

# Methods Increased Fracture Toughness Thermosetting Polyester Mixture with Vinyl Ester for Raw Materials in Ship Bodies

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## Abstract

Unsaturated polyester is a polymer that is widely used as a basic matrix to form strong composites for engineering applications such as cars, ships, aircraft, and other field applications. The advantages of this material are that it has a fairly high tensile strength when reinforced with appropriate reinforcement, is light and easy to shape. However, the weakness of this polymer is that it is brittle and cannot withstand shock loads. To do that, it is necessary to overcome the nature of the weaknesses mentioned above. One of the materials chosen to strengthen polyester with vinyl ester is because these polymers have almost identical molecular bonds. A crack test was carried out on the addition of vinyl ester with a different composition process. To find out whether this vinyl ester can provide an increase in the crack strength of unsaturated polyester. The aim is to find out what percentage of the mixture has good crack resistance properties, with a good percentage of the mixture. To determine the fracture resistance value of the polymer mixture, a crack resistance test was carried out which would produce a large critical stress intensity factor based on ASTM D 5405 by varying the composition of the vinyl ester mixture from 0%, 10%, 20%, 30%, 40%, and 100%. From the test results, the greatest critical stress intensity factor occurred in a mixture with a composition of 40% vinyl ester is 1.752 MPa.m<sup>1/2</sup>. The critical-stress-intensity factor an increase from 0.392 MPa.m<sup>1/2</sup> to 1.752 MPa.m<sup>1/2</sup> (an increase of 447 %) than pure UP.

**Keywords:** Toughness; Polyester; Vinyl Ester; Blends; Tensile Stress.

## 1. Introduction

Unsaturated polyester is a thermoset resin that has been widely used in automotive components, aircraft, ship construction, and other engineering applications [1]. Cured unsaturated polyester resins (UP) are often highly brittle and do not have impact resistance. These resins can be reinforced for increased strength by providing reinforcement, are economical, and have good aging and water resistance [2]. This is because thermosets have a macromolecular covalent bond network structure with a tight and rigid cross-link density and are mutually bonded to each other, and it is very difficult for plastic deformation to occur at the localized crack tip, which can lead to catastrophic brittle failure [3]. Therefore, the greatest effort is the effort to absorb energy in the fracture tip area of the material so that additional plastic deformation occurs and prevents this material from moving to the brittle region [4]. Some of these drawbacks limit the use of unsaturated polyester resins applications. Many attempts have been made to increase the toughness of these polyether polymers, one of which is supplementing these materials with natural fibers, bonded chain barrier materials, and other bonding materials [5, 6, 7]. Another approach to increasing the toughness of polyester is to prevent the chemical chains from bumping into each other by mixing them with crosslinked polyether chain-structuring

chemicals [6, 8]. Much research has been done on mixing with vinyl esters to disrupt the cross-linking of polyester chains due to the similarity of these two thermoset chain structures [9]. As per the results of previous studies, the addition of 40% vinyl ester resin to polyester resin resulted in an increase in tensile strength of 63.6% and an elongation of 85.7% [10, 11]. Although many studies have been carried out on the effects of mixing vinyl ester (VE) on polyesters in increasing the toughness of polyester, there is almost no information about the binding of vinyl ester polymers modifying the binding of cross-linked polyester chain structures. Several previous studies have not reported much on this material to study the cracks in the material, and this information has not been published. For this reason, several studies will be carried out at this step, including the ability of the material to resist crack loads [12, 13].

The ability of a material that has initial defects to accept external loads that have a crack propagation effect is known as fracture toughness and is characterized by a critical stress intensity factor. The factor occurs depending on various factors, such as the characteristics and direction of loading, the type of material, the dimensions of the specimen, and the direction and length of the initial crack [14]. However, the hypothesis about the mech-

anism of fracture toughness in thermoset polyester reinforced by a mixture of vinyl ester and the addition of MMA is still not known with certainty [15].

## 2. Materials and Method

The hypothesis developed is that the strength of the material that occurs is very dependent on the percentage composition of the mixture of polyether and vinyl ester. This is an important object of this research.

### 2.1. Material

Un-saturated polyester is a polymer that is commonly used as a basic material in the manufacture of composite matrix materials because this material is widely used in engineering. Here are some properties of un-saturated polyester: With the product, Yukalac 1560 BL-EX [13, 20] by P.T. Justus Kimia, SG= 1.1 g/cm<sup>3</sup> at 25°C and  $\mu$  y 4.5-5.0 poise at 24 °C), vinyl ester (RYP-OXY R-802 EX-1, S G= 1.05 g/cm<sup>3</sup> at 24 oC), *methyl methacrylate*(MMA), and methyl ethyl ketone peroxide as a catalyst [16].

### 2.2. Preparation and y Measurement

Unsaturated polyesters (UP), vinyl esters (VE), and methyl methacrylate (MA) are materials used to manufacture tough materials with the compositions shown in Table 1. Then, to homogenize the above ingredients into the right composition, a magnetic stirrer (Daihan MSH-20D) is used for 10 min at 400 rpm and about 24 oC [17]. The next step is curing at room temperature from 0 to 240 min [20]. The die was made to the ASTM D 5045 standard, with dimensions of 53 mm (length) x 48 mm (thickness) x 12 mm (width), and it was notched for crack toughness [18, 20].

### 2.3. Mechanical Characterization

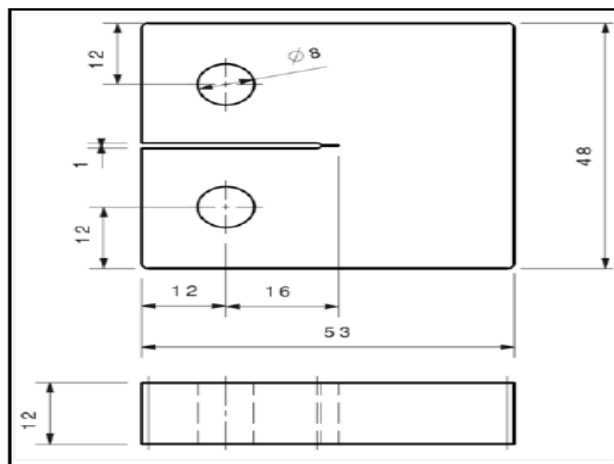
The casting sample is examined with the fracture toughness test using a universal testing machine. COM-TEN [21]. Testing of specimens with geometry considering the exact dimensions based on predetermined standards to provide good crack propagation is illustrated in Figure 1. The crack length-to-width ratio ( $A/W$ ) is limited to 0.5 and has a loading rate of 5 mm/min. The critical stress intensity factor ( $K_{Ic}$ ) is calculated from several test samples according to the formula from equation (2), and the average is taken:

$$K_{Ic} = \frac{P_{Q1}}{Bw^2} \cdot f\left(\frac{a}{w}\right) \quad (1)$$

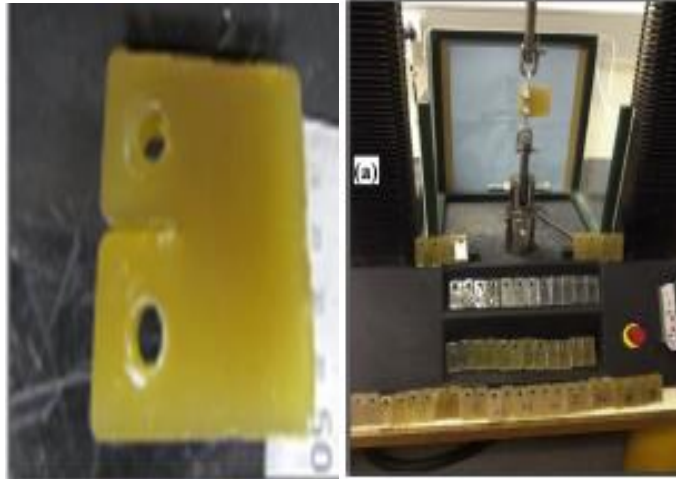
$$f\left(\frac{a}{w}\right) = \frac{\left(2 + \frac{a}{w}\right) \left\{ 0.886 + 4.64 \left(\frac{a}{w}\right) - 13.32 \left(\frac{a}{w}\right)^2 + 14.72 \left(\frac{a}{w}\right)^3 - 5.6 \left(\frac{a}{w}\right)^4 \right\}}{\left(1 - \frac{a}{w}\right)^{3/2}} \quad (2)$$

Where is the maximum load determined from the load-displacement curve, B is the specimen thickness. After checking the conditional result  $K_{Ic}$  against the size criteria following Eq (1). The

calculated fracture toughness ( $K_{Ic}$ ) is valid since the quantity of  $2.5 \left(\frac{K_{Ic}}{\sigma_y}\right)^2 <$  of specimen thickness (B), the crack length (a), and the ligament ( $w - a$ ).



**Figure 1:** Dimensions of the specimen configuration as used for determining fracture toughness



**Figure 2:** Universal testing machine Autograph Machine Merk COM-TEN 95T Series 5K to crack testing

**Table 1: Curing Characteristic Of Up/ve Blend At Room Temperatur**

Material No.	UP (wt %)	VE (wt %))	MMA (wt %)	MEKP (wt %)
1	100	0	10	4
2	70	30	10	4
3	30	70	10	4
4	0	100	10	4

### 3. Results and Discussion

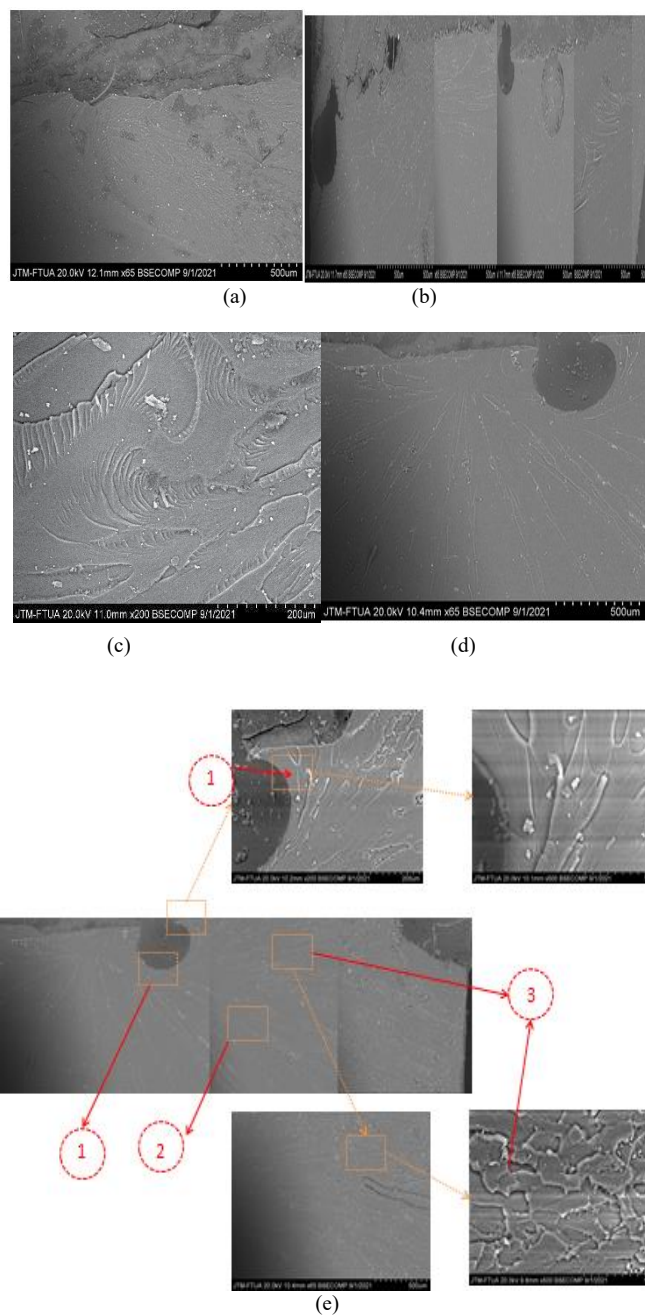
The following sections, the results of the research, data analysis and conclusions will be explained.

#### 3.1. Mechanical Properties of Polymer Blend

The fracture surface of the sample was observed under a FE-SEM model electron microscope from JEOL with an accelerating current of 5 kV and a probe current of 8 mA [25, 8]. The fracture surface of a pure unsaturated polyester fracture sample is shown in Figure 3(a), which has a smooth surface due to its low toughness. Figure 3(b) depicts the fracture surface of pure vinyl ester fracture samples, which has a slightly rougher surface than pure polyester but is still classified as a low toughness polymer. [26].

The addition of VE and MMA to unsaturated polyester resulted in a rougher, cracked surface. Figure 3(c) depicts the characterization of the crack surface for the addition of 30% vinyl ester to polyester (UP/VE 30%), with a rough crack surface forming, indicating that good plastic deformation with the meaning of the word has occurred. In this area, the brittle nature of polyester unsaturation can be reduced, resulting in plastic deformation. The addition of VE and MMA to unsaturated polyester result-

ed in a rougher, cracked surface. Figure 3(d-e) depicts the fracture surface characterization for the addition of 70% vinyl ester to polyester (UP/VE 70%), with three distinct fracture surface forms. This unscratched fracture surface shows the fracture surface area with slow fracture growth. The fracture surface characterization is shown in Figure 3(d-e) at a 70% UP/VE rate. area (1); crack surface area with a smooth cracked surface with only a small number of cracked surfaces. Region (2) is the transitional crack surface area where the rough cracked surface begins to form a region (3). The very rough crack surface has a rougher appearance due to the rapid growth of the radial cracks due to the formation of circular nano voids (red arrows) and produces different roughness lines [27, 9]. In contrast, the smooth fracture surface in the fault groove (1) results from the slow crack growth and tortuous along the fault groove, with the lowest plastic regions in the crosslinked polymer chain structure being slightly disturbed. Regions (1) and (2) reflect the characteristic appearance of transitional plastic deformation. The rougher the crack surface, the higher the plastic deformation with characteristic coastal markings as shown in Figure 3d, location (3). With the addition of failure energy, the crack growth rate increases until the collapse ends [20, 22].



**Figure 3:** SEM tensile fracture surface of (a) UP 100%, (b) VE 100% (C-e) UP/VE at 40 wt. %

### 3.2. Mechanical properties

Table 2 and Figure 4 show the magnitude of the force applied by the machine to give the fracture failure samples for pure UP, pure VE, and UP/VE polymer mixtures, respectively.

In terms of testing, the crack specimens showed unstable crack propagation under conditions of continuous loading, while the load decreased to zero after reaching the maximum, which indicates that the elastic limit of the material has reached the level of brittleness. It also implies that most of the energy is consumed in the crack initiation stage, while less energy is lost in the fast crack propagation stage. After a tensile load is applied, the unsaturated polyester is reinforced with (30 wt. %). VE undergoes further elongation (displacement) compared to pure UP. This is attributed to cracks initiated at deflected loads due to interfacial adhesion with bonded VE and UP polymers. As the cracking in-

creases, the load continues to increase, as shown in Figure 4. For specimens with up to 70 wt. %, When VE is added to the UP mixture, the VE composition is well dispersed in the UP matrix at the fracture tip location and can reduce the local stress concentration, allowing the mixture to be mixed. It enables the polymer to withstand greater loads and produce more fractures [4, 14].

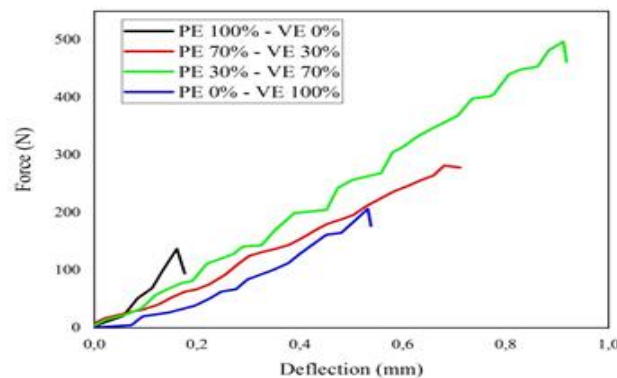
Figs. 5 and 6 show the comparison of peak energy absorption of different specimens for cracking load is presented in Table 2. Representative loads against time curves recorded for samples affected at different energy levels are shown in Figure 4. Load time curves for all laminated polymers are linear up to the point of initiation damage, then reach peak load. Following the initiation of damage, the load drops suddenly, indicating a decrease in the stiffness of the material as the polymer matrix fails. The peak

load represents the maximum load that a crack test specimen can withstand before undergoing major failure. The peak load taken by the post-impact sample for the three energy levels, 0.25, 0.63, 0.89, and 0.77 N.mm, showed a considerable reduction (Fig. 5). This drastic reduction in the peak load for the post-crack test specimen is associated with polymer failure as a result of loss of stiffness due to the effects of the post-acting load that caused the crack. Energy absorption is an important factor that is commonly used to assess the ability of polymers to withstand cracking forces. The effect of the crack test response on the absorption magnitude for various percentage crack resistance crack resis-

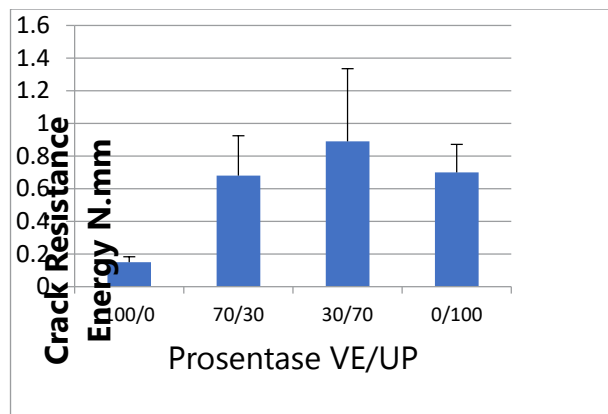
tance energy levels is shown in Figure 6. The corresponding energy plot of the experimental results obtained shows a strong influence on the post-crack resistance of the material, as indicated by the amount of energy absorbed by the specimen when subjected to a cracking load. It can be observed from the same figure that the absorbed energy increases the level to 27% for the 30% VE mixture and 38% for the 40% VE mixture and has the lowest 17% for the pure UV and 18 VE for pure VE. Energy is absorbed compared to all other sample categories. This is due to the lower sample impact resistance caused by matrix cracking at higher incident energy levels [20, 23, and 24].

**Table 2: Load Crack To Fracture Speciment Of Up/Ve Blend**

Percentage UPE - VE (%)	Speciment	Force (kN)	Average(kN)	Standart Deviation
100 – 0	1	0.1370	0.226	0.077
	2	0.2700		
	3	0.2700		
70 – 30	1	0.2820	0.362	0.164
	2	0.2500		
	3	0.5480		
30 – 70	1	0.5210	0.499	0.021
	2	0.4810		
	3	0.4970		
0 – 100	1	0.1780	0.256	0.092
	2	0.2070		
	3	0.3490		



**Figure 4: The tensile fracture of UP/VE blends**



**Figure 5: Crack Resistance Energy of UP/VE blends**

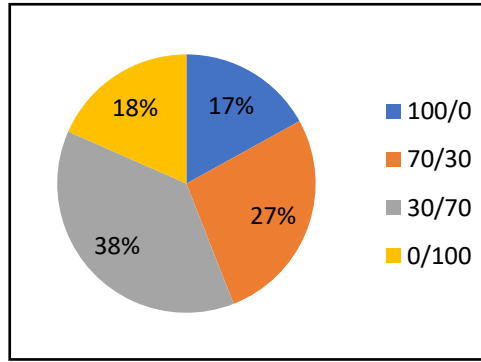


Figure 6: Percentage ratio of Crack Resistance Energy Of UP/VE blends

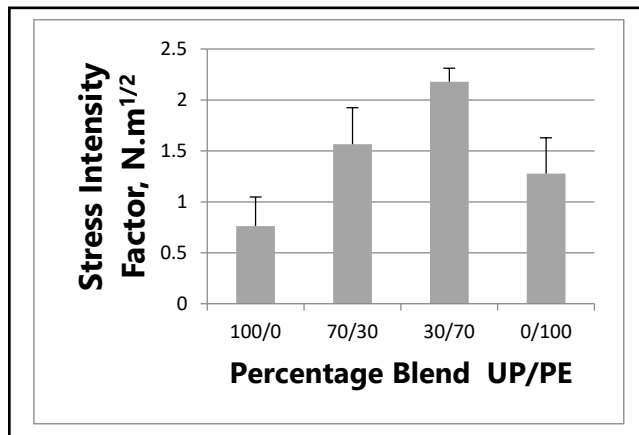


Figure 7: Stress Intensity Factor of UP/VE blends

### 3.3. Stress Intensity Factor

The stress intensity factor ( $K_{Ic}$ ) of the polymer mixture molded sample was tested against the crack load using a crack testing machine (CT). As shown in Figure 1, CT specimens were fabricated according to the dimensions of the crack test standard with ASTM D5045. The speed of movement for applying a force to the sample is 5 mm/min, and the following relationship is used to measure the Figure 5 shows the load-crack curves obtained from the crack testing results of the CT crack testing machine for various percentages of polyester blends. All samples experienced different crack propagations depending on the percentage of the mixture. Before the maximum load, the curve tends to form a straight line as illustrated in Figure 9. The magnitude of  $K_{Ic}$  of unsaturated polyester

mixed with vinyl ester and mixed slightly will increase the value of the stress intensity factor. At the time of adding 40% vinyl ester, it appeared as the highest  $K_{Ic} = 1.667 \text{ N.mm}^{1/2}$ , with an increase of 447% compared to pure unsaturated polyester  $K_{Ic} = 0.772 \text{ N.mm}^{1/2}$  [3]. The vinyl ester addition by up to 40% increases the upper  $K_{Ic}$  value due to the emergence of a tough polymer by the successful interaction of the tough vinyl ester and rigid polyester polymer. These results are similar to those reported in a previous study [18]. The comparison of  $K_{Ic}$  values for VE based on pure unsaturated polyester is much different from polyester that has been mixed with vinyl ester. The effect of combining these two polymers can increase the fracture toughness of pure polyester [10, 28].

Table 3: Stress Intensity Factor Of Up/Ve Blend At Room Temperature

Percentage UP - VE (%)	Speciment	$K_{Ic}$ (MPa.m <sup>1/2</sup> )	Average	Standart deviation
100 – 0	1	0.434	0.762	0.285
	2	0.949		
	3	0.904		
70 – 30	1	1.383	1.566	0.584
	2	1.095		
	3	2.220		
30 – 70	1	2.045	2.179	0.133

	2	2.311		
	3	2.182		
0 – 100	1	0.969	1.277	0.527
	2	0.977		
	3	1.885		

#### 4. Conclusion

This study reports the success of determining the right composition of a polymer mixture made from unsaturated polyester by adding vinyl ester to improve the brittleness of the polyester into a tough material. With this research, engineering in the field of engineering, especially in the field of raw materials for vehicle components, is greatly helped. The unsaturated polyester blend with 40% vinyl ester and 10% MMA has the highest stress intensity factor for critical stress. Which in its application is very capable of resisting good crack strength. This research resulted in an increase in stress the treatment of adding a mixture of vinyl esters to the base material of pure unsaturated polyester increased  $K_{Ic} = 1.667 \text{ N.mm}^{1/2}$  to  $K_{Ic} = 1.667 \text{ N.mm}^{1/2}$ . Adding vinyl esters and MMA to unsaturated polyesters results in an increase in the crack resistance of unsaturated polyesters due to the disruption of the UP chain linkage knots, leading to a decrease in structural rigidity and an increase in the area of plastic deformation. The mode I fracture toughness of the crack test samples at room temperature was characterized according to ASTM D5045, and the fracture surfaces were identified by SEM analysis. Incorporation of MMA up to 40% by weight into unsaturated polyester resins showed the highest stress intensity factor.

#### Nomenclature

An	initial crack length mm
B	specimen thickness mm
$K_{Ic}$	Stress intensity factor critical Mpa.
$P_0$	Load maximum displacement curve Newton
SG	Specific graph gram/cm <sup>3</sup>
W	width specimen minus initial crack length mm
Wt %	ratio mixed volume to volume neat UP %

#### Greek letters

$\sigma_y$ , Tensile stress in load crack direction N/mm<sup>2</sup>

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