Nanovoids in fracture surface of unsaturated polyester/vinyl ester blends resulting from disruption of the cross-linking of the polymer chain networks

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Abstract. A weakness of unsaturated polyester is brittle due to the cross-linking of the UP chain network. Improving the toughness may be carried out by blending with appropriate additives. This work aims to characterize the fracture surface of unsaturated polyester (UP)/vinyl ester (VE) blends with a ratio of 70% and 30% respectively. Addition of VE in UP increases the toughness of the blends resulting from disruption of the cross-linking of the UP chain network. The disrupted network was characterized by the FESEM morphology from fracture surface of the blend which exhibits three different regions i.e., the smooth zone corresponding to the slow crack growth rate (1); a transition zone, where the surface roughness steadily increases (2); a final failure zone with much rougher marks (3). The presence of more nanovoids in region 2 and 3 confirmed the bigger disruption of the crosslinking in UP networks increasing UP chain mobility and toughness of the blends. The nanovoids result in a dimpled appearance of the fracture surface and become points of high-stress concentration from which cracks can initiate. When subjected to a sudden load, many cracks can grow simultaneously forming beach marks where the cleavage from several cracks meets.

Keywords: nanovoids, fracture, polyester, crack, morphology

1. Introduction
Thermosetting like unsaturated polyester resin is widely used in automotive construction as coatings [1]. This polymer has advantages in term of high chemical and water resistance, high tensile strength, and low cost [2]. But, UP resin was brittle due to its rigid chain structure [3]. Therefore, this weakness limits the commercial applications of UP resin. A simple attempt has been conducted to enhance the toughness of this material by mixing it with VE resin [4][5]. The blending aims to destroy the crosslinking chain structure [6]. The disruption of this polyester chain network increased tensile strength and fracture strain [7]. However, there was no previous work presenting the disrupted chain structure which can be observed from the fracture surface morphology of the UP/VE blends. Thus, this work aims to characterize tensile properties of the UP resin mixed with VE resin and to relate the measured differences in the properties to the changes in polymer structures.
2. Materials and Method

2.1 Materials
Polyester resin (YUKALAC BQTN 157-EX type), vinyl ester resin (RIPOXY R-802 EX-1, methyl ethyl ketone peroxide (MEKEP) as a catalyst and methyl methacrylate (MM) were obtained from Justus Sakti Raya Inc, Indonesia.

2.2 Method
Preparation of UP and VE blends was similar as reported in our previous work [4]. The ratio of additives in UP resin was presented in Table 1. Homogenization of the mixture was conducted using a magnetic stirrer (Daihan MSH-20D) at 400 rpm and 25 °C for 10 min. The catalyst of MEKEP of 4 mL was mixed to the solution and stirred for a 5 min. This blend was then poured onto a die made from silicon material at 25 °C for 72 h. The die dimension for tensile testing was based on ASTM D638-14 standard (Type I) [8].

| Samples | VE (mL) | UP (mL) | MM (mL) |
|---------|---------|---------|---------|
| 1-UP    | -       | 100     |         |
| 1-VE    | 100     | -       |         |
| 0.9-UP/0.1-VE | 10   | 90      | 10      |
| 0.8-UP/0.2-VE | 20   | 80      | 10      |
| 0.7-UP/0.3-VE | 30   | 70      | 10      |
| 0.6-UP/0.4-VE | 40   | 60      | 10      |

2.3 Morphology investigation using field emission scanning electron microscopy (FESEM)
JIB 4610 FE-SEM model from JEOL was used for observation of the fracture surfaces from the tensile samples. An accelerating current of 5 kV and probe current of 8 mA was set up for this testing. All samples were coated with carbon and then followed by gold for two minutes using an argon plasma metallizer (sputter coater K575X) (Edwards Limited, Crawley, United Kingdom).

2.4 Tensile test
A Universal Testing Machine Gotech (GT-7001-LC-30) was used for tensile testing with a tensile test speed of 4 mm/min. All specimens before testing were stored in a closed chamber for 48 h under 50 ± 5% relative humidity (RH) at 25°C. Tensile tests were carried out five times for each sample.

3. Results and discussion

3.1 Fracture surface
The fracture surfaces of selected tensile samples were presented in Figure 1. Figure 1a and Figure 1b are smooth surfaces of UP and VE respectively. This smooth appearance corresponds to low toughness probably resulting from rigid cross-linked chain network. The fracture surface was perpendicular to the tensile stress direction resulting from a growing crack which cleaves the polymer structure along with the weakest atomic bonds [4]. This phenomenon is in agreement with the tensile testing curve (Figure 2) showing a lack of plastic deformation for both pure resin. After mixing with a blending ratio as shown in Table 1 the fracture surface of the UP/VE blend had a rougher appearance (Figure 1c, number 1 and 2). Some defect sections appeared on the surface (marked by the red arrow) probably as a result of the presence of VE polymer as a filler in UP chain network. This results in a disruption of the UP polymer chain structure causing a decrease in the number of linked chain networks which increase in the mobility of the polymer chains, consequently, improving the plastic deformation as presented in the stress-strain curve marked with a white arrow (Figure 2). For further loading, the mobility of free cross-linking chain became slower resulting from restriction of the available rigid cross-linked chain network. This phenomenon creates a nano-sized void in UP polymer chain structure. The void promotes an initial crack for a catastrophic fracture of this polymer and results in a rough fracture surface as shown in Figure 1d.
Figure 1. FESEM in a section of the fractured surface from the tensile sample.
3.2 Tensile properties
Figure 2 displays the tensile strength for each sample. Pure UP and VE stress-strain curves did not have plastic deformation. This agrees with a smooth fracture surface (Figure 1a and 1b). After blending with VE resin, the 0.7-UP/0.3-VE stress-strain curve shows an elastic and plastic deformation. This sample had tensile strength (64 MPa) and elongation at break (13.3%) are higher than those for pure VE or UP resin. This result indicates the toughness and ductility became higher. A similar phenomenon was also presented with increasing the TS of the polyester resin after blending with vinyl ester resin [7].

![Figure 2. Tensile properties of UP, VE resin and UP/VE blend](image)

4. Conclusion
This work reported the morphology of fracture surface from pure UP or VE, and the blend of both these resin materials. The blending UP and VE resin resulted in rougher fracture surface in comparison to the pure resin. The presence of VE disrupted the polyester chain structures causing an increase in mobility of UP chains. Consequently, the structural rigidity was reduced and increased in the toughness of UP resin. The area in the plastic deformation section presented the smooth surface. This is a result of slow tortuous crack growth through the zones with the lowest rigidity. The rapid rupture occurred resulting from the presence of nano-sized voids.

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