Core sandwich material development based on vinyl ester bioresin for ship structure application

Tuswan Tuswan¹, Achmad Zubaydi¹*, Bambang Piscesa², Eli Novita Sari³, Abdi Ismail¹
¹Department of Naval Architecture, Institut Teknologi Sepuluh Nopember
Campus of ITS Sukolilo, Surabaya 60111, Indonesia
*Email: zubaydi@na.its.ac.id
²Department of Civil Engineering, Institut Teknologi Sepuluh Nopember
Campus of ITS Sukolilo, Surabaya 60111, Indonesia
³Department of Mechanical Engineering, Billfath University
Siman, Sekaran, Kabupaten Lamongan, Indonesia

Abstract. Development of lightweight core sandwich based bioresin for ship structure application needs more attention. Bioresin from vegetable oils constitutes single, easily available, low cost, and biodegradable materials. In this research, the vinyl ester bioresin based Vinyl Ester-Coconut Oil (VE-CO) and Vinyl Esters-Soybean Oil (VE-SbO) containing 4 wt% vegetable oils are developed. The influence of vegetable oil addition in bioresin is characterized by visual observation and physical testing, including FTIR, density, hardness, and tensile test based on Lloyd’s Register standard. Visual testing shows that VE without vegetable oil is more transparent compared with VE with vegetable oil. The density test shows that adding vegetable oil decrease the apparent density. Vibration pattern indicates the presence of O-H, C-H, C=O, C=C, and C-O-C, which demonstrate the ability to bind, which leads to the potential formation of a polymer blend and elongation increase. Moreover, hardness decreases due to the absence of chemical bonds that occur between vinyl esters and vegetable oils. The addition of vegetable oil to vinyl ester bioresin reduces tensile strength and increases the elongation at break. So, density and tensile strength criteria meet Lloyd’s Register Standard while the other criteria are not fulfilled.

Keywords: vinyl ester-coconut oil, vinyl esters-soybean oil, bioresin, core sandwich, ship structure

1. Introduction
Sandwich material has been extensively developed in various engineering application fields, especially in ship structure. Sandwich materials usually have relatively thin faceplate and thick core in modern construction. The sandwich panel is generally applied in ship structure to increase high bending stiffness to weight ratio [1-3]. Several studies in developing sandwich material for ship structure have been carried out. Development of material types and composition for the faceplate and core for ship structure application is reviewed. Development of hybrid sandwich consisting of
steel face sheet and core from resin and waste material (clamshell and eggshell) for ship’s car deck and side hull has been reviewed in [1-4]. Other studies develop material consisting of steel faceplate and resin/talk [5] and polyurethane [6] as core material. Furthermore, the development of sandwich material available in Indonesia for application in ship structure is needed to be conducted.

The research of polymer blends is strict. Indeed, blending two or more polymers can result in new polymeric component with new, exciting properties [7-9]. The nature of the polymer blend is largely determined by the compatibility of the components blend. The purpose of the polymer blend compatibility is to obtain a stable and even dispersed phase so that the morphology and physical properties of the desired polymer blend can be achieved. Therefore, a compatibilization process is needed to modify the properties of the polymer blend. As an effort to material innovation, the development of environmentally friendly polymer materials is carried out. Vinyl ester resin is a versatile industrial resin today. Vinyl ester is an essential thermoset for polymer matrix composites due to good mechanical and adhesive properties. The processability of the vinyl ester-styrene cures at room temperature and makes them the main choice for application of large structures, especially shipbuilding application. Moreover, vegetable oil is a renewable resource that can be used as a starting material for new products with a variety of structural and functional variations. Vegetable oil-based polymers can compete with existing petroleum-based materials based on cost and positive impact on the environment. The vegetable oil can be modified easily for epoxidation of the double bonds [10]. Its abundant availability and relatively low cost make vegetable oil an attractive industrial raw material. Vegetable oils have been widely used for producing polymer composites that combine organic or inorganic particles or fibres, both synthetic and natural, and are measured from a macro scale to a micro-scale [11].

In this study, the vinyl ester based on polymer bioresin with vegetable oil polymers (coconut oil and soybean oil) is rigorously studied. The application of the bioresin will be used as the main ingredient of core sandwiches for ship structure. The aim is to investigate the properties of bioresin for core sandwich material by conducting several tests, including visual test, Fourier-transform infrared spectroscopy (FTIR), density, hardness, and tensile test. The development of core sandwich for ship structure application refers to Lloyd Register (LR) acceptance criteria.

2. **Experimental method**

2.1 **Core material development**

The sandwich panels are composite materials consisting of two different types of materials formed into a layer. Hybrid sandwich material includes of two steel face materials separated by polymer core. In this study, the development of core sandwich based bioresin using vinyl ester and vegetable oils is investigated. Vinyl ester resin (VE) is a thermosetting polymer that integrates the excellent mechanical, chemical, and thermal properties of epoxy resins. Vinyl ester resin has higher toughness compared to unsaturated polyester resins, with similar chemical structure [12]. Vinyl esters are widely used in marine structural applications. The main material used in this study is EPOXY R-802 EX-1 vinyl ester (VE) resin which is added with cobalt naphthenate and Methyl Ethyl Ketone Peroxide (MEKP) obtained from PT Justus Kimiaraya. Soybean oil is received from PT Wilmar Nabati, and coconut oil is received from PT Sukanda Djaya. The material properties and chemical structure of vinyl ester are presented in Table 1 and Figure 1, respectively.

Vegetable oil (VO) is a suitable alternative to replace mineral oil. Vegetable oil is biodegradable and safe material [14]. Vinyl ester based on polymer bioresin with vegetable oil polymers of coconut oil and soybean oil is studied to develop core material sandwich. In this
In this research, we develop the bioresin with three different variations. The first variation (pure VE) is required to provide baseline properties of pure vinyl ester resin (VE).

### Table 1. Properties of vinyl ester [12]

| Properties               | Value          |
|--------------------------|----------------|
| Tensile Strength         | 80 MPa         |
| Elongation at break      | 5%             |
| Viscosity at 25°C        | 520-620 MPa s  |
| Pot life at 25°C         | 14 – 24 Min    |

![VE chemical structure][13]

The thermoset polymer blends are mixed by mechanical blending method and cured at room temperature. The vinyl ester resin is mixed with 1 wt% cobalt naphthenate and 4 wt% catalyst (MEKP). The blend is mixed to ensure that no air bubbles formed. The second variation is the vinyl ester coconut oil (VE-CO). VE-CO is made by mixing 91 wt% vinyl ester, 1 wt% cobalt naphthenate, 4 wt% catalyst (MEKP), and 4 wt% coconut oil. The third variation, SbO is made by similar mixing composition with 4 wt% soybean oil. Next, all specimen variation is poured into wooden moulds and left under low vacuum (300 kPa) for 2 h, and cured in the room temperature for 24 h.

#### 2.2 Material test and preparation

Development of core material based on polymer bioresin is conducted by investigating several experimental tests, including FTIR test, apparent density, hardness, and tensile test to fulfill the requirement given by LR. The following report explains the preparation, test standard, and procedure for each test.

In FTIR analysis, infrared light is used to scan and analyze the chemical property of the specimens. A Fourier Transform Infrared Spectroscopy (Nicolet IS10) is performed to examine functional groups and chemical bonding of pure vinyl ester, vinyl ester with coconut oil, vinyl ester with soybean oil. FTIR analysis of vinyl ester bioresin will be compared to vinyl ester with vegetable oil. Bond changes can be used as an indication that a cross-link between vinyl esters and vegetable oil.

The density of the core is determined by calculating the mass of the specimen and then calculate the volume of the specimen. The size of the specimen must be as large as possible. The total volume of a specimen is 100 cm$^3$. In this research, the number of specimens per variation is five specimens where the dimension measurements are undertaken by pycnometer, and weight calculation uses FUJITSU FSR-B1200. The density is calculated based on ISO 845. The formula of density is ($\rho$) = $m/v$, where $m$ is mass, of the test specimen, and $v$ is the volume of specimens. For measurement accurately, wait at least 72 h after manufacturing the specimen. Moreover, a hardness test is defined as the resistance to indentation and is determined by measuring by giving indentation. In this research, Shore D Hardness is tested based on DIN 53505 using a durometer for different five indenter location of each specimen.
Determining the tensile strength of core materials is necessary so that the strength of each type of core materials can be deeply evaluated. The purpose of mechanical properties testing is to determine the ability of the core to withstand mechanical forces and loads. In this research, Tensile test is conducted by Universal Testing Machine performed employing Hung Ta HT-2402 machine in Innovative Material Laboratory, Department of Materials and Metallurgical Engineering, ITS. ISO 527 as standard operational and specimen dimension is used. The size of the specimens tested have a thickness of 10 mm, a width of 10 mm, and the total length is 150 mm. Testing is conducted on 3 specimens of each variation by finding the average value of maximum tensile strength as the value of tensile strength. The provisional rules for the application of sandwich panel in ship structure set down the criteria for the assessment of core material sandwich development. The development of core sandwich material is controlled by the following properties according to acceptable Lloyd’s Register [15] is illustrated in Table 2.

| Material Properties | Standard | Criteria |
|---------------------|----------|----------|
| Density             | ISO 845  | ≥ 1 g cm\(^{-3}\) at RT |
| Tensile strength    | ISO 527-4 / ASTM D412 | ≥ 20 MPa at RT |
| Tensile modulus     |          | ≥ 5 MPa at +80°C |
| Elongation at break | DIN 53505 | Min. 10% at -20°C, Min. 20% at RT |
| Shore D hardness    |          | ≥ 65 Shore D at RT |

RT = Room temperature in °C

3. Result and discussion

3.1 Visual inspection
The results of visual observations showed that 100% VE is more transparent than VE, which has been mixed with vegetable oil, as depicted in Figure 2. It shows that there is a bond or miscible between VE and vegetable oil. Mixing both materials cause an effect on the visual observation that the addition of vegetable oil makes the material opaque. The more additions of vegetable oil material will be much opaque. This proves that vegetable oil and VE can be used as polymer blends which are then used as bioresin.

Figure 2. Visual inspection between three different samples
3.2 FTIR result
In this section, the FTIR result will be compared for all variation of material. Figure 3 shows the allocation of the vibrational modes of FTIR. For VE vibrational modes in the range of 3392.63 cm\(^{-1}\) links to hydrogen bonded O-H. The vibrational mode for C-H stretching aliphatic is at 2965.65 cm\(^{-1}\). The vibrational modes for carbonyl are observed at 1717.12 cm\(^{-1}\) for C=O stretching, 1507.63 cm\(^{-1}\) for C=C stretching (aromatic), 1234.41 cm\(^{-1}\) for C-O-C stretching, 775.13 cm\(^{-1}\) for C-H deformation. For VE-CO vibrational modes in a range of 3434.60 cm\(^{-1}\) links to hydrogen bonded O-H. The vibrational mode for C-H stretching aliphatic is at 2964.71 cm\(^{-1}\). The vibrational modes for carbonyl observe at 1716.93 cm\(^{-1}\) for C=O stretching 1507.71 cm\(^{-1}\) for C=C stretching (aromatic), 1234.85 cm\(^{-1}\) for C-O-C stretching, 775.37 cm\(^{-1}\) for C-H deformation. For VE-SbO vibrational modes in a range of 3457.47 cm\(^{-1}\) links to hydrogen bonded O-H. The vibrational mode for C-H stretching aliphatic is at 2965.08 cm\(^{-1}\). The vibrational modes for carbonyl observe at 1716.79 cm\(^{-1}\) for C=O stretching, 1507.68 cm\(^{-1}\) for C=C stretching (aromatic), 1234.92 cm\(^{-1}\) for C-O-C stretching, 775.36 cm\(^{-1}\) for C-H deformation. Vibration pattern of all samples indicates the existence of O-H, C-H, C=O, C=C, and C-O-C which exhibit the ability to bind to other elements leading to the potential formation of a polymer blend and elongation increment value due to longer carbon chain.

![Figure 3. Comparison of FTIR result](image)

3.3 Core density measurement
The density of the core is determined by calculating the mass of the specimen and then calculate the volume of the specimen. The density test is according to ISO 845 standard. Density testing is performed to find out the density value of the core material to be used. The density shown in Figure 4 is collected from the average of five samples for each variation. This test result that by adding the vegetable oil can reduce the density compared to VE specimen. The density values of VE, VE-CO, and VE-SbO are 1.231 g cm\(^{-3}\), 1.002 g cm\(^{-3}\), 1.003 g cm\(^{-3}\), respectively. The decrease in density due to the density of VE is higher than the density of vegetable oil. The density of VE, VE-CO, and VE-SbO fulfil the LR standard.
3.4 Hardness measurement

In this section, Figure 5 shows the hardness of VE, VE-CO, VE-SbO, respectively. The test is carried out at five indentation points on each specimen, then the average value of the indented results is taken. It can be analyzed that VE has the highest hardness value reaching 67 Shore D, followed by VE-CO and VE-SbO of 63.7 Shore D and 63 Shore D, respectively. FTIR results show that there is a polar group (C=C) that has not been fully bonded. It means that mixing occurs mechanically and not chemically. The mechanical properties of the hardness decrease due to the absence of chemical bonds that occur between vinyl esters and vegetable oils. Although the hardness value of VE-CO and VE-SbO is smaller than VE, these values do not meet the minimum standard of hardness value for core sandwich material applications according to Lloyd’s Register. The composition of coconut oil and soybean oil less than 4% is recommended to be analyzed.
3.5 Result of tensile test
The tensile test is conducted to obtain the strength of the core material. Figure 6a shows the tensile test result for all variation of materials. VE-CO has the highest tensile strength compared with VE and VE-SbO gaining 30.206 MPa, followed by VE 28.894 MPa and VE-SbO 25.837 MPa. It shows that the addition of coconut oil into VE has a good effect in terms of tensile strength. Both tensile strength values between VE-CO and VE-SbO fulfil LR acceptance standard for core sandwich material applications. The addition of vegetable oil to vinyl ester bioresin decreases the tensile strength value due to unreacted bonds and molecules that are difficult to freeze and agglomeration.

![Graph showing tensile strength and elongation at break comparison for VE, VE-CO, and VE-SbO](image-url)

**Figure 6.** Comparison of: a) Tensile strength, b) Elongation at break of all variations
Figure 6b shows the comparison of elongation between VE, VE-CO and VE-SbO. They are 14.741%, 18.414%, and 19.027%, respectively. It indicates that the addition of vegetable oils could increase the elongation value of VE for core sandwich material applications. VE-SbO has the highest elongation values. The increase in the elongation value of vinyl ester bioresin is caused by the many long-chain structures of the polymer and the easy movement of molecules. Mixing vinyl ester with vegetable oil shows high elongation value and flexibility between the two ingredients, as mentioned in [16]. Both VE-CO and VE-SbO elongation values do not meet the minimum standards of elongation required by Lloyd’s Register because the values are slightly below the acceptance criteria. But another study [17] is slightly higher than the acceptance criteria. Furthermore, VE, VE-CO, and VE-SbO have the potential to be used in the marine environment, such as blade material for the vertical axis hydrokinetic turbine [18].

4. Conclusion
Development of core sandwich based on bioresin and vegetable oil is investigated by conducting several physical tests. The conclusion obtained from the tests carried out:

- Vibration pattern of all samples indicates the existence of O-H, C-H, C=O, C=C, and C-O-C that lead to the potential formation of a polymer blend and elongation increment.
- Hardness testing shows that the addition of vegetable oil decreases VE hardness and the results of VE-CO and VE-SbO hardness test values slightly below the LR criteria.
- Adding vegetable oil VE-CO increases the tensile strength value but decreases the tensile strength in VE-SbO. Both VE-CO and VE-SbO tensile strength meet LR criteria.
- From the density measurement, it can be illustrated that the addition of vegetable oil can reduce the apparent density of VE. The VE-CO and VE-SbO densities meet the LR standards given.
- The composition of vegetable oil with other vegetable oil type and composition need to be further analyzed.

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