

Surface characteristic and direct interaction measurement on Ramie (*Boehmeria nivea*) single fiber - polymer matrix

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ABSTRACT

An approach to understanding compatibility between ramie fiber as reinforcement in polymer resin was pursued by investigation of the surface porosity and contact angle measurement. Treatment the fibers is a must to obtain optimal wettability and also intimate contact as a lock and key mechanism between the fiber surface and polymer resin. Fiber surface porosity was examined by BET (Brunauer-Emmet-Teller) method. It was surprising that the fiber treated by silane (trimethoxymethylsilane) and methylethylketone (MEK) had a higher porous diameter and specific surface area compared to ethanol and acetone. Comparison of wetting process between polypropylene (PP) and epoxy resins were also provided. Improvement was also showed by optimum contact angle between the fiber and PP droplets, which had $\cos \theta \approx 0.939$. Both polypropylene and epoxy resin have a good wettability which had contact angle $\theta < 55^\circ$. From the pull-out test, the fiber embedded in epoxy and polypropylene with embedded length 1 and 2 mm (approximate) showed that epoxy matrix had a lower interfacial shear strength (ISS) than PP. Fiber-matrix pull-out fracture mechanism indicated from SEM proved that fiber embedded in PP matrix had better bonding-ability except for untreated fiber-PP. In semi-empirical stress distribution data, it was also found that ineffective lengths of ramie-PPs were remain lower than ramie-epoxy. Finally, the effect of solvent based treatment and silane coupling agent to the fiber surface proving that hydrophilic ramie fiber and hydrophobic polymeric materials can be combined and interact together to build an intimate contact due to fiber surface topography and chemical/physical interaction to the polymeric matrix.

Key words: Ramie fiber, surface porosity, BET, contact angle, pull-out, interfacial shear strength, debonding modes, critical length

INTRODUCTION

The application of natural fibers reinforced composite has attracted substantial issues on their compatibility aspects such as adhesive bonding and wettability. Adhesive bonding and wettability are variables to be optimized in order to get the best properties and performance in composite materials. Fiber surface treatment and characterization of several natural cellulose fibers are necessary to predict the properties and performance of composite¹⁻³. Ramie (*Boehmeria nivea*) fiber was

believed as the strongest fibers in term of tensile strength and Young's modulus compare to other natural cellulose fibers available today⁴⁻⁵. Utilizing and modifying ramie as reinforcement fiber in polymer composites.

This paper is focused on surface porosity and contact angle between ramie treated fiber and epoxy and polypropylene liquid droplets. Surface porosity of the fiber affected surface roughness in which the matrix can flow and fill the porous to build mechanical interlocking^{6,9}. Adhesion and wettability

are the main key of interfacial strength of the composite. Epoxy and PP liquid droplets were used to examine contact angle between the fiber surface and the droplets. Contact angle measurement is one of the simplest method to determine and understanding relationship between hydrophilic and hydrophobic materials in the creation of a beneficial fiber-matrix relationship⁷⁻⁹. Interactions between fiber surfaces and matrix also can be evaluated using single fiber pull-out method to determine interfacial shear strength and bonding fracture modes between fiber and matrix in interface region in which the fiber is embedded¹¹.

EXPERIMENTAL

Materials

Ramie fibers were decorticated from Garut, West Java Indonesia. The fibers were prepared and pretreated using 5% NaOH boiling solution for 1 hour. Washed by distilled water until pH=7. and dried at room temperature for 20 hour and continued to oven heating 110° for 1 hour. After pretreatment, the fibers were grouped into four samples and immersed in ethanol, acetone, MEK and silane for 180 minutes at ambient temperature. Allowing oven-dried 110° for 1 hour and calculated the weight differences before and after treatment. Fibers were kept at vacuum sealed bag before surface porous characterization and applied to epoxy and PP liquid droplets. Ethanol, acetone and MEK were bought from Merck Indonesia. Silane (trimethoxymethylsilane) was from Fluka-Sigma Aldrich Corp. Epoxy was obtained from Bratachem, Bandung. Recycling disposal grade 5 uniform PP was used and melted by electric solder as liquid droplets.

Methods

Saturated Nitrogen gas covered the fiber surface

To investigate surface porosity using BET method, the fibers were firstly vacuumized for 6 hour to remove water trapped at the fibers surface. Nitrogen was used as gas adsorbate in operational temperature 77 K and allowing the fiber to absorb the gas until saturation in isothermal condition. BET's computer controlled provided BET isothermal graph which contains some information about diameter porous, total pores volume and specific surface area. Fig 1. shows BET procedure schematically.

Bubbles indicated Nitrogen molecules concentrated at the fiber surface. This happened until Nitrogen become saturation in liquid phase and all surface were covered by the Nitrogen liquid which had relative pressure P/P_0 range between 0.05-0.3 Nitrogen liquid not only covered the surface but also penetrated into fiber porosity in monolayer condition. All procedure was measured at Quantachrome Instrument-High Speed gas sorption Analyzer. Contact angle measurement was prepared to the fibers as shown in fig.2. The fibers were arranged horizontally in a jig. Epoxy droplets were pushed from a disposal syringe and solid PP was melted using electric solder applied to the surface directly and allowed for 2 hour curing time.

Saturated Nitrogen gas covered the fiber surface

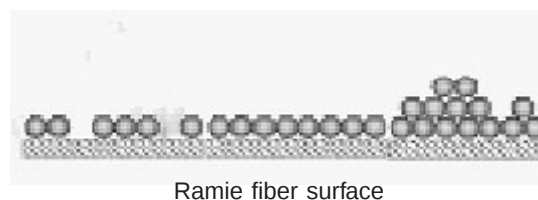
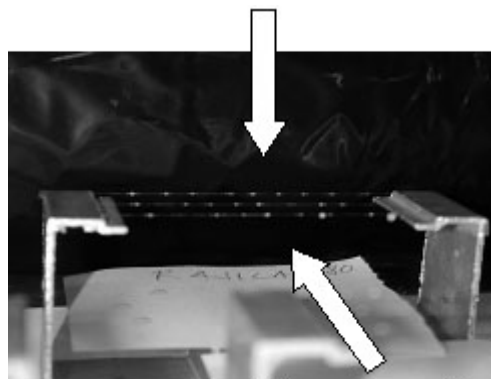


Fig. 1: BET method in which Nitrogen gas covered and penetrated into the ramie solid fiber surface porosity to obtain surface characteristics.

Droplets injected from a syringe for epoxy and electric solder for solid PP



Taken pictures of the droplets from this side

Fig. 2: Epoxy and PP droplets on the fiber surface to build contact angles

The droplets were then examined using microscope optic to take pictures of the droplets and calculate the contact angles assisted by Image Analysis software.

Pull-out test was conducted in Mesdan-Tensolab strength tester with 100 N load cell and lowest test speed 7 mm/min. The pull –out specimens were attached using special jig and the fibers above the matrix were glued to paper board as seen in Fig. 3.

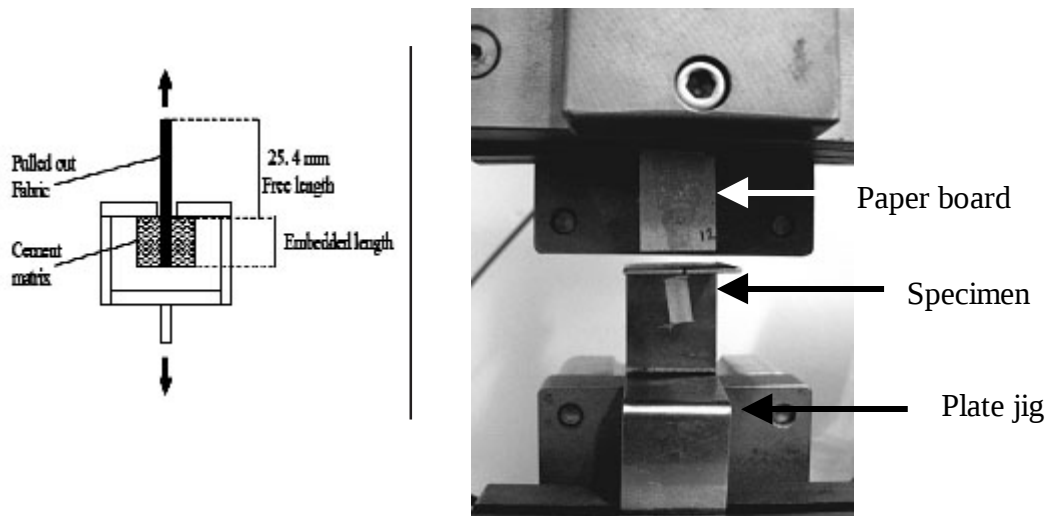


Fig. 3: Fiber-matrix pull-out test and the specimen's jig

The interfacial shear strength (ISS) are calculated from force balance equation for the maximum pull-out load (σ_p) obtained from the test results with embedded length l_c .

...(1)

$$\tau_i = \frac{(\sigma_f)^d}{4l_c} \quad \dots(2)$$

RESULT AND DISCUSSION

Linier BET plots

The Brunauer-Emmet-Teller (BET) method is the most widely use procedure for the determination of the surface area of solid materials and involves the use of the BET equation [3] and simplify as below:

$$\sigma_f \frac{\pi d}{4} = \tau_i \pi d (l_c) \quad \dots(3)$$

$$W_m = W \left(1 - \frac{P}{P_0}\right) \quad \dots(3)$$

Ramie surface fibers showed response linier BET graphs. Linier equation obtained from the graph that is in general form $y = ax + b$, has a slope a and intercept b to calculate the weight of monolayer absorbate W_m .

$$W_m = \frac{1}{a+b} \quad \dots(4)$$

And total surface area of the fiber is written as

$$S_t = \frac{W_m N A_c}{M} \quad \dots(5)$$

where N is Avogadro's number (6.023×10^{23} molecules/mol). M is the molecular weight of the Nitrogen adsorbate and A_c is cross-sectional area of Nitrogen molecules 16.2 Angstrom^2 .

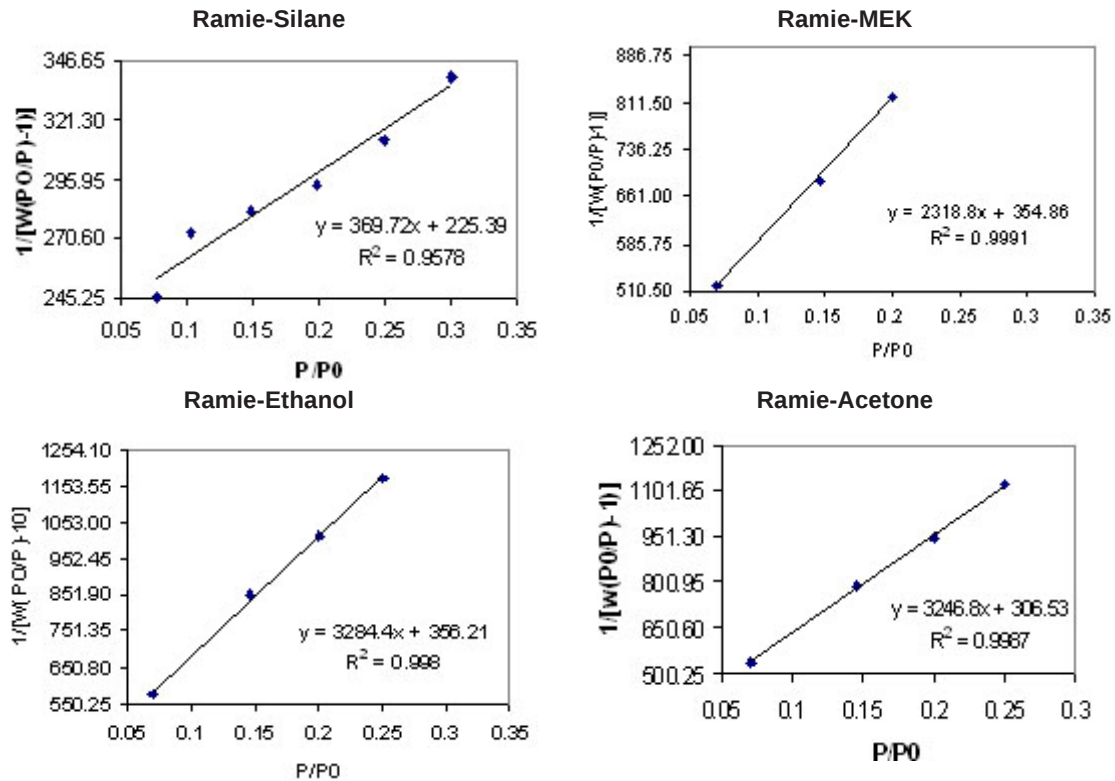


Fig. 4: Typical linear BET plots of ramie fiber-treated surfaces

Assuming cylindrical pore geometry, pore radius can be written as follows:

$$r = \frac{2V_{liq}}{S_t} \quad \dots(6)$$

where V_{liq} is the volume of liquid Nitrogen and S_t is BET surface area of the fiber.

From the BET characterization, linear BET plots for ramie fibers were identified. (Fig. 4).

Ramie-silane showed the lowest slope a and intercept b . It means ramie-silane has optimum monolayer weight W_m compared to ramie-silane, ramie-ethanol and ramie-MEK. The lower slope and intercept the wider surface area and impacts on more porous surface. Silane as a coupling agent has an effect on improving fiber surface to provide a better wettability between fiber surface and polymer matrix⁵.

Ramie-silane had a maximum pores distribution compare to the others. It means the fiber to be predicted had ability to catch the liquid matrix into the surface fiber porosity wider coverage area.

Contact angle measurement

Contact angle measurement is the simplest method to examine wettability between solid and liquid interaction. Contact angle also related to surface tension¹⁰ as seen on Fig.5.

$$\cos \theta = \frac{(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} \quad \dots(7)$$

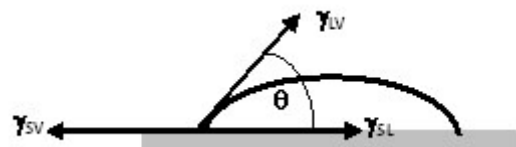


Fig. 5: Schematic diagram of contact angle θ and its surface tension components

Measuring the angle that droplets made with the solid surface using optical method, table 2 showed more common occurring contact angle between the fiber surface and both epoxy and PP matrix. Some researcher^{6,9} classified a good wettability if the angle is lower than 90°. Contact angle closed to zero means there is no wetting relationship or called spreading phenomenon. Lower wettability is shown by contact angle higher than 90°. In this measurement, there was not

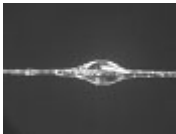
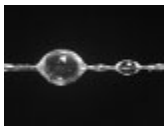
founded that contact angle lower than 10° and higher than 60°.

From this point of view, both epoxy and PP liquid droplets had ability to interact with ramie surface effectively. Figure 6 showed mean and deviation standard of contact angle measurement for each epoxy and PP droplets on ramie treated-fiber surfaces.

Table 1: Quantitative of ramie surfaces topography

Fiber treated	Density, g/cm ³	Porous diameter, Angstrom	Spesifik volume porous, cm ³ /g	Specific surface area, m ² /g
Green ramie	1.668	93.633	0.134	0.742
Ramie-Silane	1.433	118.988	1.442	3.257
Ramie- Ethanol	1.531	65.719	1,572	0,957
Ramie-Acetone	1.306	108.067	1.325	0.980
Ramie-MEK	1.385	96.87	3.154	1.303

Table 2: Observation result of the most occuring contact angles between Ramie and both epoxy and PP liquid droplets

Contact angle (q)	Epoxy droplet	PP droplet	Cos θ value
$10^\circ \geq \theta > 0^\circ$	n/a	n/a	$\cos \theta \approx 1$, spreading liquid matrix
$10^\circ < \theta \leq 30^\circ$			$\cos \theta \approx 0,707$ to $0,985$, optimum wetting
$45^\circ \geq \theta > 30^\circ$			$\cos \theta \approx 0,5$ to $0,694$, medium wetting
$65^\circ \geq \theta > 45^\circ$			$\cos \theta \approx 0,423$ lower wetting
$90^\circ \geq \theta > 65^\circ$	n/a	n/a	$\cos \theta \approx 0$ lowest wetting

It can be seen on fig.6 that ramie-silane and ramie-MEK remain had a lower contact angle both of epoxy and PP droplets compared to ramie-green, ramie-acetone and ramie-ethanol. Decreasing contact angle means higher wettability. This can be related to surface porosity that ramie-silane and ramie MEK had specific surface area and pores diameter higher than the others table 1.

Calculation of interfacial shear strength using equation 2, the ISS to be constant along the fiber embedded length¹¹. Figure 7 showed comparison of the ISS ramie treated both embedded in epoxy and PP matrix with the embedded length of 1 and 2 mm.

Ramie-silane1 and ramie-ethanol1 both embedded in epoxy and PP matrix showed the optimum ISS value for 1 mm embedded length. ISS of ramie-silane1-PP was 9.72 ± 0.37 MPa and ramie-ethanol1-PP was 10.28 ± 0.45 MPa compared to ramie-silane1-epoxy and ramie-ethanol1-epoxy with the ISS 7.09 ± 0.69 and 8.05 ± 0.72 MPa lower than ramie fiber embedded in PP matrix. For embedded length 2 mm, ramie-acetone2-PP had the highest ISS about 7.14 ± 0.23 MPa and ramie-MEK2-epoxy had ISS 3.24 ± 0.31 MPa.

From SEM analysis (fig.8), the fracture modes of fiber pull-out showed that ramie-PP has better fiber surface and matrix interaction with no

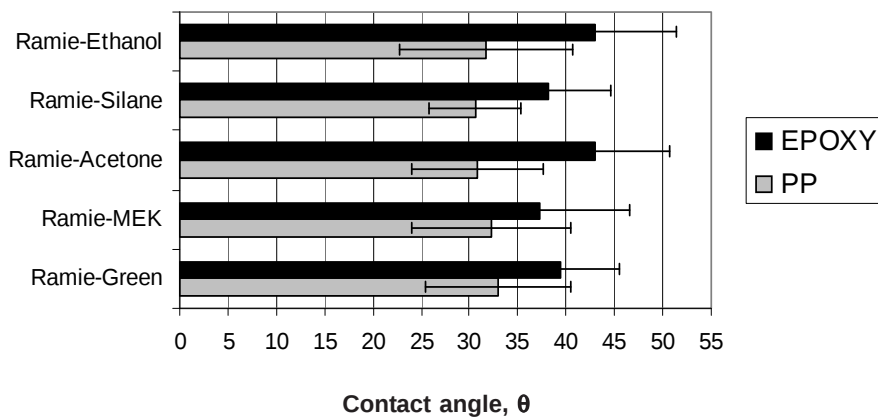
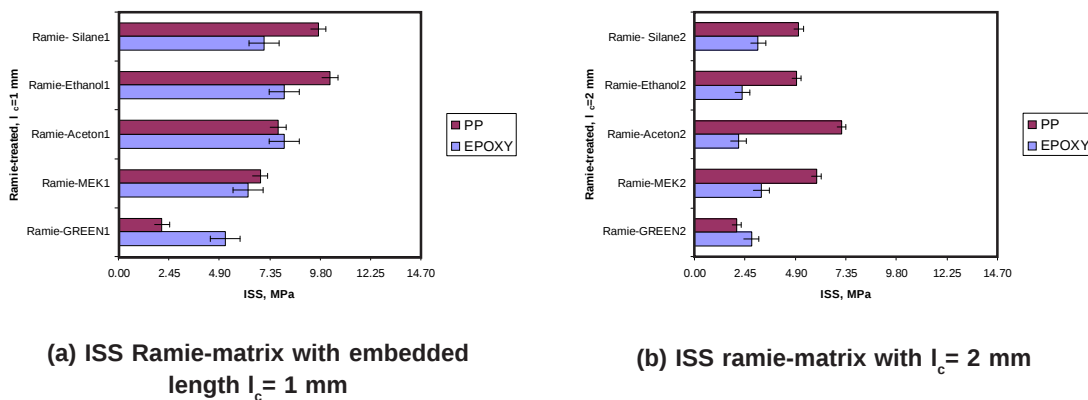


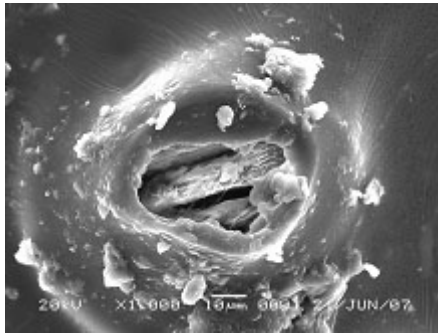
Fig. 6: Comparison of the contact angle between epoxy and PP liquid droplets on ramie-treated fiber surfaces



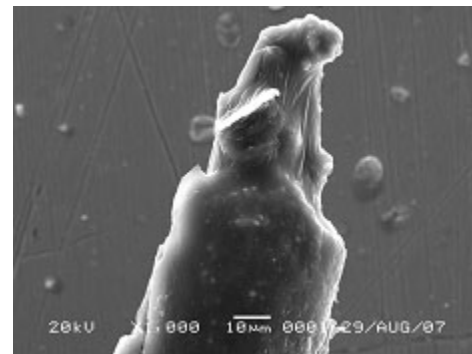
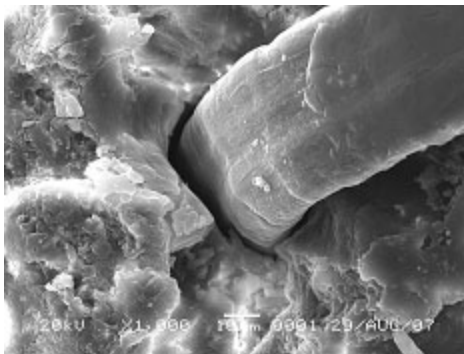
(a) ISS Ramie-matrix with embedded length $l_c = 1$ mm

(b) ISS ramie-matrix with $l_c = 2$ mm

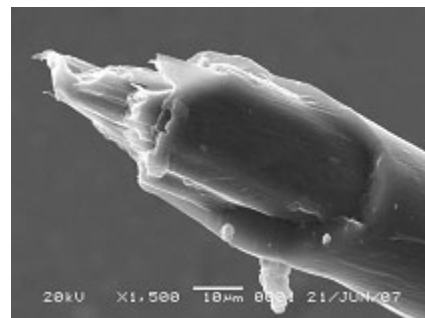
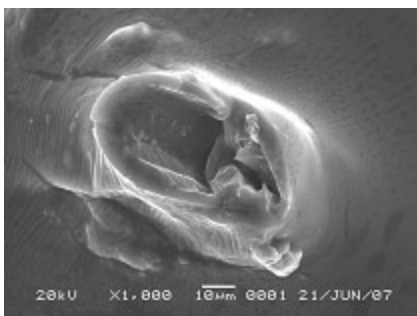
Fig. 7: ISS ramie both embedded length 1 and 2 mm in epoxy and PP matrix



(a) Ramie-Green1-epoxy shows fiber pull-out and there is no epoxy still stuck on the fiber end surface(right). The embedded fiber seems to be pull-out easily from the matrix (left).

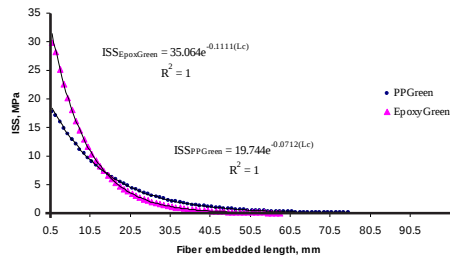


(b) Ramie-Green1-PP showed no pull-out but the region around embedded fiber and matrix surface indicated debonding between two surfaces due to pull-out load and arising broken fiber (right)

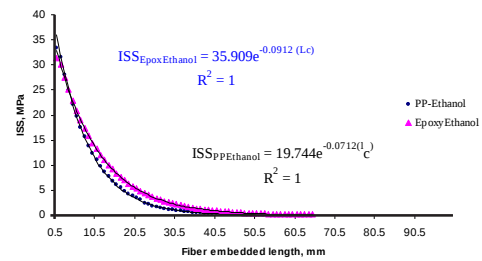


(c) Ramie-silane1- PP has a good bonding mechanism indicated by fracture of embedded fiber (left). The fiber was still embedded on the matrix surface and look alike the matrix was covered the broken fiber surface area (right)

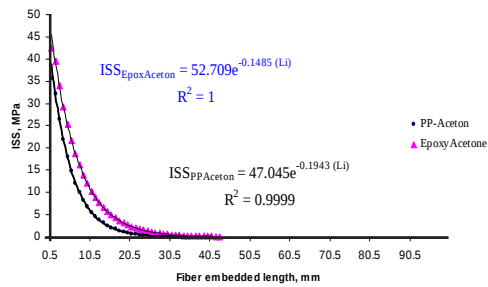
Fig. 8: Pull-out fracture mechanism of ramie fiber embedded in epoxy and PP matrix.



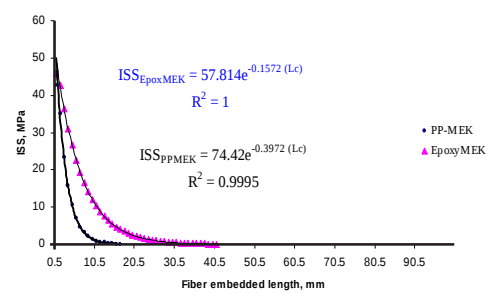
(a) Ramie Green in epoxy and PP matrix



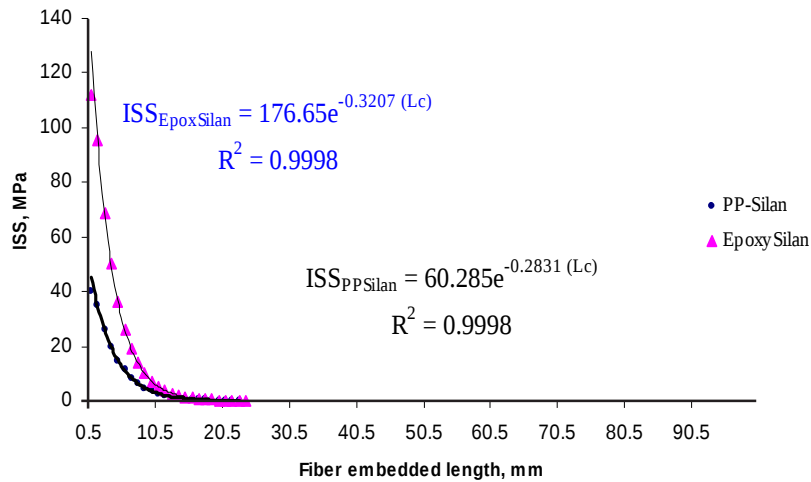
(b) Ramie Ethanol in epoxy and PP matrix



(c) Ramie Acetone in epoxy and PP matrix



(d) Ramie MEK in epoxy and PP matrix



(e) Ramie silane in epoxy and PP matrix

Fig. 9: Empirical stress distribution ramie solvent based treatment in epoxy and PP matrix pull-out test

pull-out occurred and except for ramie-Green-PP. In epoxy matrix, fiber pull-out from matrix were founded at embedded length 1 and 2 mm.

According to Zhong and Pan¹² in single fiber pull out process where the shear strength criterion is used and simulated, interaction between ramie fiber-polymer both epoxy and PP showed the effect of fiber strength (σ_f) and also embedded length (l_c) on the pull out behavior indicated occurring fiber breakage before being pull-out and the lower fiber strength the earlier the break occurs. To find out the critical length of ramie single fiber-polymer, it could be simulated using an extrapolation of maximum stress distribution of the fiber various embedded length in which ineffective fiber length could be semi-empirically determined when the stress close to zero. Fig. 9 showed extrapolation of stress distribution of the fiber embedded length performed from pull-out experiment embedded

length varied 1, 2 and 3 mm. The stress distributions have an empirical equation in exponential form.

Comparison from figure 9 stated above, the ineffective length can be predicted and the fiber critical length approximately twice of ineffective length¹³ and can be seen on table 3.

From the point of view, PP matrix had more optimum wettability than epoxy matrix. Contact angle and ISS ramie-PP showed a lower $\cos \theta$ and higher ISS than embedded in epoxy matrix. Critical length of ramie treated-PPs predicted from semi empirical stress distribution data were also shorter than ramie treated-epoxy. Finally, revealing the interaction between natural cellulose surface fiber and polymer matrix in term of micromechanic approach might the best agreement before entering macromechanic of the composite system in a wider application.

Table 3: Prediction of critical length of various treatment Ramie single fiber embedded in PP and epoxy matrix

Fiber treated	PP		Epoxy	
	Ineffective length (mm)	Critical length (mm)	Ineffective length (mm)	Critical length (mm)
Ramie Green*	74.5	149	64.5	129
Ramie Ethanol	30.5	61	45.5	91
Ramie Acetone	24.5	49	42.5	85
Ramie MEK	16.5	33	40.5	81
Ramie Silane	20.5	41	23.5	47

* untreated fiber

CONCLUSIONS

In this study, utilizing natural cellulose ramie fiber as reinforcement in polymer composite materials that should be treated and modified of the fiber surface to achieve compatibility when combined to polymer material to build up better wettability and adhesion performances using micromechanic approach. This paper presented some interaction between surface topography of ramie fibers treated by solvent based and silane compatibilizer agent. Ramie-silane and ramie-MEK remained to be a choice for reinforcement because of their surface porosity and lower contact angle θ .

Generally, all ramie fiber had value of θ range in between 20° to 55°. Both epoxy and PP droplet had no θ value occurred up to 20° and higher than 55°. In average, PP had a lower contact angle θ than epoxy and PP can be predicted more compatible to ramie fiber than epoxy matrix. The ramie-PP also showed higher ISS than ramie-epoxy due to PP matrix has a wetting capability to penetrate into fiber surface porous. Fiber porosity has been categorized into mesoporous rather than microporous. Moreover, critical length of ramie-PP especially treated by MEK and silane coupling agent had the value shorter than ramie in epoxy matrix. As we know that the shorter critical length the better to

utilized as various fiber-form reinforcement. Revealing the knowledge of the ramie fiber surface topography and interaction to the polymer matrix are important as representing the key in fiber performance in the composite system.

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