1. Introduction

Unsaturated polyester is a widely used thermosetting resin. Unsaturated polyester has a reactive vinyl (carbon-carbon double) bond. Styrene is added to unsaturated polyester as a solvent and acrylating agent for curing reaction. The organic peroxide is used to initiate the reaction. Organic salt is added to accelerate the reaction. The polymer is achieved as a result of random condensation copolymerization reaction between styrene and unsaturated vinyl double bonds by free radical mechanisms forming crosslinked network structure [1,2]. Unsaturated polyester is a resin (prepolymer) with low price, light weight, easy processing and water resistance. Unsaturated polyester commonly used in laminating resin, composites, coating, adhesive, microelectronic, aerospace, building, automotive, and shipbuilding. However, unsaturated polyester shows limited mechanical and thermal properties. It is necessary to enhance the properties of unsaturated polyester. The properties of unsaturated polyester have been enhanced by the addition of carbon fiber, fly ash, carbon nanotube, and polyamide [3-6].

Vinyl ester is an attractive high-performance thermoset polymer. Vinyl ester has reactive double bonds with rigid epoxy structure. Vinyl ester is synthesized by the reaction of epoxy with methacrylic...
acid. Styrene is added as a copolymer agent (crosslinker)diluent for the polymerization reaction. Styrene has a low price and high reactivity [2,7]. Vinyl ester has a high mechanical, thermal properties and easy processing. Vinyl ester commonly used in industrial applications such as laminating resin, composites, coating and adhesive. Vinyl ester has a potential for enhancing mechanical and thermal properties of unsaturated polyester [8,9].

This study evaluates the addition of vinyl ester (VE) into unsaturated polyester (UP) containing aromatic benzene ring forming thermoset polymer blend. The mechanical and thermal properties of the polymer blends are investigated. The unsaturated polyester/vinyl ester blends were prepared by mechanical blending method and cured at room temperature. The aim of this study is enhancing unsaturated polyester properties by blending with vinyl ester resin by keeping the advantages of both the resin such as easy to use and fast in processing (cured at room temperature). The polymer blend of unsaturated polyester/vinyl ester is cured using methyl ethyl ketone peroxide (MEKP) as a catalyst initiator reaction at room temperature without catalyst accelerator.

2. Experimental Methodology

2.1. Materials

YUKALAC BQTN 157-EX unsaturated polyester (UP) resin and RIPOXY R-802 EX-1 vinyl ester (VE) resin were obtained from Justus Sakti Raya Inc, Indonesia. The UP has specific gravity 1.1 g/cm³ at 25 °C and viscosity 4.5-5.0 poise at 25 °C. The VE has specific gravity 1.05 g/cm³ at 25 °C, acid value 7-13 KOH mg/g, viscosity 2-6 poise at 25 °C and styrene composition 46%. Methyl ethyl ketone peroxide (MEKP) was obtained from Kawaguchi Kimia Inc, Indonesia, as an initiator.

2.2. Preparation of the unsaturated polyester/vinyl ester blends

The thermoset blends were achieved by adding vinyl ester (VE) into unsaturated polyester (UP) at 10, 20, 30, 40, 50, and 80 wt.% by physical mechanical blending method with styrene as crosslinker diluent. Methyl ethyl ketone peroxide (MEKP) is added as a catalyst initiator at 4 wt.% without catalyst accelerator. Unsaturated polyester, vinyl ester, and MEKP were blended by mechanical mixer stirring at room temperature for 5 min affording a transparent colorless solution. The mixture was poured into an aluminum mold and cured at room temperature for 30 min until 240 min by increasing vinyl ester composition to achieve cured yellowish transparent solid hard materials.

2.3. Characterization of the unsaturated polyester/vinyl ester blends

The unsaturated polyester/vinyl ester blends were examined. Fourier-transform infra-red (FTIR) spectroscopic analysis was done using Thermoscientific Nicolet I S10 spectrophotometer equipped with a smart orbit diamond plate sampling technique at resolution 4 cm⁻¹ in the range 400-4000 cm⁻¹. The tensile test was done using a universal testing machine Autograph10TE at a crosshead speed of 1 mm/min using dumb-bell shaped samples according to ASTM D638 standard. Hardness tests were done using durometer Shore D. Scanning electron microscopy (SEM) was done using FEI Inspect S50 at voltage 20 kV on the tensile fracture surface. The specimen was gold coated. Thermogravimetric analysis (TGA) was done using Mettler Toledo TGA/DSC at a heating rate of 10 °C/min under nitrogen atmosphere.

3. Results and Discussion

3.1. Preparation of unsaturated polyester/vinyl ester

Vinyl ester (VE) was mixed with unsaturated polyester (UP) containing aromatic benzene ring to form UP/VE blends. The thermoset polymer blends were mixed by mechanical blending method and room temperature curing. Table 1 shows curing characteristics of UP/VE blends. UP was cured at curing time 20 min affording yellowish transparent solid hard material. Figure 1 shows the appearance of cured resin blends. UP/VE blends were cured at various curing time allowing yellowish transparent
solid hard rigid material. UP/VE blends showed homogeneous appearance without phase separation corresponding to high compatibility of UP and VE. The curing time increased with increasing vinyl ester composition at 30 to 240 min. VE was not cured after 4320 min affording yellowish transparent liquid material. It suggests that VE needs catalystaccelerator such as organic salt for curing process the resin.

UP/VE blends were investigated by FTIR. Figure 2 shows the IR spectra of UP and VE virgin resin. Figure 1(a) shows IR spectra of UP virgin resin. The peak at 3482 cm\(^{-1}\) is O-H hydroxyl bond. The peak at 3077 cm\(^{-1}\) is C-H aromatic benzene ring group. The peak at 2978 cm\(^{-1}\) is C-H aliphatic group. The peak at 1717 cm\(^{-1}\) is C=O carbonyl bond. The peak at 1493 cm\(^{-1}\) is C-H aromatic benzene ring. The peak at 1248 cm\(^{-1}\) is CO-O-C ester linkage. The peak at 1111 cm\(^{-1}\) is C-O-C ester linkage. The peak at 979 cm\(^{-1}\) is C=C unsaturated vinyl double bond. The peak at 697 cm\(^{-1}\) is C-H monosubstituted aromatic ring group. Figure 1(b) shows IR spectra of VE virgin resin. The peak at 3415, 3059, 2963, 1715, 1507, 1232, 1180, 989, 696 is O-H, C-H aromatic benzene ring, C-H aliphatic, C=O, C-H aromatic benzene ring, C-O ester, C-O ether, C=C unsaturated vinyl, C-H monosubstitutedaromatic benzene ring, respectively [3, 5, 6]. The peak at 826 cm\(^{-1}\) is C-H para-substituted aromatic ring group. VE shows high aromatic benzene ring composition.

### Table 1. Curing characteristics of UP/VE blends cured at room temperature

| Material   | Vinyl ester composition (wt.%) | MEKP composition (wt.%) | Curing time (min) | Appearance                  |
|------------|--------------------------------|-------------------------|------------------|------------------------------|
| UP         | 0                              | 4                       | 19               | Solid, yellowish transparent |
| UP/VE(10)  | 10                             | 4                       | 36               | Solid, yellowish transparent |
| UP/VE(20)  | 20                             | 4                       | 64               | Solid, yellowish transparent |
| UP/VE(30)  | 30                             | 4                       | 101              | Solid, yellowish transparent |
| UP/VE(40)  | 40                             | 4                       | 164              | Solid, yellowish transparent |
| UP/VE(80)  | 80                             | 4                       | 236              | Solid, yellowish transparent |
| VE         | 100                            | 4                       | 4320 / 3 days    | Liquid, yellowish transparent, Not cured |

![Figure 1. Photographs of UP/VE blends appearance](image-url)
The curing process of UP/VE blends were investigated by FTIR. Figure 3 shows the IR spectra of UP/VE blends at various VE composition cured at room temperature. It is observed from Figure 3(a) and 3(b), the peak at 1506 and 826 cm\(^{-1}\) corresponds to C-H para-substituted aromatic benzene ring of vinyl ester. The peak at 2920 cm\(^{-1}\) increased corresponding to the formation of long chain molecule structure. The peak at 979 cm\(^{-1}\) decreased corresponding to the vinyl functional group reaction. Figure 4 shows curing reaction and the formation of UP/VE cross-linked chemical structure network. It is suggested that UP/VE proceeded free radical chain crosslinking polymerization. It begins at the thermal decomposition of catalyst initiator MEKP producing free radical in the system. The free radical continued reaction to the vinyl group. Afterward, it is linked to the adjacent vinyl group and styrene crosslinker achieving the formation of crosslinking molecular network structure solid UP/VE polymer. The UP/VE chemical structure suggests the formation of thermoset copolymer. Figure 3(c) shows UP/VE at high VE composition (80 wt.%). The peak at 697 cm\(^{-1}\) corresponds to C-H monosubstituted aromatic benzene ring shows high intensity. It suggests remaining benzene ring and unreacted molecule. UP/VE at high composition VE is more difficult to cure and not easy to process.
3.2. Mechanical properties of unsaturated polyester/vinyl ester

Mechanical properties of UP/VE blends were examined. Figure 5 shows tensile strength of UP/VE blends. Table 2 shows the results of mechanical properties of UP/VE blends. Cured UP showed high tensile strength which corresponds to cross-linked chemical structure network [3, 9]. The addition of vinyl ester composition increased the tensile strength of UP/VE blends up to 40 wt.% of VE. The increase in tensile strength is due to an increase in rigid structure composition of aromatic benzene ring vinyl ester. At high VE composition, the tensile strength of UP/VE blends decreased due to unreacted bonds and difficulty of the molecule to be cured.

Figure 6 shows elongation at break of UP/VE blends. Cured UP showed high elongation at break. The addition of vinyl ester composition increased the elongation at break of UP/VE even at high VE composition (80 wt.%). The increasing of elongation at break is due to the high long chain chemical structure of the polymer and easier movement of the molecule chain. The UP/VE shows high elongation at break and flexibility.

Figure 7 shows hardness value of UP/VE blends. Cured UP showed high hardness value. The addition of vinyl ester composition increased the hardness value of UP/VE blends up to 20 wt.% VE composition. At high VE composition, the hardness of UP/VE decreased due to the unreacted molecule.
Figure 5. Tensile strength of UP/VE blends

Figure 6. Elongation at break of UP/VE blend

Figure 7. Hardness of UP/VE blends

Figure 8. Thermogravimetric curves of (a) UP, (b) UP/VE at 30 wt.% and (c) VE and UP/VE at 80 wt.% VE

Table 2. Mechanical properties of UP/VE blends cured at room temperature

| Material     | Vinyl ester composition (wt.%) | Tensile strength (MPa) | Elongation at break (%) | Hardness (Shore D) |
|--------------|--------------------------------|------------------------|-------------------------|-------------------|
| UP           | 0                              | 22 ± 3                 | 7 ± 1                   | 79 ± 1            |
| UP/VE(10)    | 10                             | 26 ± 1                 | 10 ± 1                  | 80 ± 1            |
| UP/VE(20)    | 20                             | 30 ± 1                 | 10 ± 1                  | 81 ± 1            |
| UP/VE(30)    | 30                             | 32 ± 3                 | 12 ± 3                  | 79 ± 1            |
| UP/VE(40)    | 40                             | 36 ± 4                 | 13 ± 4                  | 78 ± 1            |
| UP/VE(80)    | 80                             | 33 ± 3                 | 15 ± 3                  | 76 ± 1            |
| VE           | 100                            | Not cured              | Not cured               | Not cured         |
Table 3. Thermal properties of UP/VE blends cured at room temperature

| Material     | Vinyl ester composition (wt.%) | Degradation Temp. at 5 wt.% (°C) | Degradation Temp. at 10 wt.% (°C) | Weight residue at 500 °C (wt.%) |
|--------------|--------------------------------|-----------------------------------|-----------------------------------|---------------------------------|
| UP           | 0                              | 234                               | 285                               | 6                               |
| UP/VE(30)    | 30                             | 247                               | 304                               | 7                               |
| UP/VE(80)    | 80                             | 322                               | 355                               | 8                               |
| VE           | 100                            | Not cured                         | Not cured                         | Not cured                       |

Figure 9. SEM tensile fracture surface of (a) UP, (b) UP/VE at 30 wt.% and (c) VE and UP/VE at 80 wt.% VE

The morphology of UP/VE blends were examined. Figure 8 shows SEM of the tensile fracture surface of UP/VE blends. Figure 9(a) showed Cured UP morphology. It showed void and homogeneous one-phase which corresponds to transparent appearance. Figure 9(b) showed cured UP/VE blends. It showed homogeneous two-phase which corresponds to transparent appearance [3, 9]. The UP containing aromatic benzene ring shows high compatibility with VE containing aromatic benzene ring which corresponds to high compatibility and transparency. The UP/VE shows copolymer blend thermoset polymer. The surface morphology shows rough surface and plastic deformation which corresponds to high elongation at break.

3.3. Thermal properties of unsaturated polyester/vinyl ester

Thermal stability of UP/VE blends was examined using TGA. Figure 8 shows TG curves of UP/VE blends. Table 3 shows the results of thermal properties of UP/VE blends. Cured UP showed high thermal degradation and weight residue which corresponds to cross-linked chemical structure network. The addition of vinyl ester composition increased the thermal stability of UP/VE blends. The thermal degradation was due to volatilization of the unreacted molecule (diluent, moisture), fragmentation of chemical structure and gasification process [5, 7, 8]. The increasing of thermal degradation temperature and weight residue is due high composition of therigid structure of aromatic benzene ring vinyl ester.

4. Conclusion

The unsaturated polyester (UP)/vinyl ester blend was studied. UP and VE contains anaromatic ring. UP/VE was prepared by mechanical blending method and cured at room temperature using styrene as crosslinker and MEKP as catalyst initiator. UP/VE showed solid and transparent material. VE could not be cured by this reaction condition. UP/VE reacted at the vinyl bond and formed copolymer crosslinking network chemical structure. The addition of vinyl ester composition increased the mechanical properties of UP/VE blends. UP/VE showed homogeneous two-phase blend morphology corresponding to high compatibility. The addition of vinyl ester composition increased the thermal properties of UP/VE blends.
5. References

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