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UNSATURATED POLYESTER FRACTURE TOUGHNESS MECHANISM WITH BLENDING TO VINYL ESTER AND MMA

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ABSTRACT

In this research, a method was used to increase the brittleness of unsaturated polyester polymer by mixing it with vinyl ester. The choice of vinyl ester to increase the toughness of this polyester is because it is easy to form and this material has wide applications in engineering. However, this polyester has several weaknesses, namely, it is very stiff, brittle, and unable to withstand cracking loads and breaks easily due to impact. Polyester has a rigid nature because this material has cross-chain links of material that are tightly locked and interconnected with each other. With the addition of this vinyl ester, this tightly connected rigid chain is disrupted by the vinyl ester chain, thereby increasing the toughness of the polyester. Steps were taken to increase the crack resistance of unsaturated polyesters with the addition of vinyl esters, starting with the percentages of 10%, 20%, 30%, and 40% and comparing them with pure polyester. The results obtained showed that the crack resistance of polyester increased with the addition of 40% wt vinyl ester. The results show that the highest fracture toughness value is indicated by the value of the stress intensity factor of K_{1c}=1.752 MPa.m$^{0.5}$.

Keywords: fracture toughness, load tension, stress intensity factor.

NOMENCLATUR

a   initial crack length mm
B   specimen thickness of mm
K_{1c} stress intensity factor critical Mpa.$\sqrt{m}$)
P_Q load maximum displacement curve Newton
w   with specimen minus initial crack length mm
wt%   ratio mixed volume to volume neat UP %

Greek Letters
σ_{yy} Tensile stress in load crack direction N/mm^2

INTRODUCTION

Unsaturated polyester is a thermoset resin that has been widely used in automotive components, aircraft, ship construction, and other engineering applications [1]. Unsaturated polyester is a thermoset resin that has been widely used in automotive components, aircraft, ship construction, and other engineering applications This is because thermosets have a macromolecular covalent bond network structure with a dense and rigid cross-link density and are bonded to each other, and it is very difficult for plastic deformation to occur at the localized crack tip, which can lead to brittle catastrophe failure [3].To reduce the brittle nature of polyester is to take the largest energy addition step, namely by absorbing energy at the crack tip area of the material, resulting in additional plastic deformation and preventing the material from moving to the brittle region [4]. Several drawbacks limit the use of unsaturated polyester polymers in applications. Many efforts have been made to increase the toughness of these polyester polymers, one of which is to strengthen the material with natural fibers, adjacent molecular chain bonding agents, and other bonding agents [5][6][7]. Another approach to increasing the toughness of polyester is to prevent chemical chains from bonding with each other by mixing chemicals that are capable of bonding their molecular chains to the polyester molecular chains, thus preventing the polyester chains from being crosslinked with the polyester chains themselves[6][8].

Many studies have been carried out on mixing polyester with vinyl esters to disrupt the cross-linking of the polyester chains due to the similarity of these two thermoset chain structures[9]. According to 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]. In previous studies there has been no information reported about the crack resistance binding of this polyester polymer to the addition of vinyl esters and how this material retak polimer polyester ini api modifying the polyester chain reinforcement so that not all cross-links occur. Several previous studies have not reported much on the crack resistance of polyester polymer materials mixed with polyester, and not much information has been published. For this reason, several studies will be carried out at this stage, including the ability of the material to withstand crack loads by mixing polyester and vinyl ester [12][13].
The ability of a material having an initial defect to accept external loads that have a crack propagation effect is known as fracture toughness and is characterized by a critical stress intensity factor (K_{IC}). The ability of a

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material having an initial defect to accept external loads that have a crack propagation effect is known as fracture toughness and is characterized by a critical stress intensity factor [14]. However, the hypothesis about the mechanism of fracture toughness in thermo set polyester reinforced with a vinyl ester mixture and the addition of MMA is still not known with certainty [15].

MATERIAL AND METHODS

Material
The hypothesis developed is that the toughness of the polymer to crack propagation caused by the load acting on the polymer is very dependent on the percentage of the composition of the polyester and vinyl ester mixture added. This is an important review of this research. Unsaturated 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, especially in vehicle components, tourist boat bodies, and light aircraft wings. The following are some of the chemical and physical properties of unsaturated polyesters with the product Yukalac1560 BL-EX [16].

Preparations and Measurement
Polyester, vinyl ester, and MMA resin were mixed and stirred with the composition as shown in Table-1. A comparison of each material was carried out according to previous studies [2] [8]. To be more perfect, each mixture was homogenized so that the composition was uniform using a magnetic stirrer for 10 minutes at a speed of 400 rpm and an ambient temperature of 25°C. The accuracy of each mixture's viscosity was measured, then 4% MEKP was added to the mold, and the mixture was cast into a glass-based mold for approximately 3 days at room temperature. The dimensions of the die are made according to the ASTM D 5045 standard, namely the width, length, and thickness are 53 mm x 48 mm x 12 mm, and are grooved for fracture toughness [14] [18] [20]. The treatment of mixing vinyl esters into unsaturated polyesters was carried out with the following percentage compositions: 10, 20, 30, and 40% by weight by the physical-mechanical mixing method with an aqueous solution of crosslinking breaker.
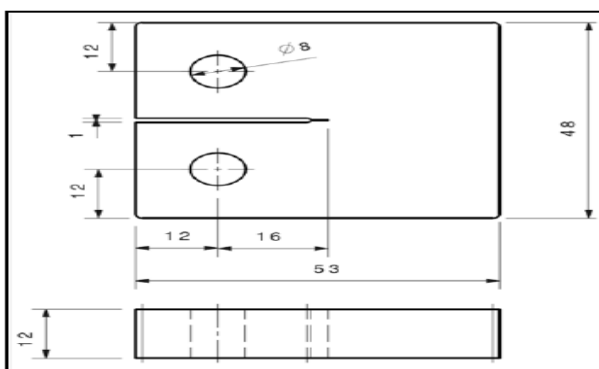
Figure-1. Dimensions of crack specimens according to ASTM D 5405 standard.

Mechanical Characterisation of Polymer
Crack testing is carried out using a crack testing machine by providing vertical tensile loads up and down simultaneously with the COM-TEN brand universal machine [2][15]. The geometry of the crack test specimen tests the fracture toughness due to the stretching of the material more accurately because it provides more room for crack propagation, as 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 (KIc) is calculated from at least five samples according to the following formula:

$$K_{1c} = \frac{P_Q}{Bw^{\frac{1}{2}}} \cdot f\left(\frac{a}{W}\right) \tag{1}$$

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

Where K_{1c}, P_Q this is the maximum load obtained from the curve read on the crack test machine display graph and B is the thickness of the specimen. Value of K_{1c} According to the dimensions given from the image of the crack test specimen and calculated by equation (1). Calculation of crack resistance for (K_{1c}) must meet the following values; $2.5(\frac{K_{1c}}{\sigma_y})^2 <$specimen thickness (B), Crack length (a), and the whole part (w − a).

(a) Crack Testing machine (CNT). (b) Molded specimen

Figure-2. Universal testing machine to crack testing.

RESULT AND DISCUSIONS
The research results, data analysis, and conclusions will be explained in the following the research results, data analysis, and conclusions will be explained in the following sections.

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Mechanical Properties of Polyester Blend

The main work in this research is to produce a good mix of vinyl ester and polyester UP/VE, and freezing the material at room temperature according to the composition of the mixture is shown in Table-1. The mixture of UP and VE was molded and dried for 3 days to produce a transparent, solid, hard, rigid material as shown in Figure-1 of the cured mixture [4][16]. The drying time increases with the increase in the vinyl ester composition in the mixture. This indicates that VE requires a longer drying time.

Table-1. Composition of UP/VE blend.

Material No.	Polyester (wt %)	Vinyl ester (wt %))	MMA (wt %)	MEKP (wt %)
1	100	0	10	4
2	90	10	10	4
3	80	20	10	4
4	70	30	10	4
5	60	40	10	4
6	0	100	10	4

The graphic pattern generated by the FTIR curve pattern can be used to determine whether the level of homogeneity of the vinyl ester mixture in unsaturated polyester can be mixed properly, indicated by the shift of the peak of the infrared wave transmittance curve from the pack [13][18]. The functional groups of each sample can be observed on the FTIR graph shown in Figure 3. The neat vinyl ester curve shows a maximum of the OH group curve at 3400-3389 cm-1, and this peak is different from the neat polyether, which peaks at 2567-2918 cm^{-1}. However, after adding 30% VE to the UP, a corresponding peak did not appear, possibly indicating an inhomogeneous dispersion of VE in the UP during sample preparation [19] [17]. As Figure-3 shows, pure vinyl ester displays OH chain peaks at 3400-3392 cm-1, and this peak is different from pure polyester, showing a decrease in the value of OH peaks and CH functional groups. See Figure-3. These results indicate that the addition of MMA allows VE to be evenly distributed throughout the UP [19][20].
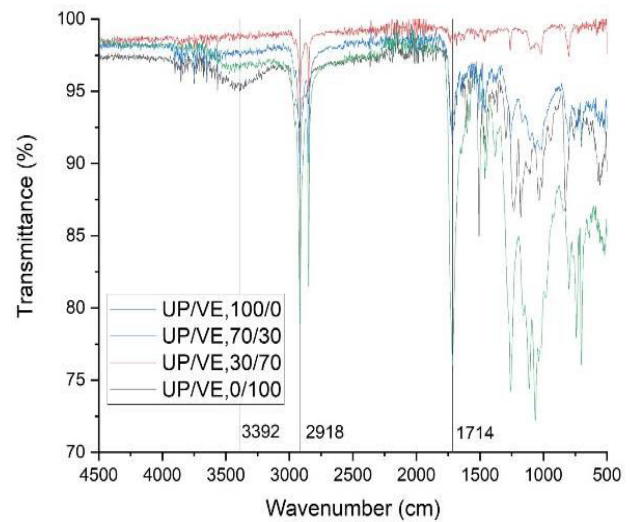

Figure-3. FTIR curves for samples mixed polymer.

Morphology Characterization

The deformation of the fracture surface of the crack test sample was identified with 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 [2][21]. Figure-4 shows the cracked surface of the crack test sample by moving the load-driving machine charge in a vertical direction. The pure UP fracture surfaces in Figure-4 (a) and pure VE fracture surfaces in Figure-4 (b) have smooth fracture surfaces that correspond to fracture surfaces with low plastic deformation. The appearance of this smooth fracture surface is due to the breaking of the cross-linked rigid chain network in front of the fracture surface leading to the fracture surface perpendicular to the direction of the load causing the crack. [22]. The growing cracks propagate and continue to cleave the polymer structure together with the weakest atomic bonds. The addition of 4% MMA and 30% VE to the UP results in a rougher fracture surface due to the mixture's large plastic deformation, as shown in Figure4(c).This picture shows that polyester, which has been mixed with 30% VE, has undergone a very large deformation because the material has experienced good crack resistance, as evidenced by the shape of the surface.

Figure-4 (d) illustrates the results of a representative TEM micrograph of the UP/VE. The figure shows a fairly rough surface characterization of these cracks, indicating that considerable plastic deformation has occurred for the polymer by adding 40% VE to the UP, [2][23][4].

(a)

(b)

(c)

(d)
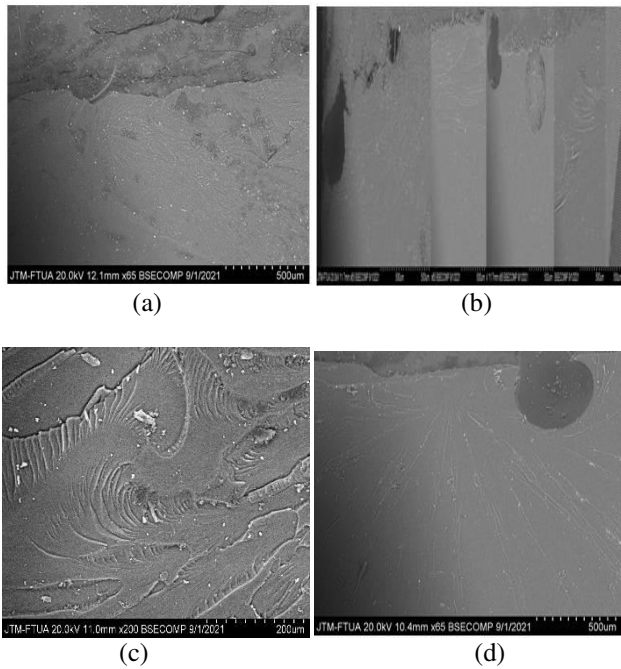
Figure-4. SEM tensile fracture surface of (a) UP 100%, (b)VE 100%   (c) UP/VE at 30 wt.%.(d) UP/VE at 40 wt.%.

## Fracture Toughness Properties

The stress intensity factor (K1c) of the molded polymer mixture samples was tested against the crack load using a crack testing machine (CT). As shown in Figure-1, specimen CT dibuat sesuai dengan dimensi standar uji retak sesuai dengan ASTM D5045. The speed of movement of the force on the sample is 5 mm/min, and the magnitude of the load on the deformation that occurs is shown in Figure 5. The curve shown in the figure shows that the load-crack curve obtained from the crack test results for various percentages of vinyl ester mixtures on polyester polymers have been described in the figure above. All samples experienced different crack propagation depending on the percentage of the mixture. Before the maximum load, the curve tends to form a straight line, as illustrated in Figure-5 above[24][25][12]. Table-2 shows the results of the mechanical properties of the UP/VE mixture. The figure shows that pure polyester produces a fairly high tensile strength but little deformation is formed, which is in accordance with the polyester chemical structure network, which is cross-linked with each other so that it has little movement and is very stiff. The addition of a vinyl ester composition to polyester increases the tensile strength of the UP/VE mixture up to 40% by weight of VE and the occurrence of plastic deformation in the mixture according to the amount of vinyl ester added. The increase in tensile stress is caused by the improvement of the cross-chain structure, which is rigidly bound to be slightly disturbed and causes movement of the polyester. At very high VE compositions, the tensile stress of the UP/VE mixture decreases due to the excess amount of vinyl ester in the mixture, and not all the molecular chains of the mixture

are bounded[27-31]. Figure-6 shows the amount of strain that occurs when the test sample experiences total breaking strain at the breakpoint for each percentage of each UP/VE mixture. The addition of the vinyl ester composition increased the breaking strain of UP/VE, reaching the highest value in the VE composition (40 wt.%.). The increase in elongation at break is due to the long-chain chemical structure of the polymer and the easier movement of the molecular. [26][27]. The UP/VE polymer mixture showed that the addition of vinyl ester function resulted in elongation at break which tends to increase, and the vinyl ester composition increased the hardness value of the UP/VE mixture up to 40 wt. % VE composition. n the VE composition, after passing 40 wt.%, the hardness of UP/VE decreases due to unreacted molecules [28].
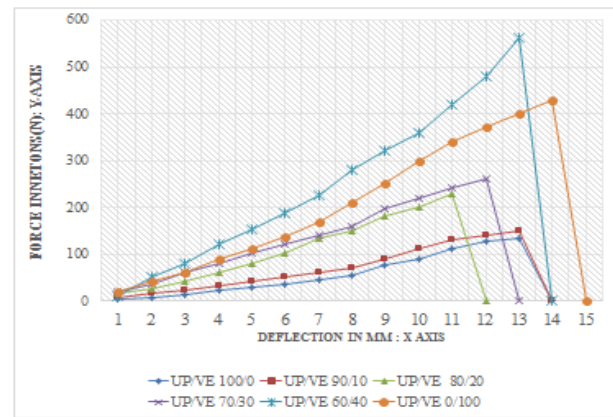
Figure-5. The typical loads versus crack opening displacement (COD) curves.
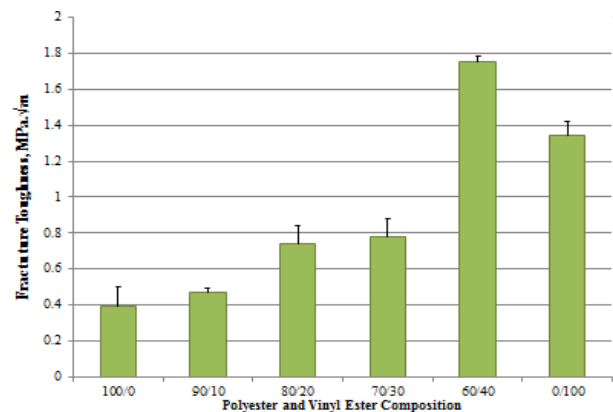
Figure-6. Fracture toughness of UP/VE blends.

Stress Intensity Factor

The stress intensity factor (K_{1C}) of the mixed polymer VE and MMA on the printed polyester (UP) polymer was evaluated using a compact stress (CT) configuration. The CT specimen was prepared according to ASTM D5045, as shown in Figure-1. The loading rate was adjusted at a rate of 5 mm/min based on previous studies, and the following relationship was used to calculateK_{1c}. Figure-5 shows a set of fracture load versus

displacement curves obtained from a crack testing machine of a mixture of VE and MMA materials against an UP-based polymer material. For samples with pure polyester, the cracks form like a straight line. This pure UP coating is brittle. All samples that were composed of a mixture consisting of a mixture of polyester and vinyl ester cracked differently from those of pure polyester. The crack test results showed that the crack propagation did not form a straight line but formed a jagged or unstable line when the maximum loading was reached. The addition of 40% and 10% MMA to the weight percentage of the mixture to the UP polymer resulted in the highest applied load on the crack resistance of the mixed polymer. The crack resistance of the K_{IC} to VE mixture (10-40% weight) is shown in Figure. The K_{IC} value of polyester can be increased with the addition of VE and MMA. This is because these two materials affect the molecular composition of pure polyester. The addition of 40% VE and 10% MMA to the process weight of the material appears to be the highest price for K_{IC}, with a value of 1.752 MPa.m$^{0.5}$ to improve the crack toughness of pure polyester [30-33]. Increasing the addition of VE up to 40% by weight of the material increases the K_{IC} value to the highest value. The addition of a vinyl ester mixture to the above composition will reduce the K_{IC} price due to the appearance of a soft polymer and weak interactions in the molecular bond matrix of the vinyl ester and polyester. These results are similar to those reported in previous studies [18]. The comparison of K_{IC} values for VE based on different pure UP can be seen in Table 2. [2][30].

Table-2. Values for crack toughness of UP/VE mixtures cast at room temperature.

No	Material	Fracture toughness MPa.m$^{0.5}$	
1	UP/VE,100/0	0.392 $\pm$	0.036
2	Polyester/Vinyl Ester,90/10	0.473 $\pm$	0.008
3	Polyester/Vinyl Ester,80/20	0.744 $\pm$	0.0327
4	Polyester/Vinyl Ester,70/30	0.778 $\pm$	0.033
5	Polyester/Vinyl Ester,60/40	1.752 $\pm$	0.011
6	Polyester/Vinyl Ester,0/100	1.342 $\pm$	0.027

CONCLUSIONS

This research reports the success of determining the exact composition of a polymer mixture made from an unsaturated polyester matrix by adding vinyl ester and MMA to increase the brittleness of the unsaturated polyester polymer into a tough This research reports the success of determining the exact composition of a polymer mixture made from an unsaturated polyester matrix by adding vinyl ester and MMA to increase the brittleness of the unsaturated polyester polymer to become a crack-resistant material. With this research, engineering in the field of engineering, especially in the fields of vehicle component raw materials, tourist boat bodies and fishing boats, is very helpful. This blend of unsaturated polyester with 40% vinyl ester and 10% MMA has the highest critical stress intensity factor. With the highest performance, this material is able to withstand good crack strength, so it is good and useful for engineering applications. This research resulted in an increase in the toughness and crack resistance of pure polyester material by treatment with the addition of a mixture of vinyl ester and MMA to the base material of pure unsaturated polyester. The increase in fracture toughness of K_{IC} from 0.392 MPa.m$^{0.5}$ for pure polyester increased to $K_{IC} = 1.752$ MPa.m$^{0.5}$ with the addition of a mixture of 40% vinyl ester and 10% MMA by weight of the mixed polymer processes. This achievement shows the highest fracture toughness value for the right mix.

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