Zvolen, Faculty of Wood Sciences and Technology, SK-96001 Zvolen, Slovak Republic

⁵Universitas Sumatera Utara, Faculty of Forestry, Padang Bulan, North Sumatra, ID-20355, Indonesia

⁶Universitas Padjadjaran, Department of Agro-industrial Technology, Jatinangor, ID-40600, Indonesia

⁷Universiti Teknologi MARA (UiTM) Cawangan Pahang Kampus Jengka, Faculty of Applied Sciences, MY-26400 Bandar Tun Razak, Pahang, Malaysia

Abstract

The purpose of this research was to create bio-based non-isocyanate polyurethane (Bio-NIPU) resins derived from the tannin of *Acacia mangium* Willd. bark for the impregnation of ramie fibres (*Boehmeria nivea* L.) and to investigate the properties of impregnated fibres. Tannin was extracted from the bark of *A. mangium* using hot water. Tannin-bio-NIPU resin was created using dimethyl carbonate and hexamine. Based on the findings, it is possible to conclude that tannin extract from the bark of *Acacia mangium* can be used effectively as a renewable alternative to toxic polyols in the development of tannin-Bio-NIPU resins. FTIR spectroscopy was used to confirm the urethane bond formed on the tannin-Bio-NIPU resins. Thermal and mechanical analysis were used to investigate the properties of tannin-Bio-NIPU resins and ramie fibres before and after impregnation. This study shows that the impregnation time of ramie fiber using tannin-Bio-NIPU resins is 30 minutes. The reaction between tannin-Bio-NIPU resins with ramie fiber forms the C=O urethane group as confirmed by FTIR Spectroscopy. The characterization results show that tannin-Bio-NIPU resins has ability to modify ramie fiber via impregnation in order to increase its mechanical properties, thus enhancing its potential for wider industrial application as a functional material.

Key words: *Acacia mangium* bark; bio-based resins; non-isocyanate; polyurethane resins; ramie fibers; tannin

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1. Introduction

The area of mangium (*Acacia mangium* Willd.) plantations in Indonesia reaches 67% of the total mangium plantations worldwide. It was reported that around 46.4 million ha of mangium plantation forest was built in Indonesia, with the highest mangium producers being the provinces of Central Java and East Java, mainly used for the pulp and paper industry. However, Industrial Plantation Forests and cen-

tres of wood processing industry activities in Indonesia, such as the pulp and paper industry, fiberboard industry, and other industries, do not use bark as an industrial product. They tend to avoid the presence of bark in the production process because it contains substances with relatively high extractive content, so it can cause black color, reduce the glueing process, and deteriorates product quality. This mangium tree consists of 30–50% wood and 10.5–12.1% bark (Sukmawi et al. 2020).

*Corresponding author. Rita Kartika Sari, e-mail: rita_kartikasari@apps.ipb.ac.id

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The availability of mangium bark as a by-product of pulp and paper is increasing every year, and most of it becomes waste because it is not used correctly. Therefore, the bark must be utilized so that it does not become waste that can harm the environment and interfere with company activities and as a form of support for the Ministry of Forestry's policy on optimal utilization of forest products aimed at reducing the amount of waste (zero waste). One of the uses of the bark is by utilizing its tannin extractive substances. The bark has a high content of tannin compounds but has not been extracted or produced commercially, so mangium bark has the potential to be used as a tannin raw material (Wina et al. 2010; Mohamad Hafiz et al. 2020). On the other hand, the resulting viscous tannin extract can be used to make polyurethane (PU) resins.

PU resin is a urethane-characteristic group ($-NCO$) polymer widely used in packaging, adhesives, coatings, and other industrial sectors. Polyurethane's wide application is due to its good mechanical properties and biocompatibility (Ionescu et al. 2016). According to Gama et al., (2018), traditional PU synthesis involves a polycondensation reaction mechanism between diisocyanates and polyols, both of which are petroleum-derived materials. The high demand for PU from various industries has resulted in environmental issues due to the depletion of fossil resources, so using environmentally friendly renewable resources is highly desirable. Polyol materials, commonly used, can be synthesized from renewable sources, including tannins (Alinejad et al. 2019).

As a result, in this study, we attempt to use viscous tannin extract to synthesise PU resin so that it is more environmentally friendly and economical and can be used to modify other materials. Previous bio-PU developments used toxic isocyanates that required phosgene, a deadly gas also harmful to the environment, to synthesize (Aristri et al. 2021c). Because of the toxicity of these isocyanates, several studies are being conducted to focus on replacing isocyanates in the PU production process with alternative materials that are more environmentally friendly and harmless. The diol/polyol is reacted with cyclic and bicyclic carbonate, and the resulting carbonated polyol is then reacted with a diamine, resulting in a polyhydroxy-urethane reaction and the production of non-isocyanate polyurethane (Aristri et al. 2021a).

Because of its low cost, abundant availability in nature, and environmental friendliness, the production of PU from materials based on living organisms, such as plants and trees, can be more efficient, attracting much attention in the development process. These materials derived from living organisms can include lignin, tannins, vegetable oils, terpenes, and sugars (Gholami et al. 2021). Thus, it is necessary to develop alternative materials that can substitute isocyanate to manufacture non-isocyanate bio-polyurethane. In this study, tannins will be used as an alternative to polyol as well as dimethyl carbonate and hexamethylenediamine which are used as isocyanate substitutes which are harmful to

health and the environment. Therefore, in this research, a Non-Isocyanate Tannin-based Bio-Polyurethane resins (Tannin-Bio-NIPU resins) will be produced which will then be used as a modified ramie fiber.

On the other hand, synthetic fibers are in great demand as materials in developing polymer composites, but they are not environmentally friendly. According to Mahir et al. (2019), carbon, aramid, and kevlar are commonly used synthetic fibers. Along with the increasing awareness and concern for the environment, more environmentally friendly materials have begun to be in demand. In addition, Indonesia has the potential for abundant and varied natural fiber wealth. One type of natural fiber that has the potential to be developed as an alternative raw material for polymer composites is ramie fiber (*Boehmeria nivea* [L.] Gaudich).

Ramie fiber is one of the plants found in almost all regions in Indonesia which contains relatively high amounts of cellulose. Ramie fiber has good strength and stiffness properties, is resistant to decay, and has a strength two times greater than ordinary wood fiber (Twite-Kabamba et al. 2009). Research conducted by Lee et al., (2020) shows that ramie fiber has better physical and chemical characteristics than other natural fibers. Paiva et al. (2004) discuss a polyester/cotton ramie composite that is printed using compression, the study concluded that ramie fiber has potential as a fiber reinforcement in resin matrix composite materials, indicating an increase in tensile strength in pure resins by up to 338%. Margem et al. (2010) reported that the strength of ramie fiber is excellent when compared to other natural fibers, so it has the potential to be developed as a polymer composite.

Although ramie fiber has several advantages and is more environmentally friendly than synthetic fiber, there are also some disadvantages, such as the relatively high water absorption capacity that can cause weak interfacial bonds between the polymer matrix and the fiber, and cause damage to mechanical properties. In addition, the maximum processing temperature for natural fibers is relatively limited, and ramie fiber also has flammable properties, so additives such as halogen, nitrogen, and phosphorus-based compounds are needed to increase the heat resistance of polymer composites (Bachtiar et al. 2019). Therefore, modification of ramie fiber by impregnation using a tannin-Bio-NIPU resin needs to be done.

2. Material and method

Acacia bark (*A. mangium*, 40–60 mesh) was obtained from PT Tanjung Enim Lestari Pulp and Paper (Palembang, Indonesia). Aquades, hydrogen peroxide 7% (Merck, Emsure), isopropyl alcohol 4%, urea 1%, dimethyl carbonate (DMC, SigmaAldrich, 99%), and hexamethylenediamine (HMDA, SigmaAldrich).

The first procedure is the extraction of tannins using the maceration method. The sample:solvent ratio was 1 : 10 [w/v] using distilled water, and the extraction temperature was 60 ± 2 °C. The resulting filtrate is then collected, and repeated extractions are carried out on the remaining residue until the extract or the resulting filtrate is clear. Then the filtrate was concentrated using a rotary evaporator with a pressure treatment condition of 74 mbar, a temperature of 60 ± 2 °C, and a speed of 100 rpm to produce viscous tannin extract.

The second procedure synthesises a tannin-based non-isocyanate bio-polyurethane resin (Tannin-BioNIPU), beginning with the synthesis of carbonated tannins. Tannins were reacted with dimethyl carbonate (DMC) with a 1 : 1 [w/w] tannin:DMC, heated and stirred at a temperature of 50 ± 2 °C for 15 minutes. The resulting carbonated tannins were then reacted with hexamethylenediamine (HMDA) with a ratio of 4 : 1 [w/w] carbonated tannin:HMDA, then stirred with a stirring speed of 500 rpm for 30 minutes.

The third procedure is to apply tannin-Bio-NIPU resin as a modified ramie fiber. Ramie fiber was pre-treated using 1% urea and 7% hydrogen peroxide (T: 85 °C t: 60 min) and isopropyl alcohol (T: 100 °C t: 60 min), and then ramie fiber was impregnated using an impregnant in the form of a tannin-Bio-NIPU resin produced in the previous step with different time variations (30, 60, and 90 minutes). Impregnation was carried out using degummed dried ramie fibers in a 1L vacuum with a 2-stage vacuum pump (VC0918SS, VacuumChambers. ue., USA). A sample of 3 g of ramie fiber was soaked in 30 mL of tannin-Bio-NIPU resin and then impregnated at 27 ± 2 °C under a pressure of 50 kPa for 30, 60, and 90 minutes. The impregnated fibers were dried at room temperature of 25 ± 2 °C for 24 hours. The dry ramie fiber was weighed to determine the weight gain after impregnation (%WPG).

The next procedure was to characterise samples of viscous tannin extract, tannin-Bio-NIPU resin, and impregnated ramie fiber which were compared with ramie fiber before impregnation. The oven drying method was used to determine the solids content of the viscous tannin extract. In a nutshell, 1 gram of tannin extract was placed in a petri dish. The sample was placed in an oven at 105 ± 2 °C for 3 hours. The sample was then removed from the oven and placed in a desiccator for 30 minutes, and re-weighed after from the oven. A sample of viscous tannin extract and tannin-Bio-NIPU resins in 20 mL was placed in a measuring glass and on a rotational rheometer (RheolabQC, Anton Paar, Austria). A spindle CC No. 27 was used with a constant shear rate of 250 s at 25 °C for 120 seconds to determine the average viscosity. The RheoCompass application displays viscosity results (Version 1.33, Anton Paar, Austria).

The Universal Attenuated Total Reflectance (UATR) method was used to analyze the functional groups of viscous tannin extracts, tannin-Bio-NIPU resin, and ramie

fiber before and after impregnation using FTIR (Spectrum Two, Perkin Elmer, USA). The average accumulation was measured in 16 scans at a resolution of 4 cm^{-1} and wavenumbers ranging from 4,000–400 cm^{-1} . The measurements were taken at a temperature of 25 ± 2 °C.

DMA (DMA 8000, PerkinElmer, USA) dual cantilever mode with a constant frequency pull of 1 Hz was used to measure the thermomechanical properties of viscous tannin extract and tannin-BioNIPU on filter paper at range temperatures from 20 to 50 °C. By heating each sample at rates of 1 °C min, the response was expressed in terms of storage modulus [E'], loss modulus [E''], and damping properties [$\tan \delta$]. Pyris 11 software creates graphics (Version 11.1.1.0492, Pyris, USA).

The tensile strength and modulus of elasticity (MOE) of ramie fiber before and after impregnation was tested using UTM according to the ASTM D 3379-75 (ASTM 2000) standard. The specimens used were single fibers separated from their strand bonds. The specimens used are 20–30 mm long, and the overall fiber length is approximately three times the length of the specimen. Specimens were tested with a loading of 5,000 N and a crosshead speed of 1 mm min. The experiment was carried out in a room with a temperature of 252 °C.

3. Results

3.1. Characteristic of viscous tannin

The highest concentration of tannins is in the bark of trees, so in this study, tannin was extracted from the bark of *A. mangium*, a by-product of the pulp and paper industry. The moisture content of mangium peel powder can be seen in Table 1, which is 5.47%, the water content is determined one of them to determine the resistance in the storage process and to know the best way of handling a material to be able to inhibit the influence of microbial activity, because water is a medium for microbial growth and a medium that good in the occurrence of chemical reactions (Labbé et al. 2002; Putra et al. 2021).

The FTIR spectra of viscous tannin extract and tannin-Bio-NIPU resins are shown in Fig. 1. There are differences in the characteristic groups between polyphenol tannins before being reacted with dimethylcarbonate (DMC) and hexamethylenediamine (HMDA) and those after being reacted to form a polymer called tannin-Bio-NIPU resins. Fig. 1 also shows the difference between the

Table 1. Characteristics of *Acacia mangium* bark and viscous tannin extract.

Properties	Results [%]
Moisture content of <i>Acacia mangium</i> bark	5.47
Solids content of viscous tannin extract	93.46
Yield of viscous tannin extract	26.43

spectra and absorption peaks seen between the tannin-Bio-NIPU in liquid and solid state.

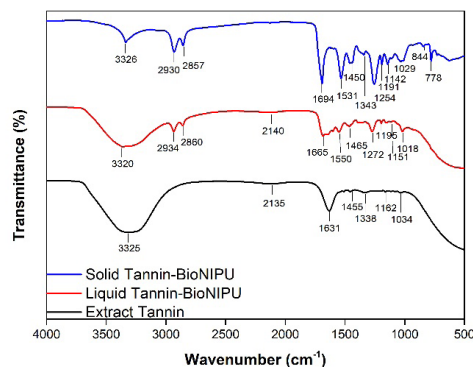


Fig. 1. Spectra FTIR of viscous tannin extract, liquid and solid tannin-Bio-NIPU resins.

3.2. Possible scheme reaction of tannin-Bio-NIPU resins

The reaction scheme that occurs can be seen in Fig. 2 where the monomer in the viscous tannin extract will initially react with the carbonyl group on the DMC to form an intermediate product before finally reacting again with the amine group on HMDA and forming a urethane group on the tannin-Bio-NIPU resin.

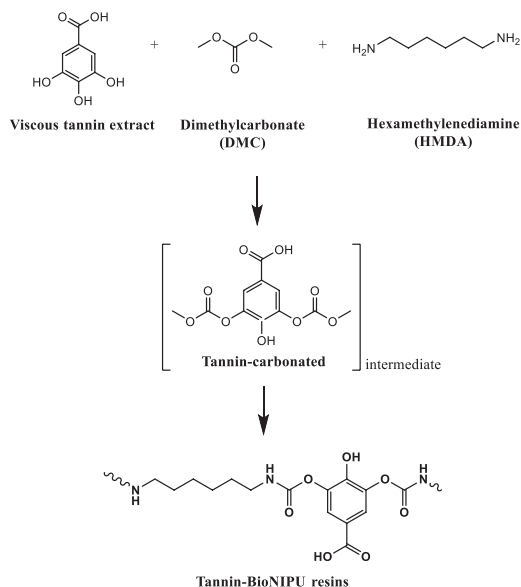


Fig. 2. Scheme reaction of tannin-BioNIPU resins.

3.3. Rheological properties of viscous tannin and tannin-Bio-NIPU resins

Basic rheological properties are needed to determine the absorption ability of the impregnants used for modifica-

tion of ramie fiber through the impregnation process. The basic rheological properties were determined, including: viscosity, torque, cohesion strength, and relaxation modulus where each was measured at the same temperature of 25. Viscosity is important to determine because it relates to the viscosity of a liquid which can affect the fluid flow of the impregnant material used. Table 2 shows that the viscosity of viscous tannin extract is the lowest when compared to tannin-DMC, and tannin-Bio-NIPU resins which are 0.49, 2.99, and 20.35 mPa s, respectively.

Table 2. Basic rheological properties of viscous tannin extract, tannin-DMC, and tannin-BioNIPU resins.

Sample	Viscosity [mPa s]	Torque [mN m]	Cohesion strength [Pa]	Relaxation modulus [mPa]
Viscous Tannin Extract	0.49	0.01	0.05	0.02
Tannin-DMC	2.99	0.04	0.75	0.11
Tannin-Bio-NIPU	20.35	0.27	5.09	0.70

3.4. Termomechanical and viscoelastic properties of tannin-Bio-NIPU resins

Tannin-Bio-NIPU resins were further characterized to determine the viscoelastic and thermomechanical as well as the molecular structure of the polymer formed (Fig. 3–5). The results showed the viscoelastic and thermomechanical properties of *Acacia mangium* bark, including storage modulus [E'], loss modulus [E''], and damping factor [$\tan \delta$] that related to the composite interface bond.

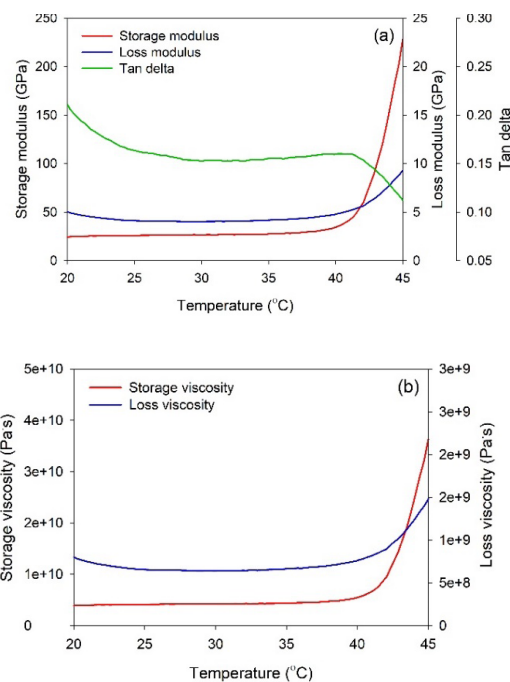


Fig. 3. DMA thermograms of tannin from *A. mangium* bark: (a) thermo-mechanical (storage modulus, loss modulus and tan delta) and (b) viscoelastic properties (storage viscosity and loss viscosity).

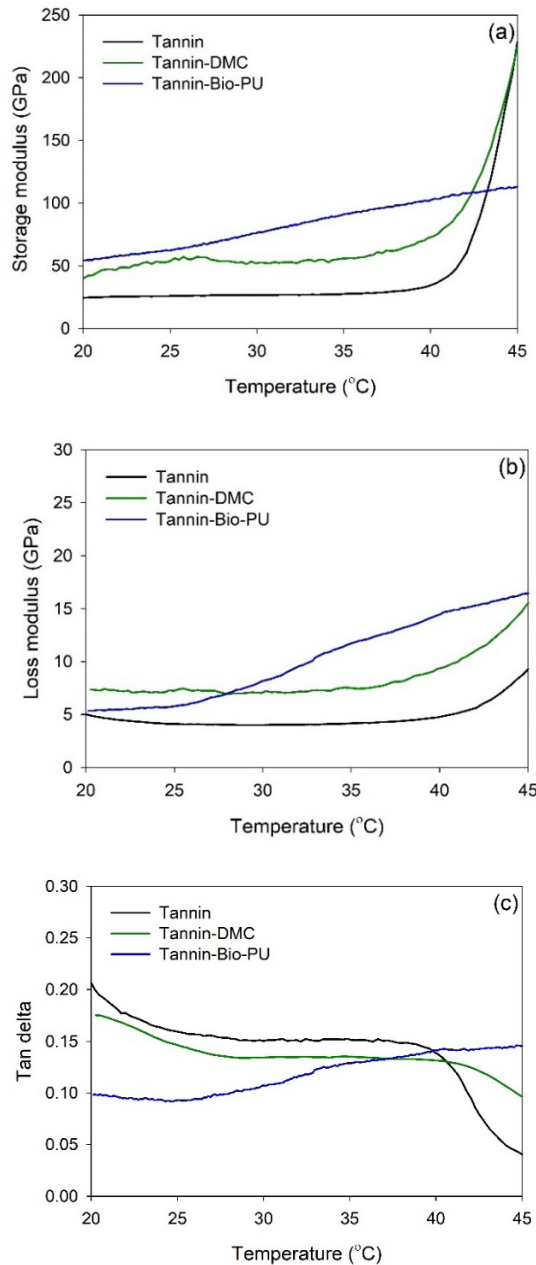


Fig. 4. Thermo-mechanical properties of tannin-Bio-NIPU resins: storage modulus (a), loss modulus (b), and tan delta (c).

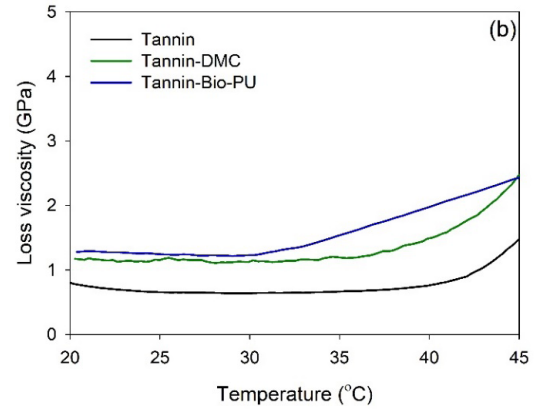
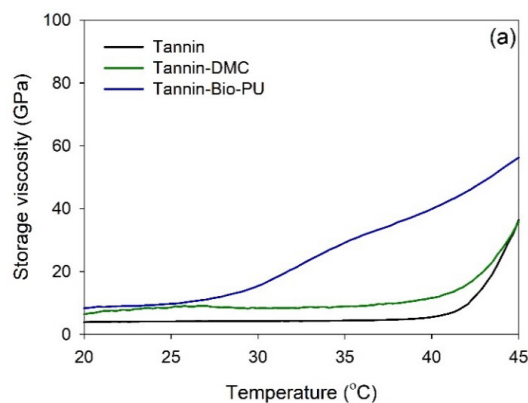


Fig. 5. Viscoelastic properties of tannin-Bio-NIPU resins: (a) storage viscosity and (b) loss viscosity.

3.5. Weight gain analysis of ramie fiber after impregnation

The increase in ramie fiber after impregnation with the time variation applied can be seen in Table 3. It can be seen that the longer the time used in the impregnation process, the fiber weight gain increases, where the highest weight gain results were shown at 90 minutes impregnation (38.29%) and the lowest occurred at 30 minutes impregnation time (19.90%). These results can also be affected by the viscosity of the tannin-Bio-NIPU resin and the diameter of the fiber used.

Table 3. Weight-Gain of impregnated ramie fiber with different times.

Impregnation time [min]	Weight gain [%]	Diameter of ramie fiber [μm]
30	19.90	30.30
60	26.47	32.12
90	38.29	37.86

3.6. Functional groups of ramie fiber after impregnation

Fig. 6 shows the comparison of FTIR results between control ramie fibers without impregnation treatment (ramie-H₂O₂) and impregnated ramie fibers with tannin-BioNIPU resins (ramie-tannin-Bio-NIPU). Based on the graph, it can be seen that there are several differences in the absorption peaks of the two types of ramie fiber before and after impregnation.

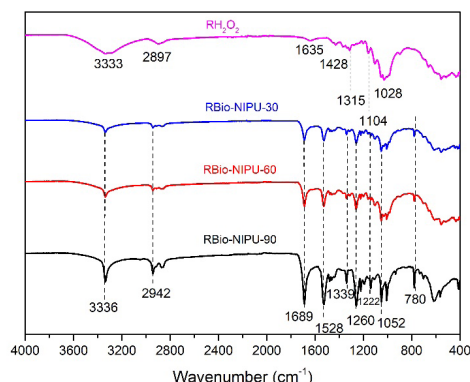


Fig. 6. Spectra FTIR of ramie fiber before and after impregnation with tannin-Bio-NIPU.

3.7. Mechanical properties of ramie fiber

The mechanical properties of ramie fiber were analyzed based on the results of the tensile strength and modulus of elasticity (MOE) tests compared to ramie fiber before and after impregnation. The value of the tensile strength of the fiber and the MOE can be seen in Fig. 7. Determination of the tensile strength of ramie fiber is important as one of the selections of ramie fibers used for textile raw materials. Kandimalla et al. (2016) stated that tensile strength indicates the ability of a fiber to withstand a given longitudinal stress. The pre-impregnated

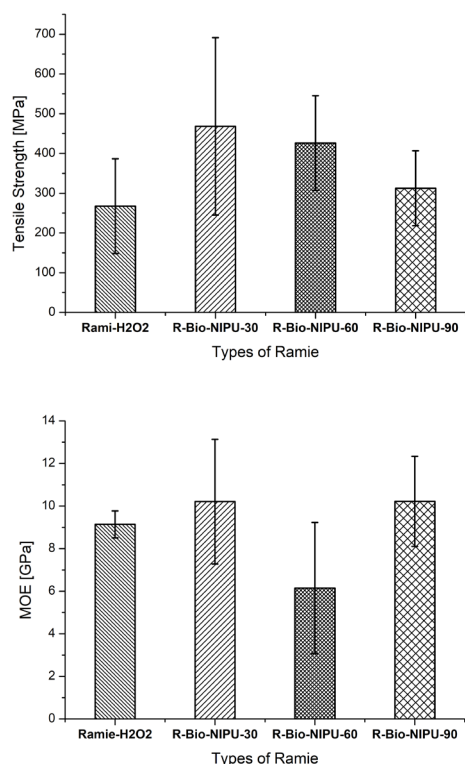


Fig. 7. Tensile strength and modulus of elasticity (MOE) of impregnated ramie fiber.

fiber had the lowest tensile strength among the post-impregnated fibers, which was 267.57 MPa, while the ramie fiber had the higher tensile strength after being impregnated.

4. Discussion

4.1. Characteristic of viscous tannin

The tannin extraction process is carried out by immersing in hot water and the extraction is carried out repeatedly until the tannin extract comes out perfectly or is marked with a clear color in the resulting extract filtrate. This extraction technique is known as maceration. Cuong et al. (2019), stated that the use of this method is quite efficient both in terms of costs and the environment because the temperature used is only in the range of 60–70 °C. During the extraction process, the bond between tannins and proteins can be broken so that the resulting extract will be more optimal. This can be proven from the yield obtained as shown in Table 1, which is 26.43%. These results are greater than the results of the research of Sosuke et al. (2003) with the same material and solvent ratio, which is 1 : 10. The resulting filtrate is then concentrated using a rotary evaporator with the principle of separating the extract from the solvent media so that a thick extract of tannin will be produced which is then tested for a solid content of 93.46% (Table 1).

The solids content indicates that the tannin extract produced has a high concentration compared to the solvent medium, which is only around 7%. Extract concentration using a rotary evaporator is considered more effective and efficient both in terms of time and cost when compared to using a freeze-dryer. The selection of the concentration method is also determined based on the process of further utilization of the tannin extract, which does not require the production of tannins in powder form.

4.2. FTIR spectroscopy of viscous tannin and tannin-Bio-NIPU resins

The FTIR spectra of viscous tannin extract, liquid tannin-Bio-NIPU resins and solid tannin-Bio-NIPU resins show each other an absorption band at a wavenumber of 3,320–3,326 cm^{-1} (OH vibration strain), but the difference can be seen in the solid form of tannin-Bio-NIPU resins which shows the band is stronger or sharper when compared to viscous tannin extract and liquid tannin-Bio-NIPU resins, which have a wider absorption band. This happens because the broad absorption band is a marker of the amount of water contained in the sample, because the solid tannin-Bio-NIPU resins have undergone an oven process first so that the solid form of the resin does not

contain much water when compared to viscous tannin extract and liquid. tannin-Bio-NIPU resins.

The spectrum of viscous tannin extract describes absorption bands occurring at wavenumbers of $2,135\text{ cm}^{-1}$ (C–H bending) and $1,631\text{ cm}^{-1}$ (strain vibration of the aromatic ring), which explains the stretching vibration of the C–H bond on the methyl group in the aromatic ring, in addition to the presence of strain on the C–O group which is also the cause of the formation of resonance in the aromatic ring (Thébault et al. 2017; Amari et al. 2021). In addition, the absorption band at wavenumber $1,455\text{ cm}^{-1}$ (C–H vibration bending methylene group), $1,338\text{ cm}^{-1}$ (O–H vibration bending phenolic group) which is a characteristic group for polyflavonoid tannins, and at wavenumber $1,162\text{ cm}^{-1}$ (C–O stretching vibration) on the ester group which is an indicator that the resulting tannin is classified as hydrolizable tannin because the ester group is classified as a monomer derived from gallic acid. On the other hand, the success of tannin extraction is also indicated by the appearance of an absorption band at a wavenumber of $1,034\text{ cm}^{-1}$ (stretching vibration of ether chain C–O–C) which occurs in the heterocyclic ring of flavonoid groups. Then, in Fig. 1 it can be seen that after the viscous tannin extract was reacted with DMC and HMDA there were several other new peaks, such as at wavenumber $2,934\text{ cm}^{-1}$ as well as at wavenumber $2,860\text{--}2,857\text{ cm}^{-1}$ (C–H stretching vibration of the methylene group in the product esterified) (Selladurai & Kathiresapillai 2017).

The reaction scheme that occurs can be seen in Fig. 2 where the monomer in the viscous tannin extract will initially react with the carbonyl group on the DMC to form an intermediate product before finally reacting again with the amine group on HMDA and forming a urethane group on the tannin-Bio-NIPU resin. The spectrum of tannin-Bio-NIPU resins in liquid and solid forms has some similar absorption peaks but in the liquid form is identical, there are fewer absorption bands or the absorption intensity is lower when compared to the solid form. This is due to the fact that in its liquid form, the resin spectrum will be more covered by the solvent media used, such as water or other solvents, so that generally the absorption intensity shown is low and does not cause absorption in the fingerprint area which can be an additional identifying group.

The form of liquid tannin-BioNIPU resins in Fig. 1 shows that there is an absorption band at a wavenumber of $2,140\text{ cm}^{-1}$ (C–H bending vibration) which is a stretching vibration of the aromatic tannin component. At wavenumbers $1,694\text{--}1,665\text{ cm}^{-1}$ (C–O and N–H stretching vibrations) and $1,550\text{--}1,531\text{ cm}^{-1}$ (CN-amide bonds) are indicators that the polymerization process and the formation of urethane bonds have been successful (Thébault et al. 2017). Absorption band $1,465\text{--}1,450\text{ cm}^{-1}$ (C–H bending vibration of methylene group). In the solid form of tannin-BioNIPU resins, there are also absorption bands at wavenumbers $1,343\text{ cm}^{-1}$ (phenolic functional

group), $1,195\text{--}1,191\text{ cm}^{-1}$ (C–O stretching vibration of ester group), at wavenumbers $1,195\text{--}1,142\text{ cm}^{-1}$ (tertiary alcohol group of resins), and at $1,151\text{--}1,142\text{ cm}^{-1}$ (stretching vibration C–O of aliphatic ether). C–O–C ether bond opening occurred in the heterocyclic ring of the flavonoid group of tannins indicated in the absorption bands at $1,018$ and $1,029\text{ cm}^{-1}$ due to the formation of new bonds due to the reaction process between tannins with DMC and HMDA resulting in stretching of the main hydroxyl groups in carbohydrates. The presence of OH from the C_3 bond of the flavonoid and OH carbohydrates resulted in a decrease in the absorption peak at both wavenumbers (Thébault et al. 2017). Based on the results of the FTIR functional group analysis, it shows that viscous tannin extract has several functional groups contained, such as hydroxy groups that allow tannins to bind to other compounds and form tannin-Bio-NIPU resins when reacted with DMC and HMDA (Aristri et al. 2021b).

4.3. Rheological properties of viscous tannin and tannin-Bio-NIPU resins

The results showed that tannin-Bio-NIPU resins have the most viscous solution compared to the other two samples (Table 2). This is because, when viscous tannin extract is reacted with DMC, a new bond is formed between the hydroxyl group of viscous tannin extract and the carbonyl group of DMC, and produces a carbonated tannin compound. Then, when compared with tannin-Bio-NIPU resins, the viscosity is increasing because more bonds are formed and the urethane bonds are produced so that the structure of the resulting compound is more bulky and is evidenced by the viscosity value which has increased drastically to 20.35 mPa s .

The use of temperature when the resin synthesis reaction process also contributes to the increase in viscosity due to the higher the viscosity value produced, the more difficult it is for the fluid to flow properly. In addition, this viscosity value is also related to the shelf life of the material. The higher the viscosity value, the easier the material will harden, thereby reducing its ability as an impregnant. However, the average viscosity produced by the tannin-Bio-NIPU resins is still categorized as low when compared to other resin types. Thus, it is hoped that the resin can be a good impregnant when impregnated as a modified ramie fiber. Torque values and cohesion strength also showed an increase in viscous tannin extract, tannin-DMC, and tannin-BioNIPU resins (Table 2). The torque value for the tannin-Bio-NIPU resins was the highest (0.27 mN m) due to the formation of a polymer so that the torsion value produced can also confirm that the tannin-Bio-NIPU resins were successfully synthesized. The torque values also indicate the melting characteristics of the compounds in the samples used when they are synthesized into a polymer.

The occurrence of the polymerization reaction can be seen along with the increase in the torque value caused by the new bonds formed. The torque value is also directly proportional to the viscosity, because it is also influenced by the increase in the molecular weight of the new bonds formed by the addition of a compound (Gogoi et al. 2014). The increase in torque value is quite sharp compared to viscous tannin extract and tannin-DMC because the torque value is strongly influenced by the presence of cross-links formed due to the reaction of tannin-DMC with HMDA so that it shows the polymerization process formed.

Table 2 also shows the value of the cohesive strength which is directly proportional to the value of the viscosity and the value of the torque. It is important to analyze the cohesive strength because it affects the process of applying the resin used later. The strength of this cohesion also shows the internal strength of the resin due to the interaction between materials that bind to each other and form a polymer bond. The strength of this cohesion is influenced by the internal strength of a material (intramolecular chemical bonds), cross-links in polymers, as well as intermolecular mechanical bonds. The intermolecular forces formed will have an influence on the properties of the resin when applied. The higher the cohesive strength produced in the resin, the easier it is for the resin to penetrate into the fiber surface during the impregnation process. Reaction conditions such as the temperature used during the polymerization process is also positively correlated with the strength of the resulting cohesion, the higher the temperature used, the stronger the cohesion will be (Fraunhofer 2012).

The relaxation modulus in Table 2 also shows results that are directly proportional to the viscosity, torque, and cohesion strength where tannin-Bio-NIPU resin has the highest relaxation modulus value, which is 0.70 mPa. Relaxation modulus shows the viscoelasticity of the material used and is related to the relaxation stress of the material with respect to the testing time. The relaxation modulus value shows the ratio of the relationship between shear stress and shear strain material, where the higher the relaxation modulus produced, the higher the shear stress obtained to maintain the shear strain.

4.4. Termomechanical and viscoelastic properties of tannin-Bio-NIPU resins

The resulting storage modulus [E'] graph shows that the value increases with the increase in temperature with an average of 25 GPa in the temperature range of 30–40 °C. The higher the temperature used, the rigidity and stiffness of the polyphenol tannin bonds will increase, resulting in a high resistance of the material to the movement of molecular chains and is directly proportional to the higher the energy required to move the bonds closer (Selvakumar & Meenakshisundaram 2019).

Loss modulus [E''] and damping factor [$\tan \delta$] are associated with loss of internal energy due to plastic deformation, internal friction, relative molecular motion, relaxation processes, phase transitions, and morphological changes (He et al. 2021). Furthermore, the results of the loss modulus E'' have a similar trend to E' where the results increase with the increase in the temperature used. The resulting E'' value can describe the viscosity of the sample based on the amount of energy lost due to viscosity deformation when a sample changes shape under a certain pressure and temperature. Figure 3a shows the $\tan \delta$ results which decrease when the temperature is above 40 °C, the $\tan \delta$ itself is the ratio between the loss modulus and storage modulus [E''/E'] which illustrates the greater the value of $\tan \delta$ which means that the value of viscous deformation and corresponds to energy loss from heat dissipation is also higher due to an increase in the bonding of OH groups (polyphenols) formed from viscous tannin extract. This $\tan \delta$ can be a measure of the ratio of energy lost to energy stored during cyclic deformation. This parameter reveals overall material behavior. The Tg value of a tested material can be determined from a graphic representation of $\tan \delta$ or E'' (Evaluation of glass transition).

Then the value of E' viscous tannin extract, tannin-DMC, and tannin-Bio-NIPU resin can be seen in Figure 4a, where the results from the graph of viscous tannin extract and tannin-DMC show constant values when below a temperature of 40 °C then above that temperature they experience an increase of up to 45 °C with the value of E' tannin-DMC greater [± 48 GPa] than the value of viscous tannin extract [± 25 GPa]. This happens because of the carbonation reaction which results in the number of bonds being formed becoming more and resulting in an increase in molecular weight and the value of molecular rigidity. Then the value of E' in the tannin-Bio-NIPU resin also increased even from a temperature of 25 °C followed by a constant increase to a temperature of 45 °C. The value of E' tannin-Bio-NIPU resins gave high results starting at the beginning of the test, which was 51 GPa and continued to increase until it reached 110 GPa. This is due to the polymerization process that occurs when tannin-DMC is reacted with HMDA, so that the molecular rigidity increases to its maximum temperature until the value of E' decreases again as described by Liang et al. (2013), which states that due to the nature of a polymer, causes a molecule to be more active in its movement. Therefore, the polymer chain and the forces between bonds become weaker along with the increase in a given temperature and this makes the storage modulus value not too high up to a certain temperature and then tends to decrease if the given temperature is higher when above its maximum temperature limit.

The value of loss modulus [E''] shows a similar trend to E' with increasing temperature giving a higher value of E'' , and a significant increase occurs starting at 30 °C in the sample of tannin-Bio-NIPU resins, in viscous tannin

extract it occurs at a temperature of 40 °C, and a temperature of 35 °C for the tannin-DMC sample (Fig. 4b). The highest value of E'' tannin-Bio-NIPU resins was 17 GPa, while tannin-DMC was 15 GPa, and viscous tannin extract was 9 GPa. This value indicates the large amount of energy dissipation at the molecular interface due to an increase in internal friction caused by polymerization reactions (tannin-Bio-NIPU resins) or carbonation reactions (tannin-DMC).

Furthermore, the general value for $\tan \delta$ is shown in Fig. 4c where the value decreases for the viscous tannin extract and tannin-DMC samples, and increases when the tannin-Bio-NIPU resins sample. The value of $\tan \delta$ can explain the viscoelasticity and damping capacity of the sample. The increase that occurred in the sample of tannin-Bio-NIPU resins was due to an increase in internal friction and dissipation of viscoelastic energy in line with the increase in temperature used. He et al. (2021) states that the polymerization reaction makes the molecule more rigid, so that the intermolecular movement becomes weaker and the polymer chain interface bonds become better (He et al. 2021).

Fig. 5a and 5b illustrate the viscoelastic properties of viscous tannin extract, tannin-DMC, and tannin-Bio-NIPU resins which illustrate the results of storage and loss viscosity based on the tests carried out. The viscoelasticity properties show an increase along with a given temperature increase. The results of the storage and loss viscosity values shown in the graph give almost the same value between the viscous tannin extract and tannin-DMC samples, only the loss viscosity value for tannin-DMC gives a higher value. The increased storage viscosity value was caused by the addition and formation of new bonds in the tannin-DMC sample due to the carbonation process so that the viscosity of the solution increased.

The results of the storage viscosity value on tannin-Bio-NIPU resins reached 60 GPa (Fig. 5a) due to the polymerization reaction that occurred so that the bonds between molecules became stronger, rigidity increased, and the strength of cohesion also increased. However, although the value of storage viscosity increases, there is also an increase in the value of loss viscosity along with a given temperature increase, although the value of loss viscosity obtained is not too large for the three samples, only about 2.5 GPa (Fig. 5b).

4.5. Weight gain analysis of ramie fiber after impregnation

Impregnation is the process of incorporating impregnant materials into media such as ramie fiber which is used to improve the properties of the fiber both thermally and mechanically to increase the use value of the ramie fiber. One of the parameters to determine the success of the impregnation process carried out on ramie fiber is to cal-

culate the weight gain. The higher weight gain produced illustrates that the impregnant material in the form of tannin-Bio-NIPU resin has been successfully absorbed by ramie fiber and forms bonds with fiber components, so they are not easily separated. The increase in ramie fiber after impregnation with the time variation applied can be seen in Table 3. It can be seen that the longer the time used in the impregnation process, the fiber weight gain increases, where the highest weight gain results were shown at 90 minutes impregnation [38.29%] and the lowest occurred at 30 minutes impregnation time [19.90%]. These results can also be affected by the viscosity of the tannin-Bio-NIPU resin and the diameter of the fiber used.

The viscosity value of the resin used is quite low, which is 20.35 mPa s (Table 2), so the tannin-Bio-NIPU resin is easier to penetrate and bond with hemp fiber components. The diameter of the ramie fiber used ranges from 30–38 μm , where the diameter is much wider than cotton, hemp, and flax, making it easier for the impregnant material to enter and be absorbed efficiently into the ramie fiber which can increase the value of the added weight of the fiber after impregnation (Handika et al. 2021).

4.6. Functional groups of ramie fiber after impregnation

Tannin-Bio-NIPU resins that have been successfully synthesized are then used as materials for modification of ramie fiber using the impregnation method with different times (30, 60, and 90 minutes). The impregnation method is carried out to provide better heat stability and fire resistance properties to ramie fiber which will later be used as a functional textile material, with the result that ramie fiber is pretreated to make the fiber look cleaner and softer, so it is expected that the impregnated ramie fiber can be applied more easily into functional textile materials because the resulting of impregnated ramie is not stiff. The main working principle of the impregnation process is by impregnating tannin-Bio-NIPU resins into the ramie fiber, so that the impregnated material can enter between the ramie fibers and not only on the surface. The impregnation process was carried out using a vacuum impregnation carried out at temperature of 25 ± 2 °C and under pressure of 50 kPa. The vacuum process itself will help the impregnants enter the fiber through the given pressure. Furthermore, to see the success of the impregnation process, characterization of ramie fiber was carried out, one of which was using FTIR.

Fig. 6 shows the comparison of FTIR results between control ramie fibers without impregnation treatment (ramie- H_2O_2) and impregnated ramie fibers with tannin-BioNIPU resins (ramie-tannin-Bio-NIPU). Based on the graph, it can be seen that there are several differences in the absorption peaks of the two types of ramie fiber before

and after impregnation. In the ramie H_2O_2 graph, there are several absorption peaks, such as the wavenumber $3,333\text{ cm}^{-1}$ (stretching vibration of O–H) which indicates the presence of water content in the fiber. Based on the research of (Kandimalla et al. 2016), the OH group can also come from the presence of cellulose, hemicellulose, and lignin content in ramie fiber. Absorption band at a wavenumber of $2,897\text{ cm}^{-1}$ (stretching vibration of C–H) which indicates the methyl group of cellulose and hemicellulose components in ramie fiber (Aristri et al. 2022). The absorption band at $1,635\text{ cm}^{-1}$ (stretching vibration of C–H carbohydrate), the absorption peak at wavenumber $1,428\text{--}1,315\text{ cm}^{-1}$ (C–H bending of methylene group), then for the absorption peak $1,159\text{--}1,028\text{ cm}^{-1}$ revealed that C=O and O–H bending of the polysaccharides present in the cellulose compounds in ramie fiber. Furthermore, after impregnation with tannin-Bio-NIPU resins, there was a shift and several new absorption bands. Thus, the absorption bands generated for each time treatment given to ramie-tannin-Bio-NIPU (30, 60, and 90 minutes) tend to be the same but have different intensities. In Fig. 6, it can be seen that there is an increase in the absorption intensity at the peak of the resulting spectrum with the addition of the impregnation time used. This indicates that the longer the time used in the impregnation process, the greater the amount of impregnant (tannin-Bio-NIPU resin) absorbed by the ramie fiber. This illustrates that there is an increase in the performance of the tannin-Bio-NIPU resin, whereas an impregnant material it can enter and penetrate well into the ramie fiber as the time it is applied increases.

Ramie-tannin-bio-NIPU spectrum also shows an absorption band at wavenumber $3,336\text{ cm}^{-1}$, indicating the presence of OH groups in the impregnated ramie fiber originating from water and several chemical components making up the fiber. Then the absorption peak at wavenumber $2,942\text{ cm}^{-1}$ showed that N–H bending groups from tannin-Bio-NIPU impregnated into the ramie fiber. The shift in the peak from $1,635$ to $1,689\text{ cm}^{-1}$ indicates a bond interaction between the tannin-Bio-NIPU resin and ramie fiber. Then the absorption band at wavenumber $1,528\text{--}1,339\text{ cm}^{-1}$ illustrates the presence of C–N group activity originating from primary and secondary amides derived from the tannin-Bio-NIPU resin structure. At wavenumber $1,260\text{--}1,103\text{ cm}^{-1}$ revealed that vibration of C–O tannin-Bio-NIPU resins and at wavenumber $1,052\text{ cm}^{-1}$ was the absorption peak indicating stretching C–O–C ether chain. Furthermore, to confirm again that there is also an absorption peak at wavenumber 1007 and in the fingerprint region of the range of wavenumber 780 cm^{-1} showed that the NCO-free group of tannin-Bio-NIPU resin reacts with the OH groups present on the surface of the ramie fiber which then forms a urethane bond. Aristri et al. (2021) stated that the absorption peak indicated the rocking of the $-\text{CH}_2$ bond from the tannins-Bio-NIPU resins. The FTIR results indirectly confirm that the impregnation has been successful so

that tannin-Bio-NIPU resins have entered the ramie fiber successfully.

4.7. Mechanical properties of ramie fiber

The results of the tensile strength of ramie fiber after impregnation, based on the difference in the impregnation time used, show that the longer the impregnation time can reduce the tensile strength of the fiber. This is made possible because of the fiber softening process, carried out as a pretreatment of the ramie fiber used, thus making the fiber smoother. Still, its tensile strength decreases because some of the chemical composition of the fiber is degraded by the materials used, such as hydrogen peroxide.

Yan et al. (2014) stated that apart from chemical modification, several other factors can affect the mechanical properties of ramie fiber, such as the relative humidity of the environment, microstructure, length, and fiber diameter, besides that the water content and drying process of the fiber can also affect its mechanical properties. The MOE value in Fig. 7 shows an inconsistent trend where the fiber before impregnation gives a higher yield [$10,819.53\text{ MPa}$] than after impregnation [$6,148.76\text{--}10,220.35\text{ MPa}$].

5. Conclusion

Based on the result, it can be concluded that the extract of tannin from the bark of *Acacia mangium* can be efficiently used as a renewable alternative to toxic polyols in the development of tannin-Bio-NIPU resins. The urethane bond formed on the tannin-Bio-NIPU resins was confirmed using FTIR spectroscopy. Characteristics of impregnated ramie fiber with tannin-Bio-NIPU resins exhibits increased the thermal and mechanical properties than ramie before impregnation. This study shows that the optimum impregnation time of ramie fiber using tannin-Bio-NIPU resins is 30 minutes and it produces better thermomechanical, tensile strength and MOE properties. The functional group of tannin-Bio-NIPU resins (NCOO^-) react with hydroxyl groups of ramie fibers and forms the urethane groups as confirmed by FTIR spectroscopy. The characterization results show that tannin-Bio-NIPU resins has ability to modify ramie fiber via impregnation in order to increase its mechanical properties, thus enhancing its potential for wider industrial application as a functional material.

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