

Surface free energy analysis of oil palm empty fruit bunches fiber reinforced biocomposites

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Abstract. Study of the size effect of natural fiber from oil palm empty fruit bunches (OPEFB) as filler, onto the contact angle and surface free energy of fiber reinforced biocomposites has been done. The OPEFB fibers were prepared by mechanical milling and sieving to obtain various sizes of fiber (long-fiber, medium-fiber, short-fiber, and microparticle). The biocomposites has been produced by extrusion using single-screw extruder with EFB fiber as filler, recycled Acrylonitrile Butadiene Styrene (ABS) polymer as matrix, and primary antioxidant, acid scavenger, and coupling agent as additives. The obtained biocomposites in form of granular, were made into test piece by injection molding method. Contact angles of water, methanol, and hexane on the surface of biocomposites at room temperature were measured using Phoenix 300 Contact Angle Analyzer. The surface free energy (SFE) and their components were calculated using three previous known methods (Girifalco-Good-Fowkes-Young (GGFY), Owens-Wendt, and van Oss-Chaudhury-Good (vOCG)). The results showed that total SFE of Recycled ABS as control was about 24.38 mJ/m², and SFE of biocomposites was lower than control, decreased with decreasing of EFB fiber size as biocomposites filler. The statistical analysis proved that there are no statistically significant differences in the value of the SFE calculated with the three different methods.

1. Introduction

Natural fibers have been used as reinforcement in polymer composites during the last decades [1-5]. Oil palm empty fruit bunches (OPEFB) as one of natural fiber biomass offer some advantages when considered for biocomposites applications. They are available in large amounts, low cost, low density, renewable and biodegradable [6]. A thermoplastic polymer, Acrylonitrile-butadiene-styrene (ABS), was used as a matrix polymer to compound with the OPEFB natural fillers for the purpose of manufacturing the bio-composite. ABS is an important engineering copolymer widely used in industry due to superior mechanical properties, chemical resistance, ease of processing and recyclability [7]. Biocomposites as fiber reinforced polymeric material can be used as an alternative material in some industries such as furniture, automotive, sports or household equipment. Studies on the properties of surface materials, including surface free energy, are the subject of intensive scientific research for over



forty years. These quantities are being assumed as important criteria for evaluation of adhesion properties of solid polymers [8]. Then the evaluation of surface free energy parameters was become a very useful tool for theoretical studies of the surface behavior of biocomposites as well as for practical developments in many technological applications, such as painting, coating, or other surface treatments of materials [9]. Thus the effect of filler on the surface free energy of biocomposites important to be studied.

Surface free energy (SFE) is one of the thermodynamic quantities describing the state of atom equilibrium in the surface layer of materials [10-11]. This quantity is characteristic for each substance. It reflects the specific state of unbalance in intermolecular interaction which is present at the phase boundary of two mediums [11]. It is measured in $[mJ/m^2]$. The surface free energy of biocomposites were measured by the contact angle measurements in order to study effect of filler fiber size on the wetting phenomena. One of the most popular methods for measuring the contact angle is the sessile drop method, which involves depositing a liquid drop on a smooth solid surface and measuring the angle between the solid surface and the tangent to the drop profile at the drop edge [12].

The basic methods of calculating SFE of a solid (γ_s) from measurements of the contact angle (θ) is due to Young equation [13]. It is given as:

$$\gamma_l \cos \theta = \gamma_s - \gamma_{sl} \quad (1)$$

where γ_l denotes SFE of liquid in contact with the solid and γ_{sl} means the interfacial free energy between the solid and the liquid. If the values of γ_l and θ are known, it is impossible to determine SFE directly from the equation (1) because of the two unknowns, γ_s and γ_{sl} . In order to solve this equation for γ_s , one has to add a second equation that correlates γ_{sl} with γ_s and γ_l . Until recently, many types of correlations have been employed.

Girifalco and Good [14] showed that interfacial free energy between the solid and liquid can be calculated from the SFE of the solid (γ_s) and the liquid (γ_l). These equations can be solved for:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s \gamma_l)^{1/2} \quad (2)$$

Fowkes [15] observed that, for solid-liquid interaction of polar materials with nonpolar ones, in van der Waals systems, only dispersion forces could effectively operate across the interface. He suggested separating the surface energy of the polar material into dispersion (γ^d) and polar (γ^p) contributions.

$$\gamma = \gamma^d + \gamma^p \quad (3)$$

Therefore, he suggests that eq. (2) be written as:

$$\gamma_{sl} = \gamma_s^d + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} \quad (4)$$

where γ_l represents the combined contributions [equation (3)] of the dispersion and polar components of the aqueous phase; γ_l^d is the dispersion component, and γ_s^d is the surface energy of the solid having only a dispersion component. Combining eq. (4) with Young's equation (1), obtains an expression known as the Girifalco-Good-Fowkes-Young (GGFY) equation [16].

$$\cos \theta = -1 + \frac{2(\gamma_s^d \gamma_l^d)^{1/2}}{\gamma_l} \quad (5)$$

Owens and Wendt [17] argued that the polar interaction could be computed using the same geometric mean mixing rule as for the dispersion force interaction. If the contact angle of at least two liquids, usually a polar and a non-polar liquid, with known γ_l^d and γ_l^p parameters are measured on a solid surface, the γ_s^d and γ_s^p parameters of that solid can be calculated [16]. Thus, Owens and Wendt suggested the following form [18]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} - 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (6)$$

With substitution eq. (6) into Young's equation (1), then can be written:

$$(1 + \cos \theta)\gamma_l = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (7)$$

By measuring θ of two different liquids against a solid, simultaneous equations are obtained which can be solved for γ_l and γ_l^d . Thus the components of surface free energy due to various forces can be approximated. The sum of these components by analogy with eq. (3) should yield a reasonable approximation of the total solid surface energy γ_s [17], where γ_s^d and γ_s^p are the dispersion and polar force components of γ_s , respectively [19].

The latest version of SFE calculation is the Lifshitz-van der Waals/acid-base approach, initiated by van Oss, Chaudhuri, and Good [20]. SFE is a sum of two components, while the first component γ^{LW} is connected with long-range interactions (dispersive, polar and inductive, referred to as Lifshitz-van der Waals electrodynamic interactions) and the second component γ^{AB} describes the acid-base interactions [11]. This vOCG method split the polar component (γ^{AB}) to the acid component (electron-acceptor: γ^+) and the base component (electron-donor: γ^-), in such a way that $\gamma^{AB} = 2(\gamma^+ \gamma^-)^{1/2}$. This method requires contact angle from three liquids, then the following correlation expressed as:

$$\gamma_{sl} = \left(\sqrt{\gamma_s^{LW}} - \sqrt{\gamma_l^{LW}} \right)^2 + 2 \left(\sqrt{\gamma_s^+ \gamma_s^-} + \sqrt{\gamma_l^+ \gamma_l^-} - \sqrt{\gamma_s^+ \gamma_l^-} - \sqrt{\gamma_s^- \gamma_l^+} \right) \quad (8)$$

which, upon combination with Young's equation (1) becomes:

$$(1 + \cos \theta)\gamma_l = 2 \left(\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right) \quad (9)$$

For any flat solid, using three liquids, γ_s^{LW} , γ_s^+ and γ_s^- can be found by contact angle determination, provided γ_l^{LW} , γ_l^+ and γ_l^- are known for all three liquids, using eq. (9). At least two of the three liquids must be polar. It usually is most expedient to determine γ_s^{LW} first, with the help of a high-energy nonpolar liquid [20].

In this paper the effect of fiber size as filler on the surface free energy of recycled ABS/OPEFB fiber biocomposites at room temperature was investigated and compared with recycled ABS as control. Surface free energy analysis using three methods GGFY, Owen-Wendt, and vOCG, through the sessile drop contact angle measurements, three liquids (water, methanol, hexane) were used in these determinations.

2. Experimental

2.1. Materials

The oil palm empty fruit bunches (OPEFB) was obtained from PTPN VIII Cikasingka, Bogor, Indonesia. The OPEFB were obtained from fresh fruit bunches, after steam treatment and stripping the fruit. The OPEFB were washed with water, drained under the sun over 2 days and then chopped into chips form. Chip samples then dried in a drying oven (Type YNC-OV, YENACO, China) at 100 °C for 8 hours. Fibers were prepared by mechanical milling (Model MDY-1000, FOMAC, China) and sieving to obtain long-fiber ($\phi > 20$ mesh), medium-fiber ($20 > \phi > 100$ mesh), short-fiber ($100 > \phi > 200$ mesh), and microparticle, fibers that have pass 200 mesh with additional treatment, hammer milling (Model HMV-4W-5.5, Vertical Hammer Mill, Indonesia) for 2×10 minutes. The average OPEFB fiber dimension was calculated from images captured by an light microscope (Model BX51, Olympus, Japan) with the software Olympus DP2-BSW integrated with DP25 Olympus Microscope Camera. The average particle size of microparticle was 468.34 nm, which was measured using Vasco particle size analyzer. The recycled ABS polymer (melt flow index 12.1 g/10 min) was purchased from PT MUB Jaya, Bogor, Indonesia.

Table 1. OPEFB fiber dimension average

	Long-fiber	Medium-fiber	Short-fiber
Length (μm)	3867.56	1535.97	230.12
Diameter (μm)	291.82	147.79	58.53

2.2. Biocomposites preparation

The biocomposites has been produced by extrusion using single-screw extruder (Model HXSJ-125/125, Kai Xin, China) with 15 wt% EFB fiber as filler, 81.7 wt% recycled ABS polymer as matrix, and 1 wt% primary antioxidant (China), 0.3 wt% acid scavenger (Germany), and 2 wt% coupling agent (Germany) as additives. In the barrel, samples blended with gradient temperature 195-215-220-220-220-225-225-225 °C. The obtained biocomposites in form of granular, were made into test piece by injection molding machine (Model HC-250, Hwa Chin, China) with gradient temperature 170-185-200 °C. The biocomposites test piece about 16.4 cm (long), 13 cm (wide) and 4 cm (thick).

2.3. Contact angle measurements of biocomposites

The sessile-drop method was chosen for contact angle measurements and the static contact angle (CA) were determined by Phoenix 300 Contact Angle Analyzer (Surface Electro Optics, Korea). Test liquids used in this study are described in Table 2 and 3. Water (equademineralized) were used as the polar liquids, methanol as semi-polar liquid, and hexane as nonpolar liquid. Three probe liquids were placed on the surface of the biocomposites test piece. Drops of 5 μL volume were employed and a total of three droplets were analyzed for each liquid. The contact angle determinations were performed through the capture of the droplet images using Surfaceware 8 software and a camera based contact angle analysis system. Image capturing continued from the beginning of the test, at 5 minutes, and 10 minutes. The angle was measured at both sides of the droplets. All tests were carried out at room condition (temperature of 25 °C).

2.4. Surface free energy determination

The surface free energy (SFE) and their components were calculated for all samples using Surfaceware 8 software, with three methods, Girifalco-Good-Fowkes-Young (GGFY), Owens-Wendt, and van Oss-Chaudhury-Good (vOCG), which uses equations (2)-(9). For GGFY, the liquid used was water (aquademineralized), with known total liquid SFE value 72.8 mJ/m^2 . The probe liquid parameters used for the determination of the biocomposites surface energy are listed in tables 2 and 3, for Owen-Wendt and vOCG, respectively. Analysis of variance (One way ANOVA) was used to determine the statistically significant differences between these methods. The ANOVA was also used to prove the differences between the SFE values of different fiber size filler on biocomposites.

Table 2. SFE and their components (in mJ/m^2) for the probe liquids used for contact angle determination according to the Owen-Wendt method

Liquid	γ_l	γ_l^p	γ_l^d
Water	72.8	21.8	51
Hexane	18.4	18.4	0

Table 3. SFE and their components (in mJ/m²) for the probe liquids used for contact angle determination according to the vOCG method

Liquid	γ_l	γ_l^{LW}	γ_l^{AB}	γ_l^+	γ_l^-
Water	72.8	21.8	51	25.5	25.5
Methanol	22.5	18.2	4.3	0.06	77
Hexane	18.4	18.4	0	0	0

3. Results and discussion

3.1. Contact angle values

Table 4. Contact angles of the test liquids on the biocomposites

Samples	Contact Angle (°)		
	Water	Methanol	Hexane
RABS	87.34	28.01	15.69
RABS/LF	87.95	26.86	13.11
RABS/MF	88.24	32.47	11.03
RABS/SF	102.58	40.05	11.09
RABS/μ	104.75	41.76	14.48

Contact angles of the test liquids (water, methanol and hexane) on the biocomposites filled OPEFB long-fiber (RABS/LF), medium-fiber (RABS/MF), short-fiber (RABS/SF), microparticle (RABS/ μ), and recycled ABS (RABS) as control are given in Table 4. The value of each contact angles was the average of three droplets. As it can be seen in Table 4, decrease of fiber size increased the contact angle. The evolution of contact angle versus time is shown in figure 1. Depletion water contact angle was slower than methanol. Furthermore, hexane contact angle depleted fastly, even at 5 minutes the droplet has been wetting perfectly, zero contact angle. Its showed the wettability of the samples decreased with decreasing of EFB fiber size as biocomposites filler. Either recycled ABS or biocomposites was nonpolar and hydrophobic materials, due to the droplets of nonpolar liquid (hexane) on its surface was wet quickly, reacted to the composite surface.

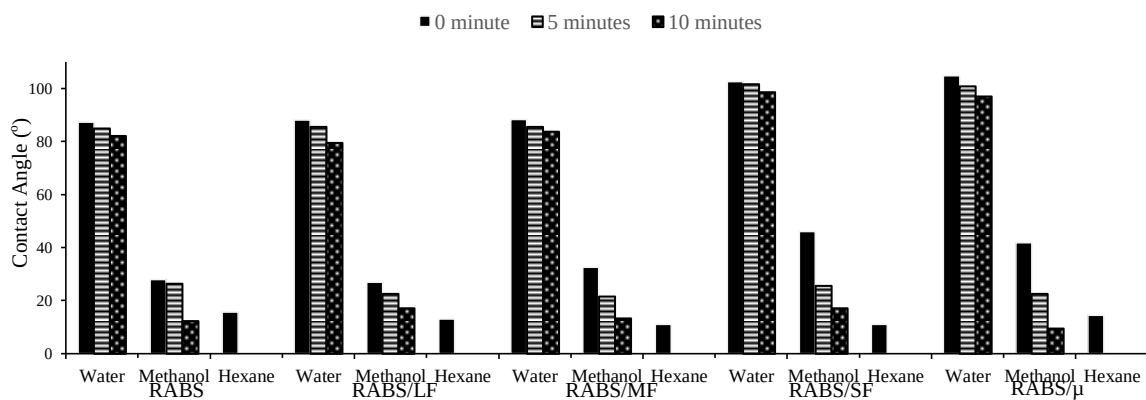


Figure 1. Contact angle depletion in biocomposites versus time (using three probe liquids: water, methanol and hexane)

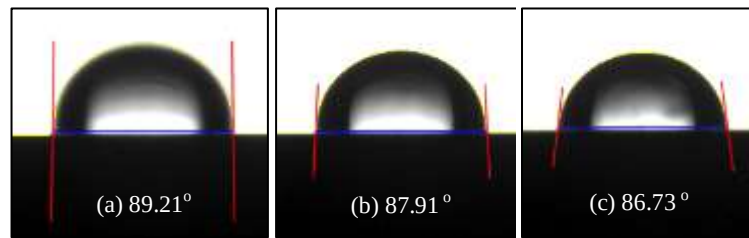


Figure 2. Representative figures of contact angle measurements of RABS/SF (a) 0 minutes; (b) 5 minutes; (c) 10 minutes with water as liquid

3.2. Surface free energy

According to the contact angle values the surface free energy (SFE) of biocomposites and their components were calculated using three previous known methods, Girifalco-Good-Fowkes-Young (GGFY), Owen-Wendt (OW), and van Oss-Chaudhury-Good (vOCG). The values of the SFE and its components are presented in Table 5.

The values of total SFE (γ_s) of biocomposites was lower than control (RABS), decreased with decreasing of EFB fiber size as biocomposites, except for RABS/LF total SFE calculated by vOCG method which higher than RABS. The dispersive components (γ_s^d) obtained by the OW are similar with vOCG (γ_s^{LW}) method and higher than its polar components, increased with decreasing fiber size. In the case for ABS/NF, the dispersive component of the surface free energy was higher than its polar components even 16 times. It can be observed as well from vOCG method calculation values that component of SFE connected with long range interaction (polar, dispersive, polar and inductive) is higher than the component describing acid-base interactions γ_s^{AB} . Lewis base (γ_s^-) surface free energy component is higher than Lewis acid (γ_s^+) for all biocomposites, where Lewis base values of biocomposites lower than RABS and decreased with decreasing fiber size filler. Owing to the insignificant γ_s^{AB} value it may be presumed that these surfaces will show properties of nonpolar materials.

Table 5. SFE and its components (in mJ/m²) of recycled ABS and biocomposites calculated with various methods

Samples	GGFY	Owen-Wendt			vOCG				
	γ_s	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^{LW}	γ_s^{AB}	γ_s^+	γ_s^-
RABS	24.61	24.3	17.72	6.67	19.57	17.72	1.85	0.07	11.4
RABS/L		9						2	
F	24.10	24.2	17.92	6.31	19.73	17.92	1.81	0.08	10.7
RABS/M		3						4	
F	23.87	24.1	18.06	6.12	19.42	18.06	1.35	0.04	10.8
RABS/SF	13.75	19.5	18.06	1.46	18.54	18.06	0.48	0.02	2.42
		2							
RABS/μ	12.48	18.9	17.82	1.08	18.21	17.82	0.39	0.02	1.75
		0							

A comparison of the total SFE calculated with three various method for RABS and biocomposites and their grouping information by using the fisher LSD method and 95% confidence, is presented in Table 6 and 7. The analysis proved that there are no statistically significant differences in the values of the SFE calculated with either the GGFY, Owens-Wendt or the vOCG method when the RABS filled with OPEFB fiber with are degraded fiber size.

Table 6. Analysis of variance for total SFE calculated with three various method

Source	DF	Adj. SS	Adj. MS	F-value	P-value
Factor	2	27.56	13.78	0.91	0.427
Error	12	181.03	15.09		
Total	14	208.59			

Table 7. Grouping information using the fisher LSD method and 95% confidence

Factor	N	Mean	Grouping
Owen-Wendt	5	22.24	A
GGFY	5	19.76	A
vOCG	5	19.09	A

4. Conclusions

Contact angle values of the test liquids on the RABS, biocomposites filled OPEFB long-fiber (RABS/LF), medium-fiber (RABS/MF), short-fiber (RABS/SF), microparticle (RABS/ μ), and recycled ABS (RABS) were increased with fiber size increasing. The values of total SFE (γ_s) of biocomposites was lower than control (RABS), decreased with decreasing of EFB fiber size as biocomposites. Owing to the insignificant γ_s^{AB} value of biocomposites, it may be presumed that these surfaces showed properties of nonpolar materials. The smaller the fiber size of biocomposites filler, the higher water contact angles, which mean the more hydrophobic the surface. It is highly advantageous since in general applications, the coating/painting materials for ABS composite were oil based (nonpolar). Therefore, the more hydrophobic material will increase the wettability of their coating. The total surface free energy values of RABS and biocomposites obtained from the different methods are similar and no statistically significant different (P -value > 0.05).

References

- [1] Singha A S. and Thakur V K 2009 *Polym. Plast. Technol. Eng.* **48** 736
- [2] Hassan A, Salema A A, Ani F N and Bakar A A 2010 *Polym. Compos.* **31** 2079
- [3] Nikmatin S, Syafiuddin A and Kueh A B H 2015 *J. Teknologi* **77** 181
- [4] Solikhin A, Hadi Y S, Massijaya M Y and Nikmatin S 2016 *BioResources* **11** 2224
- [5] Nikmatin S, Syafiuddin A, Nugroho N, Utama W and Wismogroho A S 2017 *MATEC Web. Conf.* **95** 03001
- [6] Nikmatin S, Syafiuddin A and Irwanto D A Y 2017b *BioResources* **12** 1090
- [7] Yang S, Castilleja J R, Barrera E V and Lozano K 2004 *Polym. Degrad. Stab.* **83** 383
- [8] Żenkiewicz M 2007 *J. Achiev. Mater. Manuf. Eng.* **24** 137
- [9] Oporto G S, Gardner D J, Bernhardt G and Neivandt D J 2007 *J. Adhes. Sci. Technol.* **21** 1097
- [10] Żenkiewicz M 2005 *Polimery* **50** 365
- [11] Rudawska A 2012 *Adhesive Properties Scanning Electron Microscopy* ed V Kazmiruk (Rijeka: InTech) chapter 7 pp 101-126
- [12] Njobuenwu D O, Oboho E O and Gumus R H 2007 *Leonardo El. J. Pract. Technol.* **10** 29
- [13] Young T 1805 *Phil. Trans. R. Soc. Lond.* **95** 65
- [14] Girifalco L A and Good R J 1957 *J. Phys. Chem.* **61** 904
- [15] Fowkes F M 1964 *Ind. Eng. Chem.* **56** 40
- [16] Grundke K 2005 *Surface-energetic properties of polymers in controlled architecture Molecular interfacial phenomena of polymers and biopolymers* ed P Chen (Cambridge: Woodhead Publishing) chapter 10 pp 323-374
- [17] Owens D K and Wendt R C 1969 *J. Appl. Polym. Sci.* **13** 1741

- [18] Cwikel D, Zhao Q, Liu C, Su X and Marmur A 2010 *Langmunir* **26** 15289
- [19] Sudaryanto, Nishino T, Asaoka S and Nakamae K 2001 *Int. J. Adhes. Adhes.* **21** 71
- [20] Van Oss C J, Chaudhury M K and Good R J 1988 *Chem. Rev.* **88** 927