



Experimental Evaluation on Palm Oil and Sesame Oil-based Resin Properties as Core Sandwich Material for Lightweight Ship Structure

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ABSTRACT

Research on lightweight material on ship structure has taken giant steps during the last decade. One reason is that shipping activities have increased and, therefore, the possibility of increasing the carrying cargo capacity in a realistic way using advanced lightweight material. This article summarizes a research investigation regarding the experimental tests of vinyl ester bio resin material using palm oil and sesame oil based on Lloyd's Register (LR) standard. Several tests were conducted, including density, water absorption test, Fourier transformed infrared test (FTIR), scanning electron microscope (SEM), and mechanical tests to evaluate the effect of 2-10% addition of vegetable oils on mechanical properties. The influence of the addition of vegetable oils is successfully characterized using physical measurements, which indicate the possible formation of a polymer blend to increase in elongation value. Mechanical testing shows that adding vegetable oils causes a decrease in average density, hardness, bending strength, and tensile strength. The bending strength decreases about 9.20 – 47.06% for 2-10% palm oil addition and 5.33 – 42.40% for sesame oil addition. Moreover, vegetable oil causes a tensile strength decrease of about 5-18.75% on palm oil and 3.75-13.75% on sesame oil. As summarized, bio resin based on sesame oil has better mechanical behavior with the oil addition of 4-8% fulfills all Lloyd's Register criteria.

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1. INTRODUCTION¹

The lightweight sandwich structure is developed largely in several application engineering disciplines, most notably the shipbuilding sector. Several studies on the development of sandwich material on various ship structural components have revealed benefits. It improves the strength-to-weight ratio [1-3], has good damping properties [4,5], and simplifies production and construction processes.

An intriguing issue is the progression of material types and composition for the faceplate and core sandwich for shipbuilding applications. The experimental testing procedure and acceptance properties criteria of a core sandwich as ship structure are regulated

to the Lloyd's Register [6] and DNV GL [7]. In the recent development of sandwich application in the shipbuilding sector, steel and room temperature curing polyurethane elastomer (RTC-PU) are one of the established material types which are often used as the faceplate and core materials for the sandwich panel [8,9]. However, the RTC-PU material is not cost-effective in practical application, especially for small-scale shipbuilding businesses in a developing country, where the material cost will extremely govern the overall cost of ship production [10,11]. One of the alternative solutions that have been investigated is the use of low-cost polymer and waste material [12-14] for core materials.

Low-cost core material must be tested according to the standard and meet the acceptance criteria value from Lloyd's Register [6] so that the developed material can be

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used as the core material of the ship sandwich structure. Various materials have been developed, but not many have followed the testing standards and met the acceptance criteria value from Lloyd's Register [6]. Several nanocomposites [15,16] have not been tested according to the request of Lloyd's Register to be ship material standard [6]. Various natural fibers [17-19] also do not meet the LR criteria, specifically the elongation at break criteria. The critical point is needed to be addressed, including the material brittleness and elongation threshold. Furthermore, research on the innovation of low-cost core material types with better mechanical properties needs to be conducted.

In order to substitute room temperature curing polyurethane elastomer (RTC-PU) as expensive core material and further investigation to increase the elongation value of resin polymer material, one potential alternative solution to increasing material properties can be achieved by developing a low-cost bio-resin polymer blend of two or more polymers to obtain new polymeric components from vegetable oils with excellent material properties specifically elongation parameter. Even if there are a lot of works completed on developing bio-based resin from vegetable oils to our observation, there are still limited reports on the mechanical testing development of bio-based resin as core sandwich material specifically for ship structure according to the procedure and specification standards have given by Lloyd's Register [6].

To address this issue, vinyl ester bio-based resin combined with palm oil and sesame oil with several compositions is proposed to be developed as the core material of the ship sandwich structure. The proposed core material must meet the Lloyd's Register criteria [6], such as density, hardness, tensile strength, and elongation at break. Physical tests, characterization tests, and mechanical tests were carried out to check the suitability of the proposed bio-based resin against Lloyd's Register criteria [6] and to analyze various compositions of vegetable oils further.

2. METHODS

2. 1. Material Preparation and Processing

EPOXY R-802 EX-1 vinyl ester (VE) resin type was combined with cobalt naphthenate, and Methyl Ethyl Ketone Peroxide (MEKP) were used in this study. The VE has a specific gravity of 1.05 g/cm³ at 25°C, an acid value of 7-13 KOH mg/g, a viscosity of 2-6 poise at 25°C, and styrene composition of 46%. Methyl Ethyl Ketone Peroxide (MEXP) was used as an initiator [13]. The other material used was vegetable oil (VO). In this case, palm oil (PO) was purchased from PT Wilmar Nabati Indonesia, and sesame oil (SO) was purchased from PT Sukanda Djaya Indonesia was used as an addition to the

vinyl ester bio-based resin using different compositions. Sesame oil contains a lot of unsaturated fatty acids, especially oleic acid (C18:1) and linoleic acid (C18:2), omega-6 (35.5–49.5%), omega-9 (37.5–45.4%), and several antioxidant components such as vitamin E, carotene, and lignin components [20]. The chemical structure of sesame and palm oils is depicted in Figure 1.

Because it is biodegradable and safe, vegetable oil (VO) is appropriate for mineral oil. In this case, palm oil (PO) was sesame oil (SO) was used as an addition to the vinyl ester bio-based resin using different compositions. In material development, specimen blend variations are developed based on several procedures. In the first step, all the material components, including vinyl ester, catalyst, and accelerator, are measured specified composition. Then, thermoset blending was formed by using a physical-mechanical mixing process with styrene as the cross-linker diluent, adding sesame and palm oils in 0, 2, 4, 6, 8, and 10 wt % in the vinyl ester (VE).

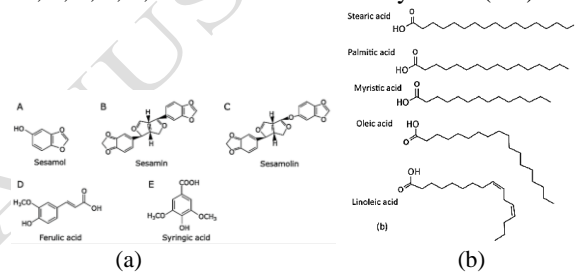


Figure 1. a) chemical structure of sesame oil [20], b) chemical structure of palm oil

In the next step, With a catalyst accelerator, Methyl Ethyl Ketone Peroxide was added as a catalyst initiator at 0, 2, 4, 6, 8, and 10% wt. A transparent colorless solution was obtained by blending vinyl ester, vegetable oil, MEKP, and accelerator in a mechanical mixer at room temperature for 2 hours. Next, the specimen is created in the wooden mold with several types according to the corresponding mechanical testing. The mixture was put into wooden molds and cured at room temperature for 24 hours after being placed under a low vacuum (300 kPa) for 2 hours. All the specimens and then removed from the mold after curing in the final step.

2. 2. Experimental testing and procedure

Shore D hardness test was conducted using a durometer with the specimen dimensions, and procedures were performed using the ASTM D2240 [21]. In this case, the average hardness test output was obtained by measuring the mean of 3 specimens of each variation with the sample thickness is 6 mm. Further, the tensile test was performed to determine mechanical properties using dumb-bell-shaped samples with Hung Ta HT-2402 at a rate of 0.1 mm/min in accordance with ISO 527-4 [22]. Besides the tensile test, three-point bending testing was carried out to obtain information on the strength of the material using the three-point bending method. Tests were carried out

with the WDW-1000 bending test machine. The specimen dimensions and testing procedure used the ASTM D790 standard [23].

Characterization tests were carried out to obtain the microscopic behavior of the material. Their tests are Fourier Transform Infrared test (FTIR) and Scanning Electron Microscopy (SEM). In this test case, both SEM and FTIR test was carried out to analyze the microscopic behavior of several specimens. Thermoscientific Nicolet I S10 spectrophotometer with smart orbit diamond crystal plate sampling technology was used for the FTIR spectroscopic investigation at resolution 4 cm^{-1} in the range of $400\text{-}4000\text{ cm}^{-1}$. Moreover, the SEM test was performed to obtain a morphological image of the sample. The morphology of composites was investigated at the fractured surface of samples using SEM, FEI INSPECT S50 at 20 kV. The cross-section of investigated samples is coated with 100 \AA thick C in the sputter coater.

Besides mechanical and characterization tests, physical properties test such as apparent density, water absorption test, and thermogravimetric analysis (TGA) was also conducted. The density test in accordance with ASTM D 70-03 [24] was conducted using a pycnometer and weighing specimens using the FUJITSU FSR-B1200. Water absorption was a test carried out to determine the absorption of material against water at a specific time. The water adsorption test procedure uses the ASTM D570-98 standard [25]. Water absorption was a test carried out to determine the absorption of material against water at a specific time. The procedure used in this test was conducted to prepare a water adsorption specimen and then weigh it when the material is dry and then immersed in a container filled with water with the amount of water that can immerse the entire area of the specimen at a specific time and then weighed again when wet conditions. The difference between the two weighing results will be used as water absorption data [26, 27]. The water absorption specimen is based on ASTM D570-98 standards. Furthermore, thermal analysis of polymers typically involves various techniques, including a well-established thermogravimetric analysis (TGA). The test determined the quantity and frequency of weight fluctuation of samples versus temperature and time in a controlled atmosphere. A TGA test was used in this case to measure the thermal stability of the material and volatile component percentage by measuring the weight change that occurred while the material was heated at a consistent rate. TGA examines changes in the weight of a sample while it is heated at a regulated temperature, and the changes are continually recorded.

3. RESULT AND DISCUSSION

In this section, the results of experimental testing in all sample variations are reviewed. As the result of physical

testing, the comparison result of apparent density due to addition of an epoxidized vegetable oil into vinyl ester bio-resin is shown in Figure 2. It can be found that the results of standard deviation depicted by a vertical line in Figure 2 for VE-palm oil specimen with different volume fractions are in the range of 0.0002-0.001 and for VE-sesame oil in the range of 0.007-0.002. The result of both specimen types experiences a decreasing trend as the fraction volume of vegetable oil increases. It can be found that pure vinyl ester specimens experience the highest density, whereas the lowest one is the specimen with the highest addition of palm and sesame oil. It can be found that the addition of 2-10% palm oil causes a density decrease in the range 10.08-10.61% and 10.43-10.88% decrease for the addition of sesame oil. A similar result was noticed by previous literature [28] that density value decreases due to the addition of vegetable oil (soybean and coconut oils) to vinyl ester specimens. Compared to the two types of material, it can be analyzed that the density of vinyl ester with palm oil is slightly higher than polymer-based sesame oil. Compared to the LR standard, both material types fulfill the minimum standard, except for 10% of VE-sesame oil specimens.

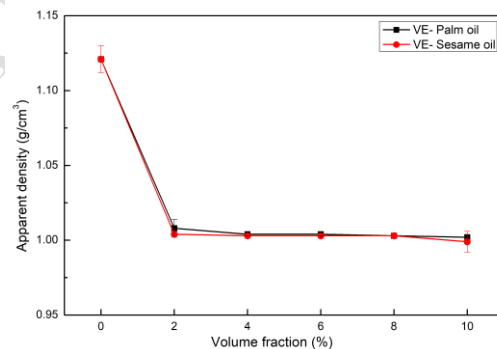


Figure 2. Apparent density between VE-palm oil and VE-sesame oil

Figure 3 illustrates the comparison of water absorption percentage between polymer based on sesame and palm oils for 7 days. The results of standard deviation depicted by a vertical line in Figure 3 for VE-Palm oil specimen with different volume fractions is in the range of 0.022-0.050 for palm oil and for VE-sesame oil in the range of 0.03-0.0076. It can be analyzed that the percentage of water absorption increases with an increase in absorption time from day 1 to day 7. It can be found that water absorption on VE-sesame oil increases from 0.285 to 0.611%, which is calculated as about 114.7% increase. Moreover, VE-palm oil experiences a water absorption increase from 0.278 to 0.61%, which calculates 118.8% increase.

Water absorption experiences an increasing trend from day 1 and day 5. However, from day 5 to day 7, it experiences constant water absorption. Water absorption becomes less from day 5 to 7 because the material experiences a state of saturation with water.

Therefore, it causes the water absorption of the specimen to decrease. The ability to absorb water in the sample occurs in the surface area. It is due to the basic nature of vegetable oils, which are non-miscible or insoluble in water. It can be seen from the plot that water absorption by bio resin increases monotonically with immersion time until an equilibrium condition is reached after 168 h, where saturation is experienced in all samples [29].

The result of the thermogravimetric analysis is presented in Figure 4a. TGA test only gives information for substances that show a change in mass for every sample analyzed at the temperature change between 0 - 600°C. It can be found that the mass change in the samples with a higher volume fraction (10%) of sesame and palm oils is greater compared to samples with a lower volume fraction (2%). It can be summarized that the lowest one can be found in the sample with vinyl-ester-sesame oil (2%). In this case, the difference in the weight changes of samples can be caused by decomposition and oxidation reactions and physical processes such as sublimation, vaporization, and desorption.

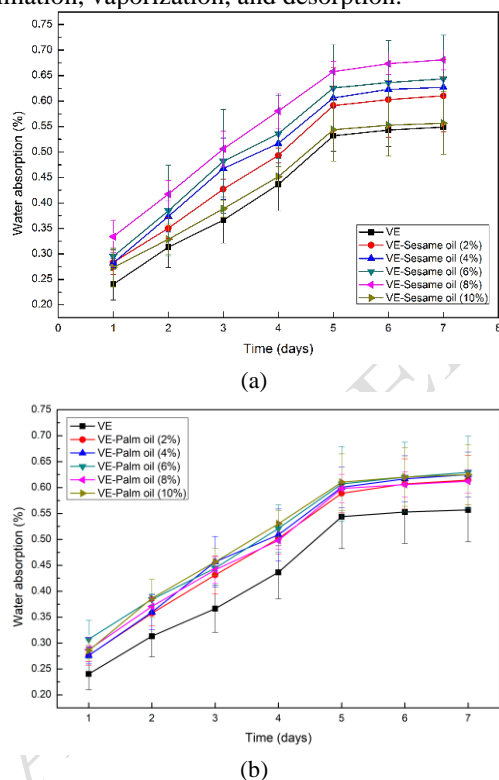


Figure 3. Water absorption a) VE-sesame oil b) VE-palm oil

Figure 5 shows the FTIR result of each variation of the specimen. At the absorption peak of 3392.63 cm^{-1} , the O-H bond is stretched, which is a ketone functional group. Then, C-H bonds stretch at the absorption peaks of 3024.59 cm^{-1} , 2918.77 cm^{-1} , and 2849.48 cm^{-1} . This phenomenon indicates the presence of an alkane functional group (CH_2 or CH_3).

At the absorption peak of 1724.31 cm^{-1} , the C=O bond is stretched, which is the functional group of the ester. Further, there is a C=C bond that vibrates at the absorption peak 1603.40 cm^{-1} and 1507.50 cm^{-1} , which show functional groups of aromatic homocyclic. Then, the C-O bond stretching at the absorption peaks of 1179.42 cm^{-1} and 1031.32 cm^{-1} show the ester and alcohol functional groups. At the peak of 826.11 cm^{-1} , the C-H bond is deformed, indicating the presence of an aromatic ring. The FTIR spectrum of vinyl esters can be identified by the dominance of the $-\text{CH}_2$ and $-\text{CH}_3$ alkane groups in the absorption regions of 2960 cm^{-1} , 2923 cm^{-1} , 2871 cm^{-1} , and 2851 cm^{-1} . Then aromatic rings appear in the absorption region of 1604 cm^{-1} and 826 cm^{-1} . The absorption area of 1712 cm^{-1} is identified by the presence of C=O stretching bonds, and there is a $-\text{C}-\text{O}-\text{C}$ group in the 1220 cm^{-1} region.

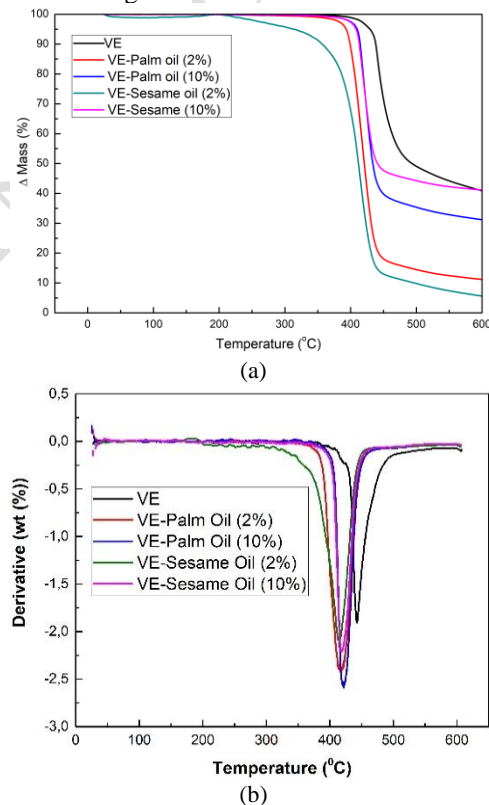


Figure 4. (a) TGA and (b) DTG of different material types

The FTIR spectrum in Figure 5 shows a new absorption peak area that appears in vinyl ester bio-resin, at the absorption peak area of 750 cm^{-1} - 760 cm^{-1} and 690 cm^{-1} - 700 cm^{-1} . The absorption peak region in the range of 735 cm^{-1} - 770 cm^{-1} is the absorption region of the deflected C-H bond with the benzene ring functional group with 4 free H atoms. The absorption area of 690 cm^{-1} - 710 cm^{-1} is the absorption region of the deflection C-H bond with the benzene ring functional group with 5 free H atoms.

As expected, the spectra present the same band patterns due to the similar structures of vegetable oils. The spectra presented in Figure 5 show bands corresponding to the stretching vibration of the carbonyl group of the ester linkage (at ca. 1700 cm^{-1} C=O functional group double bonds) from the vinyl ester and the oil structure [30]. The band appearing (at ca. $1600 - 1500\text{ cm}^{-1}$ C=C functional group double bonds) can be ascribed to the stretching vibration of the double bond from maleic anhydride [31]. C=O in the absorption at ca. of 1200 cm^{-1} . It proves that vegetable oil esters form new bonds with pure vinyl esters in the form of a benzene ring with 4 free atoms and a benzene ring with 5 free atoms. Vinyl ester polymer bio-resin with 2% palm oil filler has a steeper wave transmittance than other sample types.

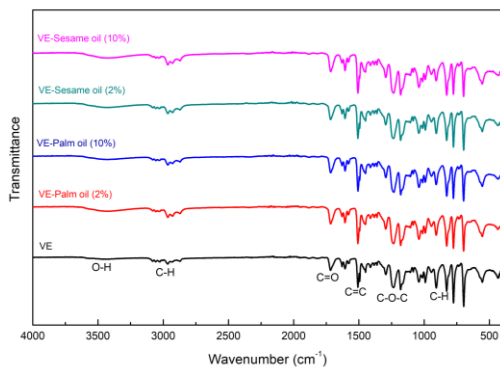


Figure 5. FTIR spectrum of different material types

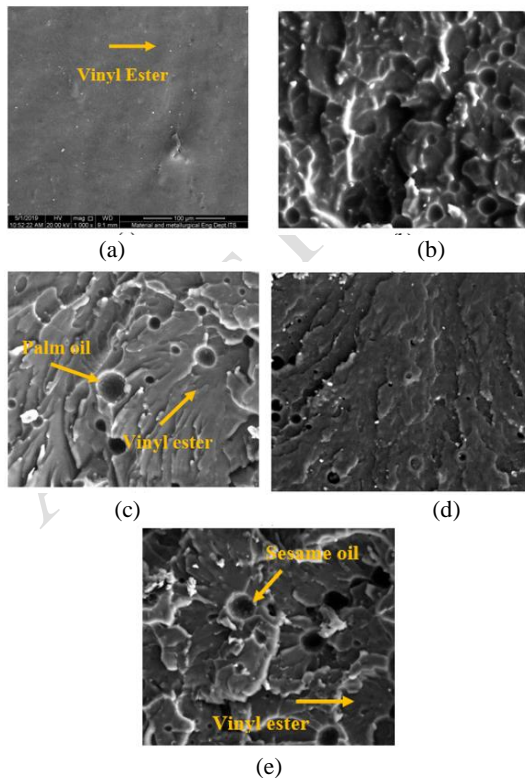


Figure 6. SEM a) VE, b) VE-palm oil (2%), c) VE-palm oil (10%), d) VE-sesame oil (2%), e) VE-sesame oil (10%)

The texture in Figure 6a is smooth and flat because there is no addition of vegetable oil. Figure 6b shows the morphology of VE-palm oil (2%). The effect of the triglyceride bond on the vinyl ester can be seen as rigid and rough-textured. It can be seen from the results that there are several forms of hemispherical basins. This basin is known as a spherical ball. Figure 6c shows a texture that is almost the same as the VE-Palm oil (2%) sample but looks smoother. Moreover, Figure 6d shows the smoothest texture among all specimens. This picture also shows the presence of spherical balls that have a varied distribution. Figure 6e shows a much coarser texture than VE-sesame oil (2%).

Figure 7 compares the average hardness value of pure VE, VE-sesame oil, and VE-palm oil. The hardness value in each specimen variation is the average result of 3 samples with the range of standard deviation 1 - 3.21 for VE-palm oil and 0.58 - 2.52 for VE-sesame oil specimen. It can be analyzed that pure VE has the highest hardness value reaching 80 Shore D. The addition of 2-10% vegetable oil into vinyl ester specimen causes a decrease of about 5.00 - 18.75% for palm oil and 3.75 - 13.75% for sesame oil. The obtained result is linear to the previous findings where the addition of 4.wt% vegetable oil causes a decrease of about 4.92 - 5.97% on hardness value [28].

According to the FTIR data, a polar group (C=C) is not completely attached. It denotes that mixing takes place mechanically rather than chemically. The hardness has dropped because chemical connections between vinyl esters and vegetable oils do not exist. In 10% addition of vegetable oil, it can be found that VE-sesame oil is higher about 6.15% compared to VE-palm oil. Therefore, it can be concluded that VE-sesame oil samples are better resistant to indentation. Compared with the minimum hardness requirement by LR, the hardness value of VE-sesame oil and VE-palm oil in all volume fraction variation is higher than the minimum hardness of 65 Shore D.

Figure 8 presents the comparison result of tensile strength between pure VE, VE-palm oil, and VE-sesame oil samples. The tensile strength value in each specimen variation is the average result of 3 samples with the range of standard deviation for VE-palm oil is 1.4 - 3.46 and 1.41 - 3.16 for VE-sesame oil specimen. From the result of the work, the highest tensile strength can be found in the pure vinyl ester sample, about 47 MPa. The result shows that the addition of vegetable oil causes a tensile strength decrease of about 5-18.75% on VE-palm oil and 3.75-13.75% on VE-sesame oil. The previous report shows that tensile strength decreases in the range 3.5 - 45.6% due to 5-20% palm oil addition into vinyl ester specimens [32]. The decrease in tensile strength is

caused by an increase in particle concentration which causes an increase in the agglomeration and the presence of unreacted bonds and molecules.

The more addition of vegetable oil composition, the more triglyceride groups contained in the bio-resin mixture. However, because there is no crosslink, the greater the addition of vegetable oil, the tensile strength value will decrease. Therefore, with an increase in vegetable oil composition, the concentration of polar groups in the bio-resin specimen will decrease, resulting in an increase in the component of vegetable oil, which can reduce the tensile strength value, as can be seen in Figure 8. All tensile strength values fulfill the LR standard.

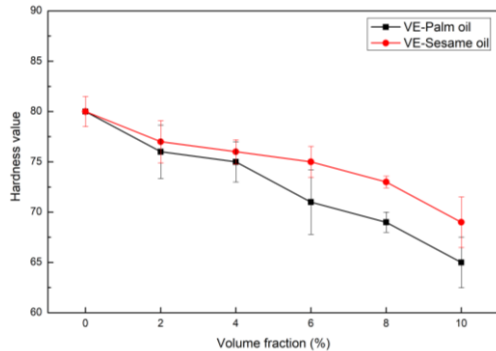


Figure 7. Result of shore D hardness test

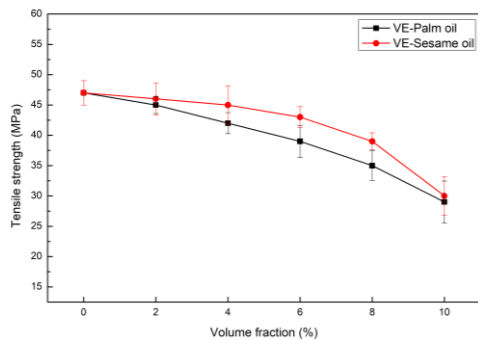


Figure 8. Result of tensile strength of different material types

Figure 9 shows the results of elongation percentage. The elongation value in each specimen variation is the average result of 3 samples with the range of standard deviation for VE-palm oil is 0.4 – 1.0 and 0.3 – 0.8 for VE-sesame oil specimen. It can be shown that adding sesame and palm oils can increase the elongation of the material. It can be found that the addition of 2-10% vegetable oil causes an elongation increase of about 46.6 – 173.3% for VE-palm oil and 33.3 - 140% for VE-sesame oil. The previous study was also noticed a similar result where the addition of vegetable oil (sesame, palm, and coconut oils) causes an increase of elongation value [28,32]. It is caused due to a large number of long-chain polymer chemical structures and the easier movement of molecules [13]. So, with the addition of vegetable oil, the elongation value increases because there are more C

chains in the bio-resin. The C chain is getting longer because of the C chain contained in vegetable oil. Compared to the LR standard with a minimum of 20% elongation at break, it can be concluded that adding vegetable oils into bio-resin is the best option and can be used as a recommendation to increase the ductility of the material. Compared to standard, only the addition of 2% sesame oil does not fulfill the minimum elongation given by LR standard.

In the last, the result of the three-point bending test is depicted in Figure 10. The bending test in each specimen variation is the average result of 3 samples with the range of standard deviation for VE-palm oil is 3.67 – 5.88 and 2.44 – 5.87 for VE-sesame oil specimen. A similar result with the tensile test can be found where the VE-sesame oil specimens have better mechanical properties due to higher bending strength than VE-palm oil. From Figure 10, it can be analyzed that the addition of vegetable oil into bio-resin causes a decrease in bending strength. The results show that the bending strength decrease is calculated about 9.20 – 47.06% for VE-palm oil and 5.33 – 42.40% for VE-sesame oil. A similar previous study showed that the flexural strength decreases by 38.9% due to addition of 5-20% palm oil into vinyl ester specimens [32].

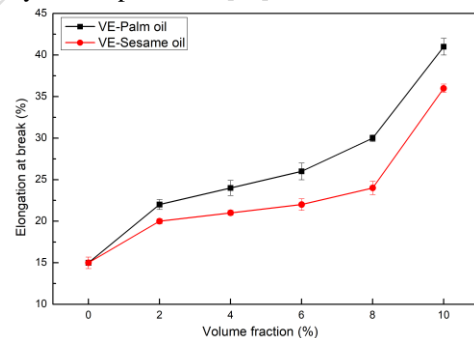


Figure 9. Elongation at break of different material types

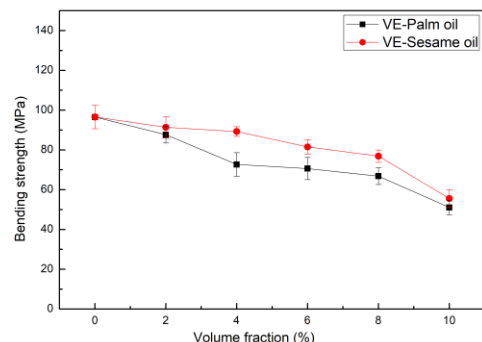


Figure 10. Result of bending of different material types

The decrease in bending strength is caused by the occurrence of porous structure in the material. However, it is found that there is no crosslink, so the greater the addition of vegetable oil, the value of the tensile strength will remain decrease. It is inversely proportional to the elongation value, which increases

because there are more C chains in the bio-resin. The C chain is getting longer because of the C chain contained in vegetable oil. The number of C carbon chains in palm oil includes C₁₈, palmitic C₁₆, linoleic C₁₈, while the C carbon chains in sesame oil include sesame C₇, sesamol C₂₀, sesamin C₂₀. The long carbon chain affects the elongation properties of a material. If the C chain of vegetable oil binds with other elements of vinyl ester, it will increase the value of the bending strength of the material. However, based on the results of the FTIR test, there is no crosslink. Therefore, only the elongation value increases without an increase in the bending strength. Although more volume fraction of vegetable oil is added to the vinyl ester mixture, only the elongation value will increase, and there is no increase in bending strength.

Several ship structures have been used to sandwich panels, including the deck [16], hull [33-35], and ramp door [1,10]. Lloyd's Register has suggested other ship parts that can also be applied to sandwich panels, including double bottom floors and girders, primary structural members, corrugated bulkheads, and any structure directly in contact with the oil cargo [6]. Furthermore, this ductile and non-corrosive composite material can be used as the blade material of the Vertical Axis Hydrokinetic Turbine [36].

4. CONCLUSION

Several experimental tests were carried out in order to measure the optimum composition and mechanical properties of bio-resin based on LR standards. The effect of the addition of volume fraction of sesame and palm oil into bio-resin is investigated. Several conclusions can be stated, as follow:

1. The oil addition indicates the ability to bind to other elements leading to the potential formation of a polymer blend and elongation increment value due to a longer carbon chain.
2. The testings reveal that adding vegetable oil can decrease the density, hardness, and strength properties but increase the elongation.
3. VE-sesame oil has better mechanical behavior than VE-palm oil, with the oil addition of 4-8% is recommended and fulfills the LR standard.

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Persian Abstract

چکیده

تحقیقات در مورد مواد سبک وزن در ساختار کشتی در دهه گذشته گام های بزرگی برداشته است. یکی از دلایل این است که فعالیت های حمل و نقل افزایش یافته است و بنابراین امکان افزایش ظرفیت حمل بار به روشی واقعی با استفاده از مواد سبک وزن پیشرفته وجود دارد. این مقاله یک بررسی تحقیقاتی در مورد آزمایش های تجربی مواد بیو رزین وینیل استر با استفاده از روغن نخل و روغن کنجد بر اساس استاندارد Lloyd's Register (LR) را خلاصه می کند. آزمایش های متعددی از جمله چگالی، آزمون جذب آب، آزمون مادون قرمز تبدیل فوریه (FTIR)، میکروسکوپ الکترونی روبشی (SEM) و آزمایش های مکانیکی برای ارزیابی اثر افزودن ۲ تا ۱۰ درصد روغن های گیاهی بر خواص مکانیکی انجام شد. تأثیر افزودن روغن های گیاهی با موفقیت با استفاده از اندازه گیری های فیزیکی مشخص می شود، که نشان دهنده احتمال تشکیل یک ترکیب پلیمری برای افزایش مقدار ازدیاد طول است. آزمایشات مکانیکی نشان می دهد که افزودن روغن های گیاهی باعث کاهش چگالی متوسط، سختی، استحکام خمشی و استحکام کششی می شود. استحکام خمشی حدود ۹۲۰ - ۴۷۰۶ درصد برای افزودن ۲-۱۰ درصد روغن نخل و ۵۳۳ - ۴۲۰۴ درصد برای افزودن روغن کنجد کاهش می یابد. علاوه بر این، روغن نباتی باعث کاهش مقاومت کششی حدود ۵-۱۸۷۵ درصد در روغن پالم و ۳۷۵-۱۳۷۵ درصد در روغن کنجد می شود. همانطور که خلاصه شد، رزین زیستی مبتنی بر روغن کنجد رفتار مکانیکی بهتری با افزودن روغن ۴ تا ۸ درصد دارد که تمام معیارهای ثبت لوید را برآورده می کند.
