Mechanical Properties and Thermal Stability of Epoxy/RTV Silicone Rubber

Fahriadi Pakaya[1], Hosta Ardhyananta[1], and Sigit Tri Wicaksono[1]

Abstract— **Epoxy products have been widely applied in industries such as in the fields of automotive, mechanical, electrical, and chemical engineering. Epoxy modified to be done to improve the mechanical properties, thermal stability, physics and chemical resistance. Using of other compounds as curing agents has long been commercialized, but the constraints posed is application of an epoxy thermoset on areas requiring impact strength and thermal stability are still low. One of the modification that has been done is addition of other material as the second material to improve properties of thermoset epoxy. Preparation of research material obtained through the provision of a second material that is RTV silicone rubber. The aim of research to analyze effect of RTV silicone rubber composition (0, 5, 10, 15, 20) wt% of the mechanical properties and thermal stability of thermoset epoxy. Testing and characterization conducted on thermoset epoxy by the addition of RTV silicone rubber. In addition RTV silicone rubber: tensile strength, elongation at break and hardness has decreased, energy and impact strength increased maximum on the addition of 15% RTV silicone rubber respectively 0.294 J and 6175 J / m^2. The maximum degradation of temperature increase in the addition of 15% RTV silicone rubber is 328 and 349^{o}C respectively at 5 and 10% degradation.**

Keywords— **epoxy, RTV silicone rubber, mechanical properties, thermal stability, impact strength.**

Abstrak— ***Produk epoksi telah banyak diaplikasikan di dunia industri seperti dalam bidang teknik otomotif, mekanik, listrik, dan kimia. Rekayasa terhadap epoksi terus dilakukan untuk meningkatkan sifat mekanik, ketahanan termal, fisika dan kimia. Penggunaan senyawa lain sebagai curing agent telah lama dikomersialkan, namun kendala yang ditimbulkan adalah pengaplikasian termoset epoksi pada bidang yang membutuhkan kekuatan impak dan stabilitas termal masih rendah. Salah satu rekayasa yang dilakukan berupa penambahan material lain sebagai material kedua untuk meningkatkan sifat dari termoset epoksi. Preparasi bahan penelitian diperoleh melalui penyediaan material kedua yaitu RTV silicone rubber secara komerisal. Tujuan penelitian untuk menganalisis pengaruh penambahan RTV silicone rubber dengan komposisi (0, 5, 10, 15, 20) wt% terhadap sifat mekanik dan stabilitas termal termoset epoksi. Pengujian dan karakterisasi dilakukan terhadap termoset epoksi dengan penambahan RTV silicone rubber. Pada penambahan RTV silicone rubber: kekuatan tarik, elongation at break dan kekerasan mengalami penurunan, energi dan kekuatan impak mengalami peningkatan maksimum pada penambahan 15% RTV silicone rubber masing-masing sebesar 0,294 J dan 6175 J/m2. Temperatur degradasi mengalami peningkatan maksimum pada penambahan 15% RTV silicone rubber yaitu 328 dan 349oC masing-masing pada 5 dan 10% degradasi.***

Kata Kunci—***epoksi, RTV silicone rubber, sifat mekanik, stabilitas termal, kekuatan impak.***

I. INTRODUCTION

Epoxy resins epoxy resin have mechanical, electrical, adhesion, chemical resistance and excellent thermal, and generally easy to process. However, epoxy also relatively hard and brittle because it takes shape from very high crosslink network [1,2]. Epoxy used in a variety of applications because of an amorphous thermoset with excellent hardness and mechanical strength. Mechanical properties of epoxy is determined by many parameters such as molecular weight, epoxide group content, curing conditions, the amount of curing agent used, curing temperature, and others [3]. Epoxy resin have low impact resistance, so less is used in applications requiring high impact strength [4].

One effort to improve impact resistance by adding elastomer carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN) on the epoxy resin. The use of CTBN best used at room temperature. However, a decline in the thermo-mechanical properties because it has glass transition temperature, T_g, high enough so it is not suitable to be used at high temperatures [5].

On the other side, many studies have been associated with the modified epoxy resin RTV silicone rubber with the aim to improve thermal stability, flexibility, water resistance, flame retardance, and to achieve important other properties. RTV silicone rubber is one type of elastomer that is rated capable of improving impact strength of thermoset epoxy. Additionally, RTV silicone rubber is also one type of elastomer which have glass transition temperature, T_g, which is very low, have high elastic properties, hydrophobic properties, as well as good resistance to thermal and oxides [6].

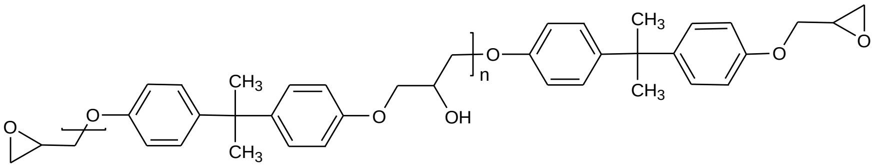
Good combination between an epoxy resin and RTV silicone rubber for applications requiring high impact strength is very promising. Therefore, we wanted to evaluate the mechanical properties and thermal stability of the mix between epoxy resin and RTV silicone rubber that can be applied.

II. METHOD

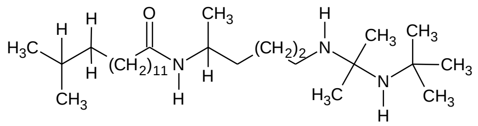
A. Materials

Epoxy resins with the basic materials is diglycidyl ether of bisphenol-A (DGEBA) (brand name: Eposchön®), EEW: 161,64 g. (equiv.epoxy)$^{-1}$, as determined by acid titration. Silicone Rubber tipe RTV 585 (brand name: Rhodorsil$^{(R)}$) with catalyst code 60R (chloroplatinic acid). Polyaminoamide (PAA) (brand name: Eposchön$^{(R)}$), eqivalent weight: 419,036 g.(equiv. active hydrogen)$^{-1}$. All of materials from PT. Justus Kimiaraya. Chemical structure of DGEBA, PAA and RTV silicone rubber can be seen in Figure.1.

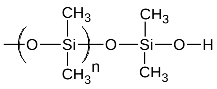
[1]Fahriadi Pakaya, Hosta Ardhyananta, Sigit Tri Wicaksono are with Departement of Materials and Metallurgical Engineering, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia. E-mail: fahriadi.pakaya@yahoo.co.id .



Diglycidyl ether of bisphenol A (DGEBA)



Polyaminoamide (PAA)



RTV Silicone Rubber

Figure 1. Chemical structure of DGEBA, Polyaminoamide and RTV Silicone Rubber

B. Preparation of Epoxy Curing System

Firstly DGEBA, PAA and RTV silicone rubber was weighed and put into to container with weight percent ratio of 0, 5, 10, 15 and 20wt% RTV silicone rubber. Samples were mixed and then put in an oven and heated at 200^{o}C, 1 hour. After curing, thermosetting epoxy then characterized.

C. Analysis of Polyaminoamide Structure

PAA chemical structure was identified using scientific Thermo Nicolet FTIR iS10 type that gives a chance from the 4000 to 500 cm^{-1} (Figure 2) and ^{1}H NMR Bruker 500 NMR instrument type shown in Figure 3.

PAA: FTIR 3285 cm^{-1} (-NH secondary), 2920 cm^{-1} (-CH aliphatic), 1648 cm^{-1} (-C=O), 1456 cm^{-1} (-CN amide), 1262 cm^{-1} (-C(CH$_3$)), dan 1123 cm^{-1} (-CN amine).

PAA: ^{1}H NMR (500 MHz, CDCl$_3$) δ ppm 0.77, m, **H**$_3$C – C – C**H$_3$,** 6.11; δ ppm 1.15, m, CH$_2$ – C**H**$_2$ – CO, 21.69; δ ppm 1.50, s, NH – C(C**H**$_3$)$_2$, 6.30; δ ppm 1.90, m, NH – C**H – C**H$_2$, 1.19; δ ppm 2.06, m, CH – C**H**$_2$ – CH$_2$, 2.41; δ ppm 2.37, m, CH – C**H**$_2$ – C**H**$_2$ – CH$_2$, 3.54; δ ppm 2.64, m, NH – C(C**H**$_3$)$_3$, 8.69; δ ppm 3.16, m, NH – CH(C**H**$_3$) – CH$_2$, 3.08; δ ppm 3,57, m, CO – N**H** – CH, 0.99; δ ppm 5.25, m, CH$_3$ – C**H**(CH$_3$) – CH$_2$, 0.69.

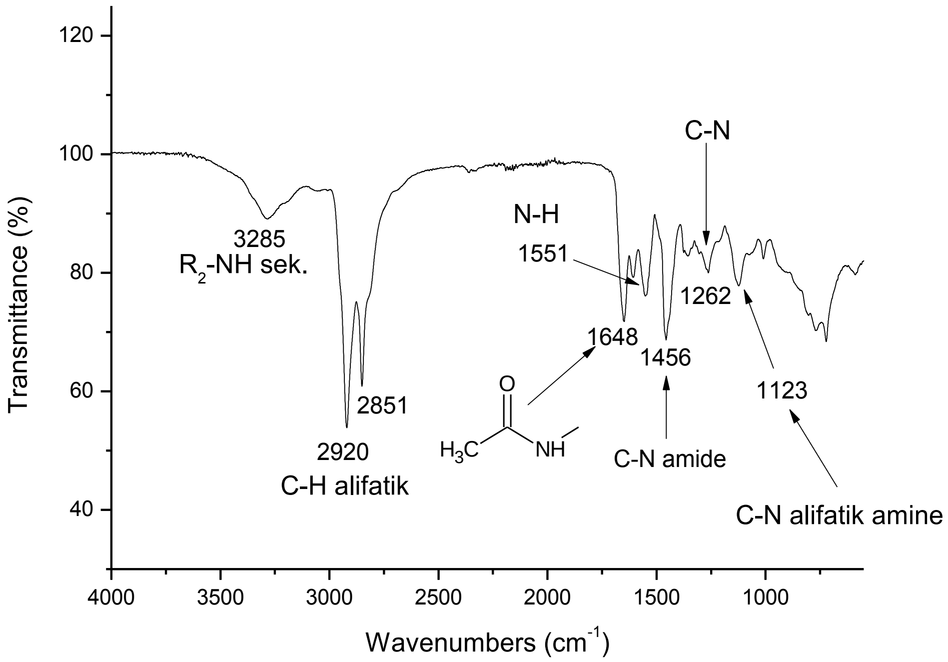


Figure 2. FTIR specra of polyaminoamide

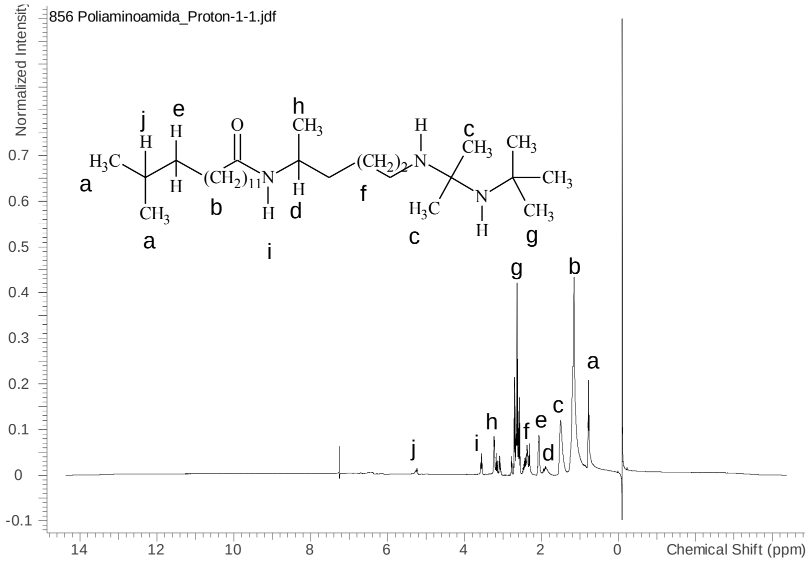


Figure 3. ^1H NMR spectra of polyaminoamide

D. Characterization of Epoxy-PAA/RTV Silicone Rubber Blend

FTIR spectra of Epoxy-PAA/RTV Silicone Rubber reported to the scientific Thermo Nicolet iS10 from the 4000 to 500 cm^{-1}.

SEM observations be done by a sample coated with Au/Pd and analyzed using the type apparatus XL30 SEM microscope (Phillips).

Mechanical properties from thermoset epoxy samples determined are tensile strength and elongation at break were measured according to ASTM D 638. Impact strength charpy type from the sample is measured based on JIS Z 2242-1993.

Thermal stability is determined by analysis using a Mettler Toledo TGA with Gas Controller GC 200. The system is operated on the temperature range from 50 to 800^oC, 10°C/min.

III. Results and Discussion

A. Curing Mechanism of Epoxy-Polyaminoamide

Curing mechanism of epoxy and PAA in Figure 4 is one of the most reactions may occur. Beginning with termination of the bond on each material. In the epoxy resin, epoxide groups which form a cyclic chain (C-O-C) experienced break the bond between the C-O. The breaking of covalent bond C-O due to the influence of temperature and the functional group N-H secondary on PAA that attack and then binds with C of epoxide ring and forming R_2HN^+-C thereby inducing reaction occurs break the bond C-O cyclic form O^- unstable. Instability R_2HN^+-C group cause hydrogen atoms break up and separated into H^+ and then captured by the O^- of secondary C-O^- group are also unstable form C-OH. This process takes place continuously until one of the material has completely reacted. In this case PAA often referred to as co-reactants and the polymer formed is usually called co-reacted polymer. Establishment and termination of the covalent bond of thermosetting epoxy/PAA can be seen of the IR spectrum of thermosetting epoxy/PAA in Figure 5. Figure 5 shows the formation of a new functional group or the loss of functional groups from the reactants. The functional groups are formed mainly C-N bonds. The functional groups are lost or diminished then forms an alcohol group (C-OH). Another group that reduced is a secondary amine group (NH) because it has formed tertiary amine.

B. FTIR analysis of Epoxy-PAA/RTV silicone rubber blend

RTV silicone rubber does not occur chemical reaction with epoxy or PAA. Bonding interface occurs between the RTV silicone rubber with epoxy-PAA. At the interface, RTV silicone rubber react with itself to form crosslinking and reacting with thermoset epoxy / PAA to form mechanically interlocking with a difficult path separated. The phenomenon of inter-diffusion and semi-interpenetrating network (IPN) occurs in the interfacial region [7]. Addition of Sn-complex catalyst by researcher was intended to occur condensation reaction with the oligomer RTV silicone rubber with crosslinker to form silicic acid ester elastomer.

IR spectrum from thermosetting epoxy/PAA with addition of 0, 5, 10, 15, and 20wt% RTV silicone rubber can be seen in Figure 6. Differences peak on the each of the IR spectrum with a particular composition are increase or decrease the intensity at some peak. At the peak 3285 cm-1 decreased the intensity of the N-H secondary PAA resin. At the peak in 1007 cm-1 there was an increase the strecting intensity Si-O-Si and Si-O-R with a growing ratio of the weight percent of RTV silicone rubber in thermoset mixture. An increase in intensity also occurs on peak 786 cm-1 that showed a growing number of C-H ratio from Si-CH3 in the thermoset epoxy/PAA/RTV silicone rubber. From the results of FTIR can be concluded that the addition of RTV silicone rubber increases the intensity in the peak in 1007 and 786 cm-1, which means the bond Si-O-Si, Si-O-R and Si-CH_3 multiply.

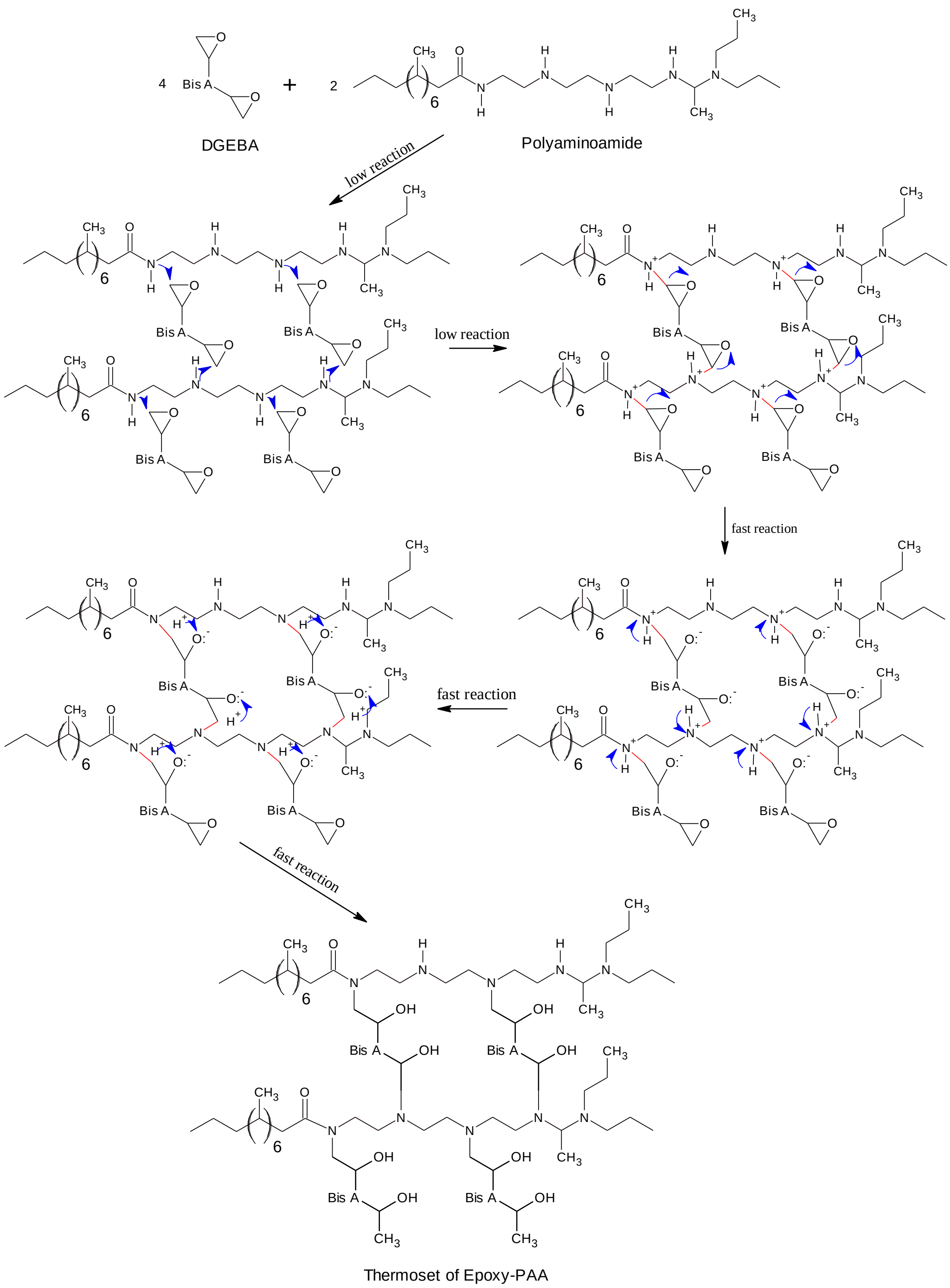


Figure 4. Schematic curing mechanism of epoxy-PAA

C. Mechanical Properties

Thermoset epoxy compared with other types of thermoset known as rigid materials that tends to have high strength, very fragile, and hydrophilic. Mechanical properties of epoxy is determined by many parameters such as molecular weight, epoxide group content, curing conditions, the amount of curing agent used, curing temperature, and others. To obtain the desired mechanical characteristics, these parameters should be optimized. Mechanical properties of thermoset of epoxy/PAA by addition of RTV silicone rubber can be seen in Table 1. Tensile strength and elongation at break of thermoset epoxy/PAA by addition of RTV silicone rubber each of which can be seen in Figures 7 and 5

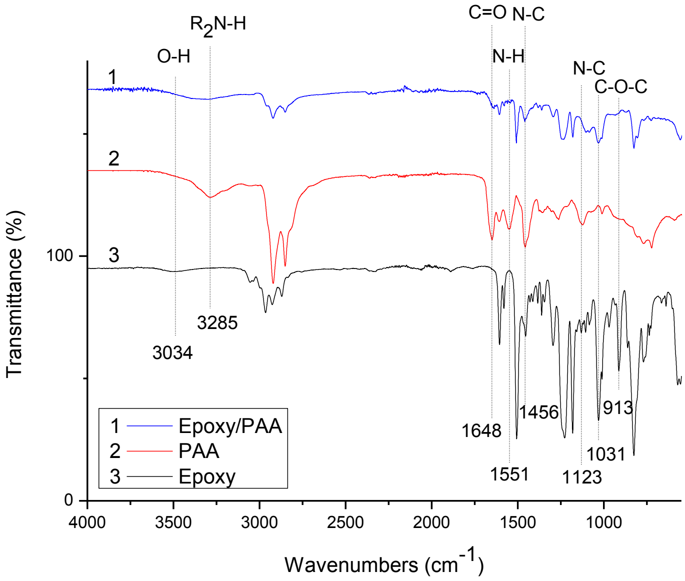


Figure 5. FTIR spectra of thermoset epoxy-PAA

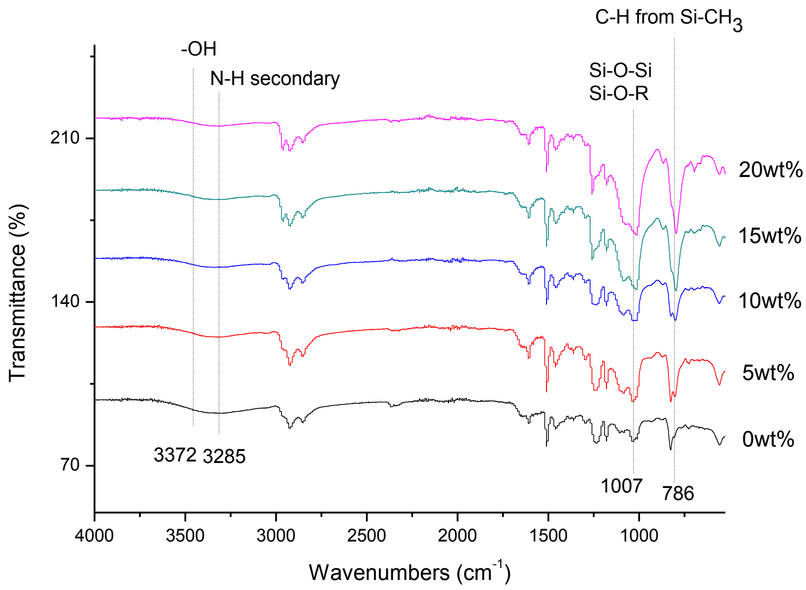


Figure 6. FTIR spectra of Epoxy-PAA/xwt%RTV silicone rubber

TABLE 1.
THE INFLUENCE OF ADDITIONS RTV SILICONE RUBBER ON MECHANICAL PROPERTIES OF THERMOSET EPOXY

RTV silicone rubber (%)	Tensile strength (MPa)	Elongation at break (%)	Impact Energy (J)	Impact Strength (J/m^2)
0	54,39	4,58	0,086	2249,91
5	42,43	3,35	0,151	3430,95
10	40,67	3,83	0,194	4071,58
15	30,86	3,39	0,279	5969,88
20	22,80	2,59	0,129	3169,35

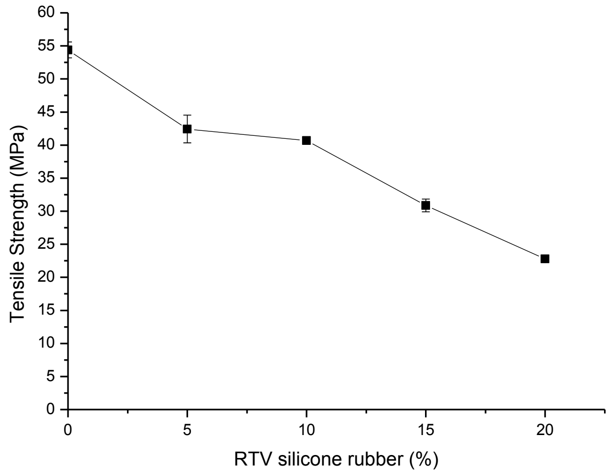


Figure 7. Effect of addition RTV silicone rubber to the tensile strength Epoxy/PAA/RTV silicone rubber on the condition of 200oC, 1 hour

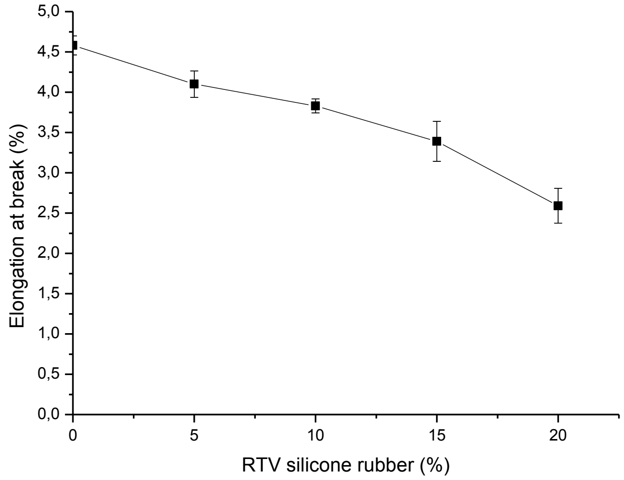


Figure 8. Effect of addition RTV silicone rubber to the elongation at break Epoxy / PAA / RTV silicone rubber, on condition of 200oC

Figures 7 and 8 shows that the addition of RTV silicone rubber causes a decrease in tensile strength and elongation at break. Addition of RTV silicone rubber which is low solubility parameter [8] cause RTV silicone rubber does not dissolve in an epoxy resin so that no covalent bonds. The bonding that is formed was interface bond (secondary bonding) wherein a small portion of RTV silicone rubber diffused and experienced mechanically interlocking that binding strength is lower than the primary bonds such as covalent bonds. No formation of covalent bonds causes the crosslink density between the three components is not formed. Addition of RTV silicone rubber is increasingly reducing tensile properties and elongation at break because besides not chemically bound, the addition of this elastomer also disturb the network crosslinks between epoxy and PAA due to additions RTV silicone rubber causes the formation of elastomer deposits. Consequently crosslink density also decreased. An increase in the amount of RTV silicone rubber is characterized by the greater intensity of the peak in 1007 cm^{-1} indicates that the Si - O - Si and a peak 786 cm^{-1} that signifies an increase in Si - CH3 on testing FTIR (Figure 6). Also from the mechanical and heating rate, a decrease in tensile strength and elongation at break due to the formation of porosity in thermoset epoxy/PAA/RTV silicone rubber was formed. Porosity are formed due to the mismatch between the time for each component to undergo a reaction to a given heating rate, the possibility of trapped solvents, or air trapped within the polymer curing. Trapped air can come from outside air while doing the stirring and air that comes from within are a byproduct formed by the heating rate is too fast to form gas (N_2 and O_2).

An increase in impact strength and energy due to additions RTV silicone rubber causes the formation of second-phase that prevents cracking and inhibiting the growth of cracks. Basically elastomer is a material with high impact strength because it is very flexible. RTV silicone rubber elastomers able to withstand dynamic loads that given quickly and absorbs the energy derived from the kinetic energy of the dynamic loads. But addition of RTV silicone rubber in the thermoset epoxy/PAA maximum time of adding 15wt% RTV silicone rubber will then decrease the impact properties of both the impact energy and strength of the material. This is because more and more RTV silicone rubber that mixed, then the space for epoxy and PAA to react and to form crosslink network more difficult. As a result, many epoxy and PAA that not binding and only annoying crosslink and elastomer formed. In some journals also mentioned that addition RTV silicone rubber have elastic properties that can increase the vibration of the atoms becomes larger. Vibration of atoms leads to easier movement of atoms in the material. The greater the vibrations of the atoms, the greater the energy and impact strength of the material.

D. Scanning Electron Microscopy

Thermoset epoxy/PAA/RTV silicone rubber that has been cured tested using Scanning Electron Microscopy (SEM) to see morphological structure from thermoset polymers that are formed. SEM testing results can be seen in Figure 9.

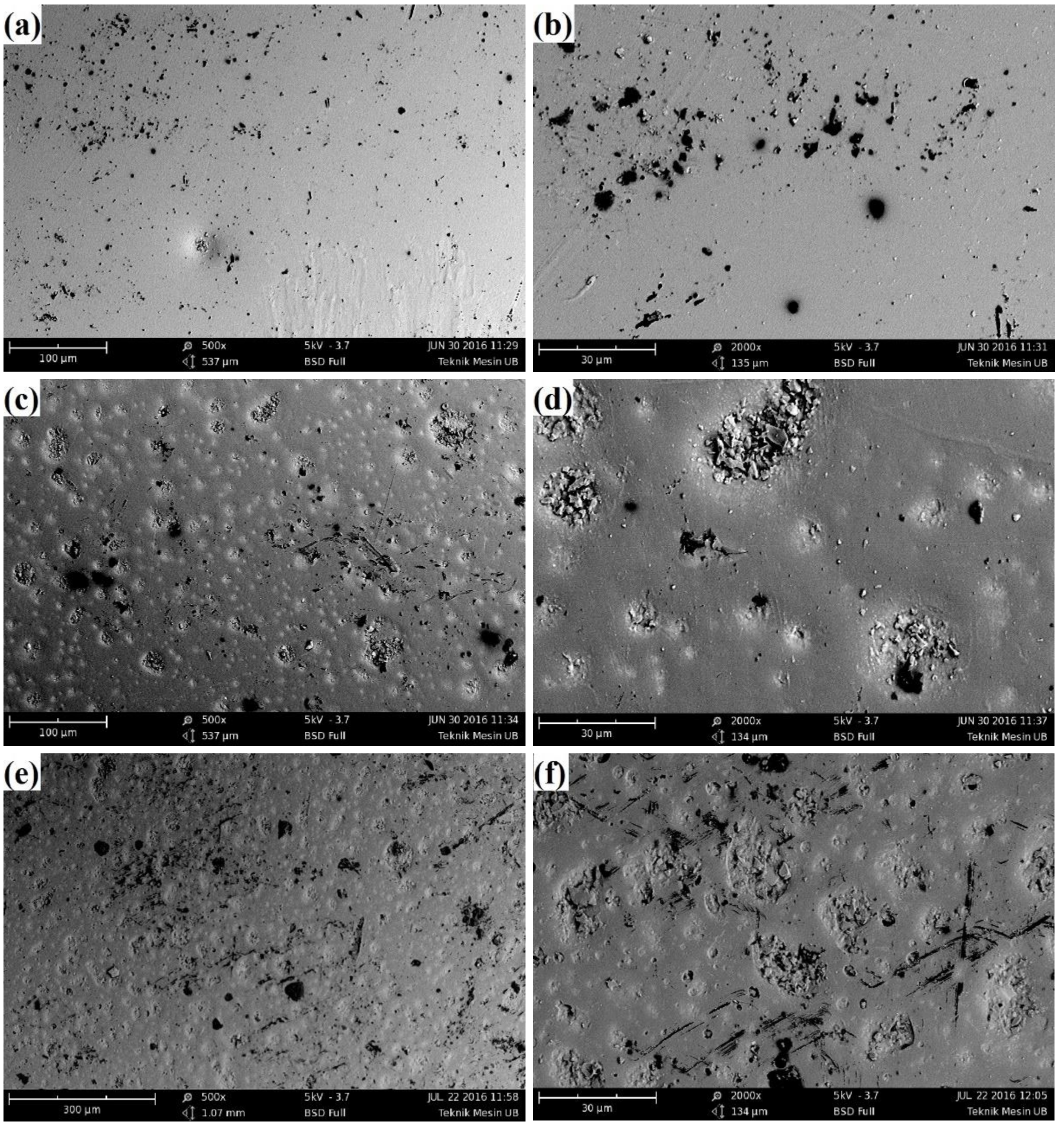


Figure 9. SEM micrograph of the cross section from thermoset epoxy / PAA pure (a and b), thermosetting epoxy / PAA / 10wt% RTV silicone rubber (c and d) and thermoset epoxy / PAA / 15wt% RTV silicone rubber (e and f)

Figure 9 shows the SEM results on thermoset epoxy/ PAA pure (Figure a and b) and thermoset epoxy / PAA by addition of 10 and 20wt% RTV silicone rubber (c, d, e and f). From Figure 9 a and b, we can see a smooth surface of thermoset with their little flecks. The smooth white surface indicates there has been a perfect curing from thermoset epoxy/PAA. The specks that appeared is the porosity from trapped air or solvent. Figure 9 c and d are micrographs from epoxy/PAA by addition of 10wt% RTV silicone rubber. From the figure can be seen the formation of two-phase separation. A large part is a thermosetting epoxy/PAA and the portions were a bit and gathering is RTV silicone rubber elastomer. The portions were slightly starts to become a lot bigger as RTV silicone rubber (Figure 9 e and f).

E. Thermal Stability

Thermal stability of thermoset epoxy by addition of RTV silicone rubber can be seen in Figure 10 and Table 2.

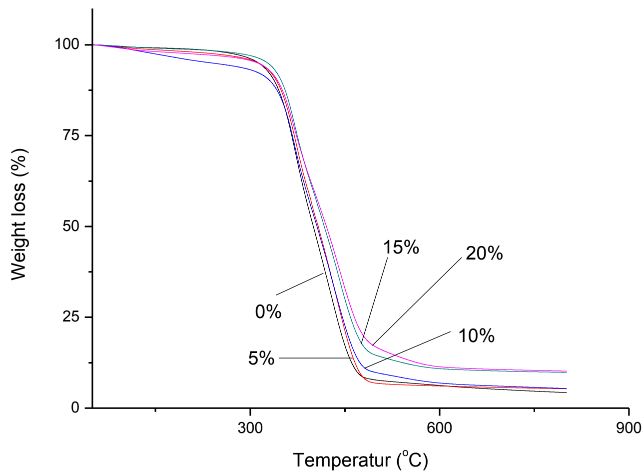


Figure 10. Thermography TG from thermoset epoxy/PAA/wt% RTV silicone rubber with a heating rate of 10°C/min

TABLE 2.
TEMPERATURES FOR DIFFERENCES IN WEIGHT PERCENT AND THE CONTENT OF ASH AT 800°C

RTV silicone rubber (%)	Temperature (°C) at varied weight loss fractions				Ash content (%) 800°C
	10%	30%	50%	70%	
0	338,44	372,04	399,99	429,72	4,271
5	341,10	375,65	406,7	436,21	5,334
10	331,81	373,48	405,53	437,74	5,394
15	349,44	381,88	416,88	449,53	9,827
20	343,8	381,45	420,5	454,98	10,190

From Figure 10 and Table 2 can be seen that addition RTV silicone rubber can improve the thermal stability of thermoset epoxy. Thermal stability increases with the addition wt% RTV silicone rubber. This is because the RTV silicone rubber containing organosilane molecules with unique capabilities that form covalent bonds between atoms from inorganic and organic (Si-O). Functional groups Si-O were covalently bonded and the bond energy is given to break covalent bond Si-O fairly large compared to other functional groups C-C or C-O at epoxy resins, so that a relatively large temperature given to the process of material degradation.

IV. CONCLUSION

This computational study has shown that the stress distribution was greatly affected by the diameter of the screws. It was found that the optimum diameter of screw was 4.5 mm with value of 126.36 MPa, and below the yield strength value of SS316L with 170 MPa. Screw must be strong and flexible to prop the broken bone, but it should not exceed the strength of the bone itself. If the value surpass the yield strength, the materials will deform plastically and broken so it is avoided. The value in this research indicates the screw's not deformed and broken so safe for femur. It is apparent that the screw diameter also greatly affects the value of total deformation. Small screw diameter is unable to sustain the bone and plate well, indicated with high value of total deformations. The maximum deformation value in screw is very small and less than 1 mm, so the shape deformation is not obvious. This research is expected the quicker recovery time and not likely to cause post-operative pain which indicated with minimum von Mises stress value (below yield strength material) and lower deformation value.

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