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Cocoon waste reinforced in epoxy matrix composite: Investigation on tensile properties and surface morphology

Jeerasak Jarupong[1], Apichart Artnaseaw*[2] and Suparat Sasrimuang[3]

[1]Department of Mechanical Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand
[2]Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand
[3]Department of Chemical Engineering, Faculty of Engineering, Ubon Ratchathani University, Ubon Ratchathani 34190, Thailand

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Abstract

There is potential for using silkworm cocoon waste such as broken, damaged, discarded and uncoiled cocoons as well as the caterpillars that remain inside. Cocoon waste is estimated to account for up to 11% of raw cocoon input in the textile industry. The aim of the present work is to use cocoon waste as the natural fiber reinforcement in an epoxy resin matrix composite. Cocoon waste with different weight fractions of 0 wt%, 25 wt%, 42 wt%, 58 wt%, and 75 wt% were used as reinforcement with an epoxy resin matrix to fabricate the composite material by hand lay-up technique. Subsequently, tensile testing and scanning electron microscopy observations were employed to evaluate the performance of the proposed composite materials. Experimental results demonstrated that the tensile strength continuously increased as cocoon waste fiber increased from 25 wt% to 58 wt%, reaching a maximum tensile strength of 61.04 MPa. Elastic modulus showed a slight difference of 25 wt% to 58 wt%, a maximum of 762.91 MPa. However, at 75 wt%, the tensile strength and elastic modulus declined by 57.07 MPa and 515.69 MPa, respectively. The 58 wt% of cocoon waste was presented as the optimum ratio for reinforcement with an epoxy resin matrix. The SEM image revealed the dispersion of cocoon waste in an epoxy resin matrix, presenting the close-packed interfacial bonding between cocoon waste fiber and matrix. This research is useful for the development of cocoon waste-based composites with improved mechanical properties.

Keywords: Cocoon waste, Composite material, Epoxy resin, Natural fiber

1. Introduction

Polymeric composite material has been interesting for decades due to its remarkable properties. They have been used in various applications such as building, automotive, aerospace, chemical, packaging, biomaterials, etc. However, such composites (e.g. glass fiber, carbon fiber) are fabricated by synthesis material made of petroleum which is non-renewable as well as high energy consumption for production [1]. It has been attempted to seek natural material as a substitute for synthetic material. Natural fibers have been interesting due to their characteristics as eco-friendly, inexpensive, lightweight, strength, and renewable materials. Additionally, natural fibers provide a feasible alternative reinforcing fiber. Bio-composites reinforced with natural fibers such as flax, jute, ramie, pineapple, hemp, etc. have been widely investigated for natural fiber-reinforced composites [2, 3]. Recently, the Alfa plant had been employed as a natural fiber to reinforce epoxy composite [4]. Cocoon produced by silkworm caterpillars is one kind of natural structure with polymeric composite materials having outstanding mechanical properties [5]. Currently, there are several studies using silk fiber as the natural fiber reinforcement in the polymeric matrix. Ranakoti et al. studied the effect of surface treatment and fiber loading on the physical, mechanical, sliding wear, and morphological characteristics of Tasar silk fiber waste epoxy composites for multifaceted biomedical and engineering applications: fabrication and characterizations. Silk fiber waste reinforced epoxy composite was successfully fabricated by compression molding method with physical, mechanical and wear behaviors [6]. Chen et al. also studied the fabrication and properties of poly (butylene succinate) or PBS bio-composites reinforced by waste silkworm silk fibers (called as spun silk fabric) obtained from silk wastes and pierced cocoons. It revealed that the spun silk fabric could improve the mechanical properties of PBS composites [7]. Recently, Xu et al. investigated a transparent, skin-inspired composite film with outstanding tear resistance based on a flat silk cocoon [8].

Silk production is one of the industries where produce waste can account for up to 25% of the raw cocoon intake. 50 wt% of silk waste is generated throughout the silk production process in the form of silkworm cocoon waste and silk waste. Silkworm cocoon waste is generated by 2 sources; cocoons remained after the silk moth leaving and damaged cocoon such as twin cocoons and dirty cocoon, which are not suitable for reeling. Silk waste is produced from silk spinning and silk weaving. The overall amount of waste in the cocoon sector is 45% [9]. As a result, silkworm cocoon waste has the potential to be used as natural fiber waste. In Thailand, there is a quite number of small, medium scale industries and some number of large-scale industries of silk production of about 5,660 ton a year, generating a considerable amount of cocoon waste [10].

*Corresponding author.
Email address: aapich@kku.ac.th
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However, it has not yet been studied for using the waste of cocoon reinforcement in the polymeric matrix composite. This work, thus, aims to reuse the cocoon waste as for reinforcement in an epoxy resin composite along with investigating the tensile properties and the fracture surface of the specimen matrix.

2. Experimental

2.1 Materials

Cocoon waste was collected from silk villages in the northeastern region and Queen Sirikit Sericulture Center Khon Kaen, Thailand. Regarding silk production, cocoons as raw material for silk production are firstly visually checked for suitable and unsuitable cocoons. The suitable cocoon is brought to boiling process and the silk reeling for further silk production. The unsuitable cocoons defined as pierced cocoons and damaged cocoons including twin cocoon, dirty cocoon, etc. are considered as cocoon waste. Reuse of cocoon waste as reinforcing material, of which cocoon waste fiber is shown in Figure 1. Epoxy resin YD 582 modified bisphenol-A based epoxy resin is used as the matrix. The hardener EPOTEC TH 7278 is modified amine, provided by J.N. TRANSOS Company, Thailand.

Figure 1 Cocoon waste

2.2 Methodology

Because of their small and inconsistent shape, cocoon wastes are difficult to use directly in the manufacture of composites. The semi-processing approach of pressing the cocoon wastes into nonwoven mats could be an acceptable choice [11, 12]. Before fabrication, the weight percent of cocoon waste was calculated as following; the volume of resin as liquid used for each mold sized 15×15 cm was 200 ml being equivalent to 240 g (calculated by density of resin is 1.2 g/ml). Different cocoon waste content used for each mold were 0 g (used as control specimen) 60 g, 100 g, 140 g and 180 g being equivalent to 0 wt%, 25 wt%, 42 wt%, 58 wt% and 75 wt%, respectively.

In the sample preparation, first, cocoon waste weighing approximately 20 g was pressed by the hydraulic press into the steel mold, obtained in a thin plate. A considerable deal of effort was expended to ensure that the cocoon waste was evenly distributed. Hydraulic pressure 6 MPa was applied to the mold for a period of 1 hour then removed from the mold. The epoxy resin was mixed with the hardener with a ratio of 4:1 by weight around 240 g as a matrix solution. Several thin plates of cocoon waste were moved into a rectangular mold box until the specified weight content was reached. The matrix solution was poured layer by layer over a thin cocoon waste plate in the mold box, cured for 3 hours, and then pressed at 6 MPa for 12 hours at room temperature. As a result, an epoxy resin adhesive was used to bond the layers together. The composite plate was then removed from the mold. After that, it was cured at a temperature of 80 °C for 4 hours. Finally, composite plate specimens with dimension 15×15 cm were displayed in Figure 2. Three cocoon waste composites were prepared with different contents of cocoon waste: 0 wt%, 25 wt%, 42 wt%, 58 wt% and 75 wt%, respectively.

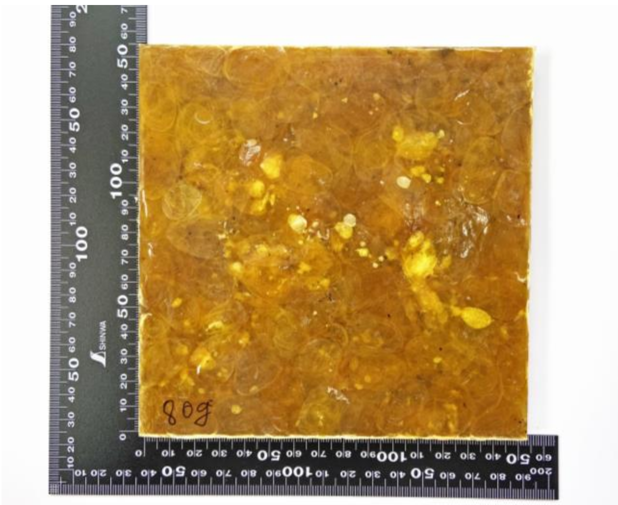

Figure 2 Cocoon waste composite specimen.

2.3 Characterization

Tensile testing of specimens was performed at room temperature using an ISO 527-4 standard with the gauge length of 25 mm. A 100 kN load cell was used with a crosshead speed of 5 mm/min. An international testing standard was used to determine the tensile properties of fiber reinforced plastic composites. The mean tensile strength and elastic modulus of three specimens with the same cocoon waste content were calculated.

The fracture mechanisms of the composite plate after the tensile test were investigated by a JEOL JSM-5900LV scanning electron microscope at an acceleration voltage of 20 kV.

3. Results and discussion

3.1 Mechanical properties of cocoon waste composite

The load vs. elongation curve of cocoon waste composite specimens is illustrated in Figure 3, demonstrating that the load is directly proportional to the elongation until reaching the fracture. It indicated that the elastic line had linear behavior until it was suddenly fractured, when it reached the yield strength. As the weight fractions of cocoon waste increased from 25, 42, 58 and 75 wt% the load and elongation increased. The composite of 75 wt% of cocoon waste had a longer elongation before fracture, 3.01 mm, compared to 1.40-2.23 mm for the other weight % of cocoon waste. Shown by elastic line, the elongation result was similar with de Oliveira et al. [13]. It is important to note that elongation represents the flexibility of the cocoon waste composite; a higher amount of cocoon waste results in greater flexibility.

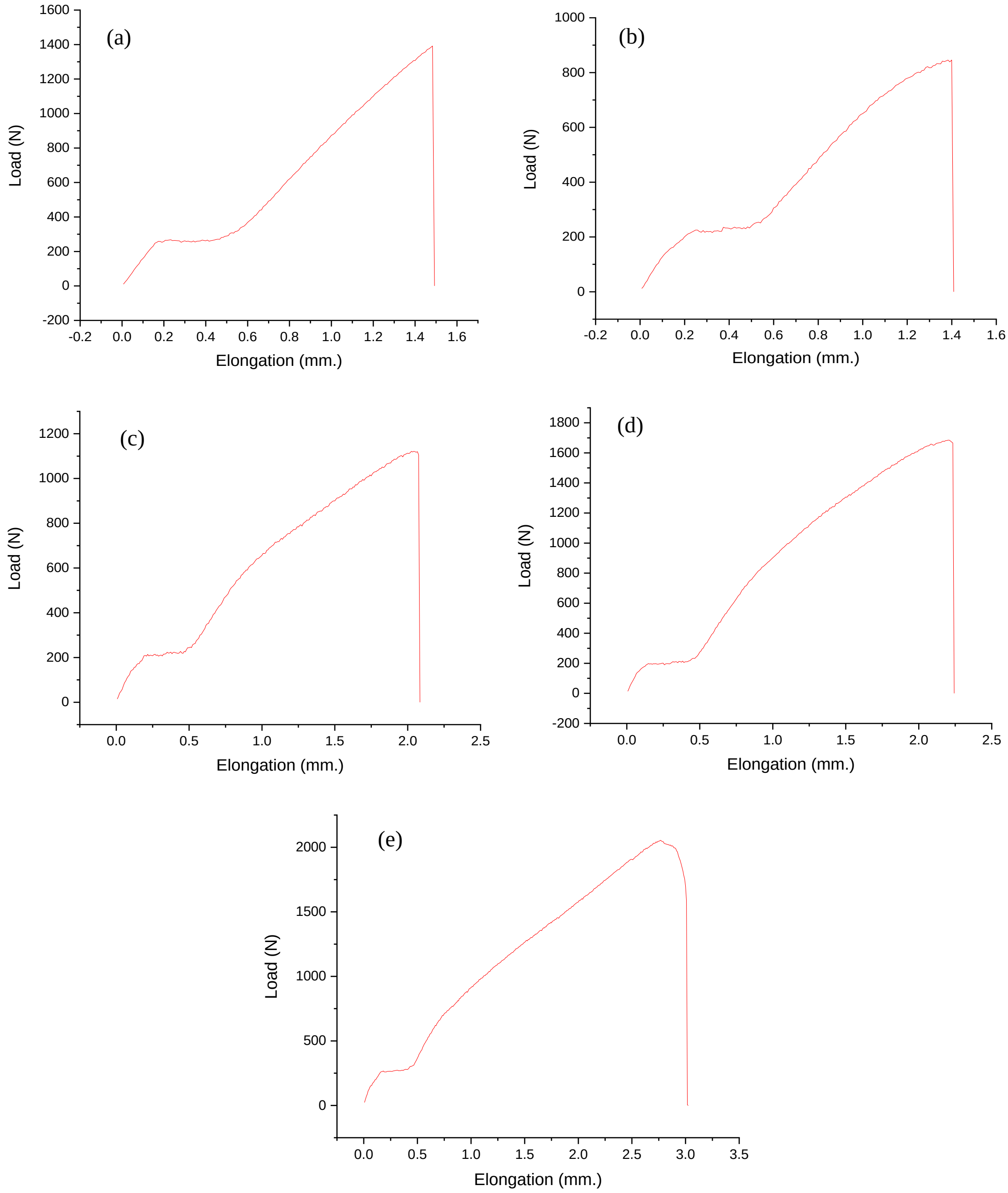

Figure 3 Load vs. elongation of cocoon waste composite: (a) epoxy matrix, (b) 25 wt%, (c) 42 wt%, (d) 58 wt% and (e) 75 wt%

Table 1 shows the tensile strength and elastic modulus of cocoon waste composites supplemented with various weight fraction of cocoon waste. Tensile data for cocoon waste composite are shown in this table, which are plotted in Figure 4 (a) and (b). The tensile strength of cocoon waste composite had a significant difference due to the mechanical properties of cocoon waste. The tensile strength of the cocoon waste composite was 42.72 MPa at 25 wt%, 58.41 MPa at 42 wt%, 61.04 MPa at 58 wt%, and 57.07 MPa at 75 wt%, of which all of them were higher than the tensile strength of unreinforced composite (41.43 MPa). Furthermore, the tensile strength in composites increased with the increase of cocoon waste fiber for 25 wt%, 42 wt%, and 58 wt% then decreased at 75 wt%, while the elastic modulus remained likely constant in the range of 691-762 MPa at 25 wt%, at 42 wt%, 58 wt% and then started decreasing downward to approximately 516 MPa at 75 wt%, of which the result were similar to Chen et al. [7], demonstrating that increasing the silk fiber content significantly improves the tensile characteristics of silk fiber biocomposites. It was concluded that the optimum cocoon waste fraction was 58 wt% as determined by the tensile strength and elastic modulus of the composite at load 1,684 N with an elongation of 2.23 mm.

The stiffness of cocoon waste fiber had enhanced the adhesion between the cocoon waste fiber and the matrix. In addition, fiber on cocoon waste consisted of two proteins namely fibroin and sericin. Fibroin protein was a crystalline microstructure that provided strength and flexibility properties, which improved interfacial adhesion between fiber and epoxy resin matrix [14, 15]. Sericin protein was an amorphous microstructure, providing a stability property [16]. Tensile strength increased along with the cocoon waste increased from 25 wt%, to 58wt%, owing to the cocoon waste fiber acting as reinforcement and being capable of maintaining the higher tensile strength. Then the tensile strength decreased as the higher cocoon waste at 75wt%. It corresponds to the results of tensile strength shown in Figure 4, following the Hook's law [17]. The decrease in tensile strength at a very high fiber content of 75 wt% was caused by insufficient filling of epoxy resin matrix in the reinforcing cocoon waste, which would result in additional microstructural imperfections during composite processing. Such incomplete filling effects were also discovered with a fiber content of 60 wt% with chopped short silk fiber reinforcement [18] and at 45 wt% with "as-separated" short silk fiber reinforcement [19].

Table 1 Tensile strength and elastic modulus for cocoon waste composite

Weight fraction of cocoon waste (%)	Tensile strength (MPa)	Elastic Modulus (MPa)
0	41.43 ± 1.62	698.36 ± 1.43
25	42.72 ± 2.02	762.91 ± 1.57
42	58.41 ± 1.95	721.06 ± 2.19
58	61.04 ± 1.82	691.02 ± 1.97
75	57.07 ± 2.63	515.69 ± 2.52

Note: Data shown means ± standard deviation (sd)

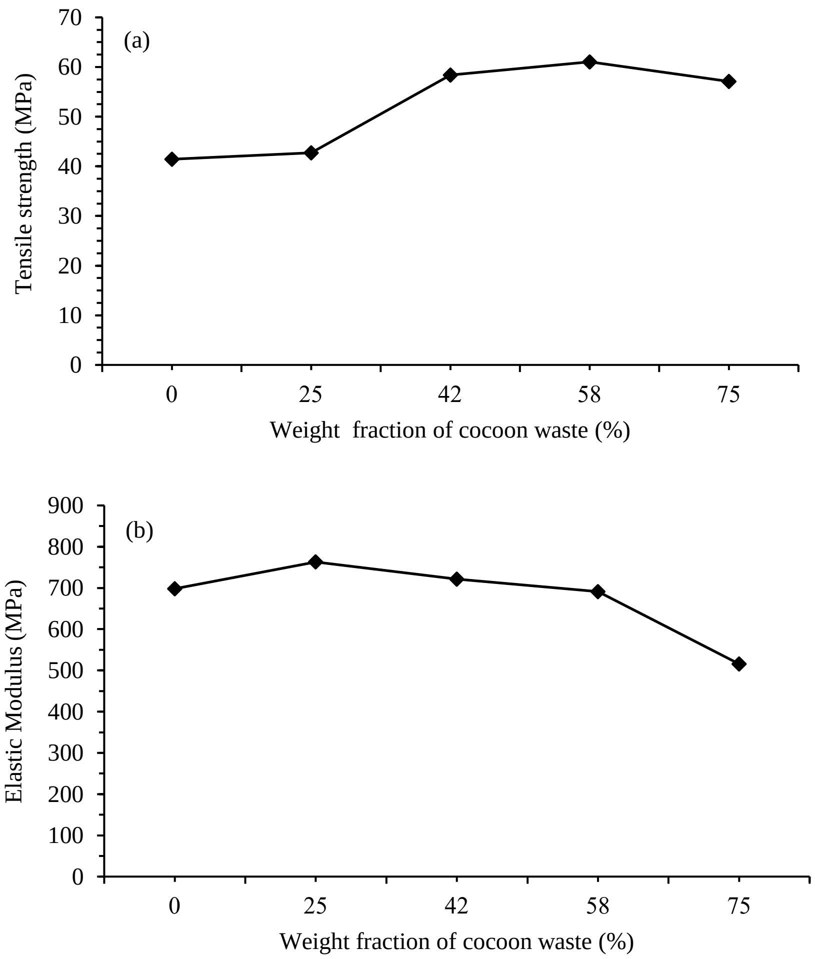

Figure 4 (a) Tensile strength vs. weight fraction of cocoon waste (%) and (b) Elastic modulus vs. weight fraction of cocoon waste (%)

Table 2 displays the P values for Analysis of variance (ANOVA) with only one factor. The level of significance in this Table is 5% (0.05). If P is more than 0.05, there should be a "**No"** difference in behavior for any weight fraction of cocoon waste in the set of values. On the other hand, if P is less than 0.05, then statistically, "**Yes"**, a difference must be recognized.

Based on the ANOVA hypothesis, incorporating cocoon waste into epoxy resin matrix results in a statistically significant difference in tensile strength and elastic modulus, as shown in Table 2. In other words, the hypothesis that the values are the same can be rejected with 95% confidence, according to the findings in Table 1 and Figure 4.

Table 3 displays the Tukey test results; the minimum significant difference (m.s.d.) is a value that may distinguish which treatment has a difference in its average values. When the difference between the average values of two groups is greater than the m.s.d value, this pair is regarded to be different. The tensile strength m.s.d. was calculated to be 4.62, and the elastic modulus m.s.d. was calculated to be 4.45. The difference between mean values that were greater than the m.s.d. was highlighted in bold.

The Tukey test results in Tables 3 reveal some remarkable points. As compared to any other weight fraction (0, 25, 42, and 75 wt%), the 58 wt% cocoon wastes were markedly different. By incorporation of 58 wt% cocoon waste, this results in a stronger reinforcement of the epoxy resin matrix that correlates with Table 1 and Figure 4 found to have the maximum tensile strength. On the other hand, no significant difference was discovered in the weight fraction values of 25 wt% and neat epoxy resin matrix. The elastic modulus differed significantly between weight fractions of 25 wt%, 42 wt%, 58 wt%, and 75 wt% cocoon waste composites.

Table 2 ANOVA decision based on values of P

Tensile strength (MPa)						
Source of variation	**SS**	**DF**	**MS**	**F**	**$F_{critical}$**	**P-value**
Between groups	1039.295	4	259.824	61.052	3.478	5.47×10^{-7}
Within groups	42.558	10	4.256			
Total	1081.853	14				
Are the different?						Yes
Elastic Modulus (MPa)						
Source of variation	**SS**	**DF**	**MS**	**F**	**$F_{critical}$**	**P-value**
Between groups	107974.70	4	26993.67	6838.378	3.478	3.91×10^{-17}
Within groups	39.474	10	3.947			
Total	108014.18	14				
Are the different?						Yes

Table 3 Results obtained for differences between the average values for 0 wt%, 25 wt%, 42 wt%, 58 wt% and 75 wt% after applying the Tukey test.

	Tensile strength (m.s.d. = 4.62)					Elastic modulus (m.s.d. = 4.45)				
	0 wt%	25 wt%	42 wt%	58 wt%	75 wt%	0 wt%	25 wt%	42 wt%	58 wt%	75 wt%
0 wt%	0.00	1.29	**16.98**	**19.62**	**15.65**	0.00	**64.55**	**22.70**	**7.34**	**182.67**
25 wt%	1.29	0.00	**15.69**	**18.32**	**14.35**	**64.55**	0.00	**41.85**	**71.89**	**247.22**
42 wt%	**16.98**	**15.69**	0.00	2.63	1.34	**22.70**	**41.85**	0.00	**30.04**	**205.37**
58 wt%	**19.62**	**18.32**	2.63	0.00	3.97	**7.34**	**71.89**	**30.04**	0.00	**175.33**
75 wt%	**15.65**	**14.35**	1.34	3.97	0.00	**182.67**	**247.22**	**205.37**	**175.33**	0.00

Furthermore, Table 4 summarizes the tensile and elastic modulus properties of particular silk reinforced composites described recently in the literature that used long continuous silk fiber [11], short chopped fiber [18], and spun silk fabric [7, 20] as the reinforcing phase. The mechanical characteristics of a composite, as is well known, were affected not only by the matrix and reinforcement properties, but also by the shape and content of the reinforcing phase, as well as the interface circumstances. Clearly, the mechanical properties of the composites have differed significantly depending on the matrix system.

Table 4 A summary of tensile strength and elastic modulus properties of silkworm silk reinforced composites found in the literature.

Composite	T.M. (MPa)	E.M. (GPa)	Fiber fraction	Reference
Nonwoven silk-epoxy	60	5.4	36.2 vol%	[11]
Plain woven silk-epoxy	111	6.5	45.2 vol%	[11]
Silk fabric-EPCNSL	69.98	1.067	25 wt%	[20]
Silk fabric-epoxy	58.35	0.844	25 wt%	[20]
Chopped silk fiber-PBS	42	1.6	30 wt%	[18]
	48	1.9	40 wt%	[18]
	50	2.3	50 wt%	[18]
Silk fabric-PBS	40.6	0.72	30 wt%	[7]
	50.1	0.88	40 wt%	[7]
	62.5	1.03	50 wt%	[7]
	42.6	0.82	75 wt%	[7]
Cocoon waste-epoxy	42.72	0.762	25 wt%	Present study
	58.41	0.721	42 wt%	Present study
	61.04	0.691	58 wt%	Present study
	57.07	0.515	75 wt%	Present study

Notations. T.M.: Tensile strength; E.M.: Elastic Modulus; PBS: Poly(butylene succinate); EPCNSL: Epoxy Phenol Cashew Nut Shell Liquid.

3.2 Morphology

The fracture surfaces of the cocoon waste composite after tension are depicted in SEM images in Figure 5 and 6. Certain common deformation, damage and failure mechanisms at the microscopic scale may be observed such as the breakage, pullout, debonding of fibers from the epoxy resin matrix as well as the matrix's ductile cracking [7]. Figure 5 shows the SEM fractography at fracture surface of cocoon waste as 25 wt%, 42 wt%, and 58 wt% in epoxy resin, displaying fiber dispersion, indicating that the surface has no uniform dispersion in the epoxy resin matrix [21]. The cocoon waste fiber and epoxy resin matrix were found to be particularly dense as the weight proportion of cocoon waste increased. Remarking that the interfacial bonding of cocoon waste fiber and epoxy resin matrix plays an important role for the mechanical properties of the reinforced composite. As stated above, the cocoon waste consists of fibroin fiber which is a semicrystalline microstructure acted as the glued-like protein, causing interfacial bond of fiber and matrix due to hydrogen bonds [22]. It is thus attributed to the high interfacial bonding between fiber and epoxy resin, resulting in the high strength of the closed pack cocoon waste composite. Figure 6 presents SEM image closeup, presenting the observed pull-out of fiber, debonding, cocoon waste fiber and epoxy resin matrix. In terms of tensile strength and elastic modulus, cocoon waste composite was a hard and tough material.

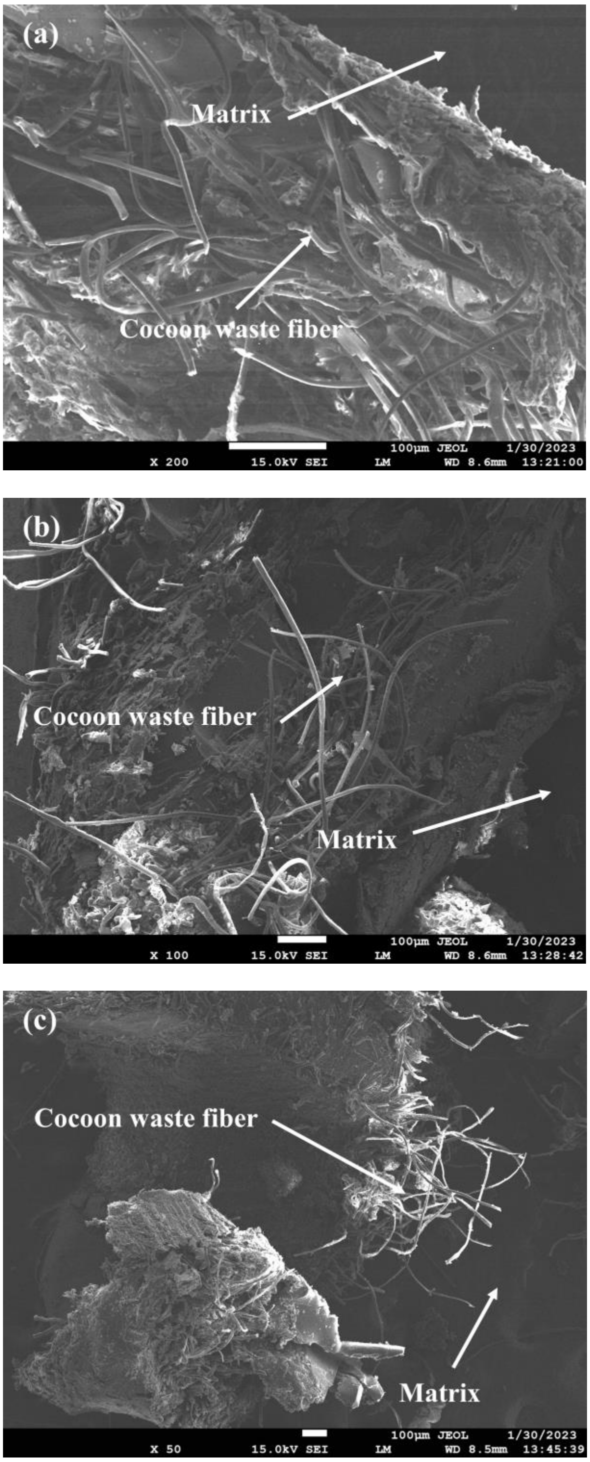

Figure 5 SEM image of tensile fracture of cocoon waste composite: (a) 25 wt%, (b) 42 wt%, and (c) 58 wt% of cocoon waste

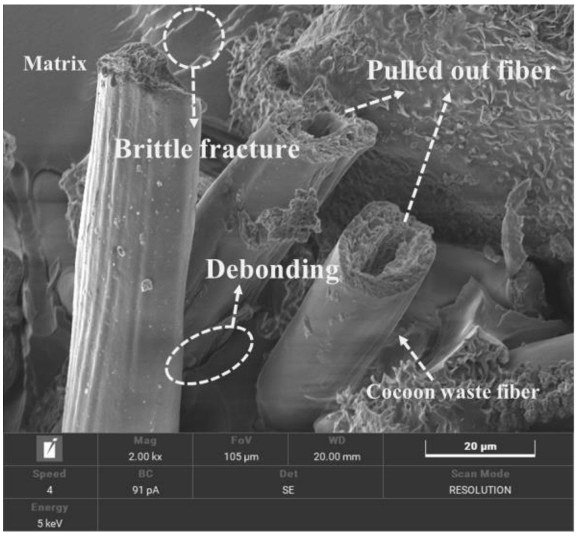

Figure 6 SEM image of tensile fracture surface specimen

4. Conclusions

The reinforcement of cocoon waste with epoxy resin composite had been potentially fabricated, with different weight fractions as 25 wt%, 42 wt%, 58 wt% and 75 wt% of cocoon waste. The experimental study of tensile strength (61.04 MPa) and elastic modulus (691.02 MPa) of the cocoon waste composite with some considerable elongation composite (2.23 mm) presented the optimum weight fraction as 58 wt% of cocoon waste. SEM image revealed the dispersion of cocoon waste fiber in epoxy resin matrix, presenting the close-packed interfacial bonding between cocoon waste fiber and epoxy resin matrix. Cocoon waste composite could be used as the reinforcement material. Based on the tensile strength and elastic mo°°dulus, the cocoon waste composite was rigid and tough material. The cocoon waste was potentially value-added material to the reinforcement composite, providing an alternative means of the renewable, eco-friendly sustainable material.

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