The Performance of Modified Silicone-Dammar Resin in Nanoindentation Test

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Abstract

Dammar plant resin (dipterocaupecea sp.) was mixed with silicone in various wt% and these two components were modified by using a volatile organic solvent to form Silicone-dammar (SD) coating material. A thin SD coating film layered on aluminium Q-panel was obtained by using spin coating method and cured at room temperature, labeled as SD0, SD5, SD10, SD15, SD20, SD25, SD30, SD35, SD40 and SD45 according to weight % of dammar. A nano-indentation test was carried out to investigate the mechanical performance of the coating film in nanoscale measurement. From the creep indentation profile, the elastic behavior of the coating material was evaluated and result shows that SD5, SD35 and SD40 have high modulus of elasticity. By using Berkovich nano-indentation with Vickers Hardness formula, SD 10 was found to be the hardest coating with hardness of 28.533 Pa and highest reduced modulus (Er) of 4.89E+02 MPa.

Keywords: *Dammar resin, silicone-dammar resin, nano-indentation, stiffness, hardness and reduced Young Modulus*

1. Introduction

The ability of coating surfaces to resist marring and scratching is particularly important in coating developments and this presents a major problem among a wide variety of coating defects occurring in polymer coating. Great attention has to be given when a new modified polymer coating is formulated. Evaluation of the coating performance, mechanical and electrochemical properties of the coating have to be evaluated. The coating materials parameters such as hardness and young modulus must be known. It is necessary to obtain the coating material's parameters from direct measurements of coated specimens since the properties of thin coating materials often differ from its bulk form. The coating is extremely thin as compared to the substrate thickness and therefore the substrate usually influences the measurement as well as the raw test data.

The nano-indentation test has been developed for determination of a coating hardness and gives an insight into the elastic properties of soft and hard thin coating [1, 2, 3, 4]. A suitable and highly technological device to carry out tests in a small scale such as nano-indentation/ nanoscratch test machine was chosen to investigate the mechanical properties of this newly developed modified Silicone-Dammar (SD). In this work, attention has been paid on *creep behaviour*, *stiffness, elastic modulus* and *hardness* of the modified silicone-dammar, SD binder by using nanoindentation testing.

2. Methodology

Fresh dammar obtained from plant was ground until it became fine powder and dissolved in volatile organic solvent. Then the solution was mixed with silicone resin. The homogenous mixture of silicone-dammar (SD) obtained was applied onto the surface of aluminium q-panel substrate using spin coater and left to dry in open air.

In the indentation experiment, creep analysis of Silicone-Dammar (SD) was done using Berkovich nanoindentation instrument bearing a serial number B-J 07 14.07.08 with a diamond tip as the indenter. The instrument was programmed, adjusted for soft coating and the load not exceeding 50mN. The measurement of acquisition rate was 10.0 Hz. with loading and unloading rate of 10.00 mN/min.

Elastic modulus (E) of the sample can be viewed during unloading. It is a measure of the sample's ability to instantly recover its former shape can be observed. Basically Oliver and Pharr defined hardness as:

$$H = \frac{p}{A} \text{...eq. 3.1}$$

Where P is the load and A is the contact area. However, modification of equation 3.1 has to be done. Nano-indentation is a famous method in measuring interfacial fracture toughness of thin coatings on substrate. The hardness of a film-coating substrate of a sample is the composite hardness, affected by the film-coated, the substrate and the interface properties [5]. The hardness of SD coated on an aluminium of panel was calculated using the basic Vickers hardness formula H_v of diamond tip, Berkovich type of indenter:

$$H_v = 1.8544 \text{ x } \frac{P}{D^2} \text{ ....eq. 3.2}$$

Where the load P is in μN and the depth D of the indent is in nm.

Young modulus of SD coating can be computed using the following equation:

$$S = \frac{dP}{dh} = \left(\frac{2\beta}{\sqrt{\pi}}\right) E_r \sqrt{A} \text{ ....eq. 3.3}$$

Where S is the contact stiffness, β is a constant of Berkovich indenter = 1.034, A is the contact area and Er is the reduced modulus.

3. Result and Discussion

3.1 Creep Indentation Profile

3.1.1 Creep Indentation Profile of Silicone coating: Figure 1 shows the results of indentation test performed on Silicone coating without modification. The indenter was driven into the silicone coating with continuous and increasing loading in mN, then the load is held constant and allowed to pause in 120.0 s prior to unloading. The value of the maximum depth (h_{max}) can be obtained directly from the unloading portion of the load versus depth curve or at the end of creep shown in Figure 1.

In this creep indentation test of pure Silicone coating, the maximum depth (h_{max}) of 3600 nm is observed. The coating is found to be very soft even when it was cured and can bear maximum load of 5.00 mN. During the holding period, the indenter continues to penetrate into the coating layer and the pause or the holding stage is the indentation creep portion of the experiment. When the stress is unloaded, the curve at the upper part of the profile is not similar to the loading profile. The two profiles do not coincide with each other and large hysteresis can be observed, indicating low modulus of elasticity of the sample. However at the lower part of the unloading curve, the coating slowly recover it elastic property.

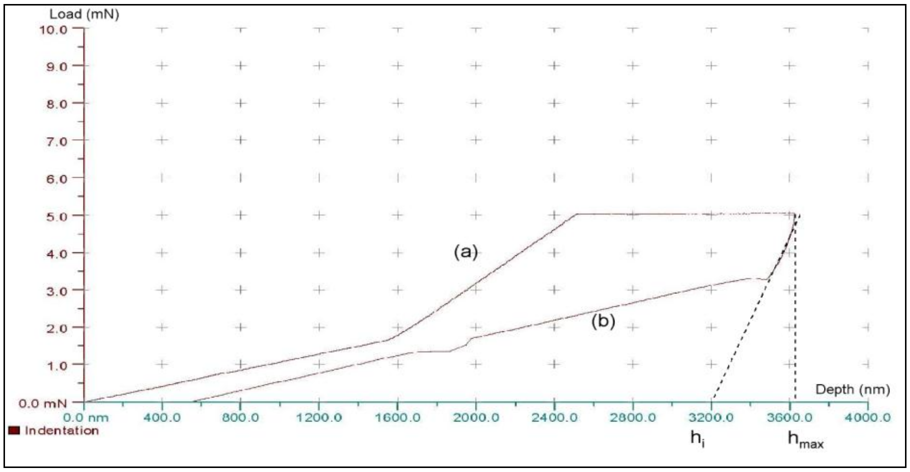


Figure 1. Load versus displacement (depth) in nanoindentation test of Silicone coating (SD0) showing the loading profile (a) and unloading profile (b)

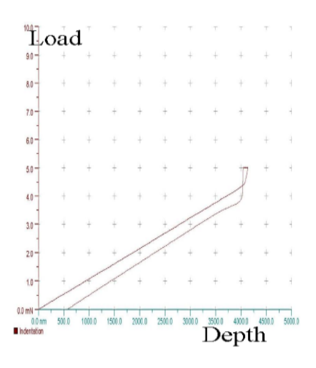
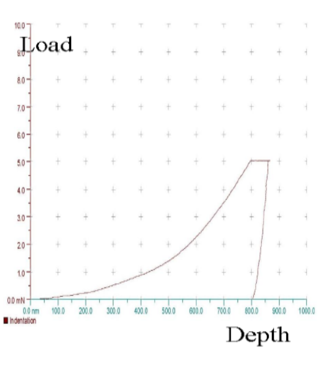
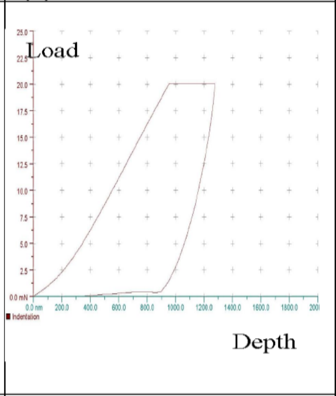
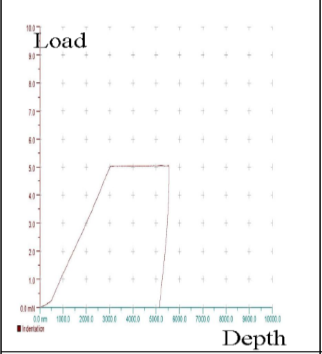
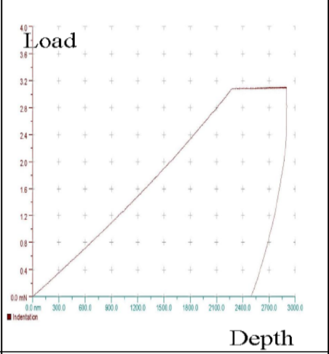
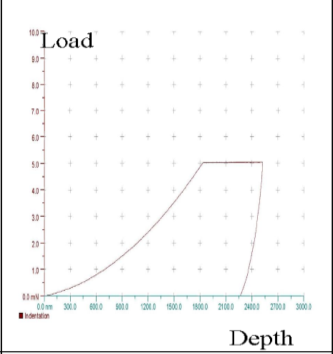
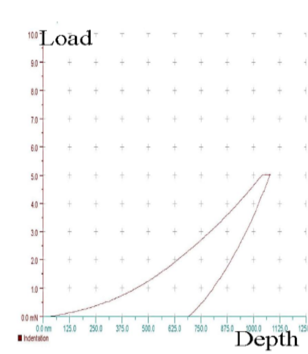
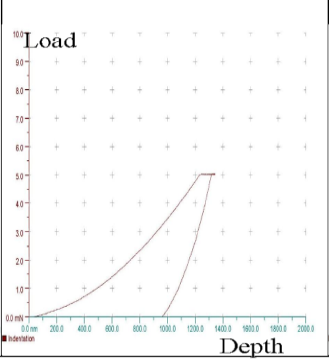
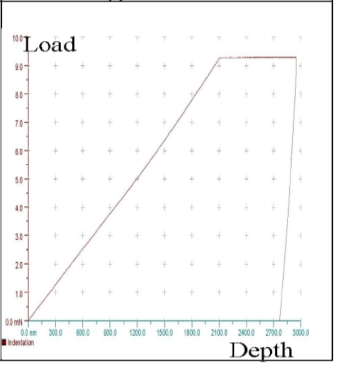
According to [6], silicone has some unique features among which, they are extremely flexible and rotate at about silicone bonds freely. This explains why the lower part of the unloading curve is elastically recovering and almost similar to the loading curve.

3.1.2 Creep Profile of modified Silicone-Dammar (SD) : Table 1 shows the overview of the creep indentation curve for the Silicone-Dammar obtained by holding the load constant and monitoring the change in depth for SD coatings with different compositions of dammar. From the various load-displacement curves shown in Table 1, SD coating with increased composition of dammar (SD45) is confirmed to be very brittle due to the crystalline nature of dammar. The creep performance for each and every one of the sample was then analyzed and from the indentation curve the value of the coating stiffness, hardness and elastic property are obtained using the Oliver and Pharr method.

Table 1(a) depicts the curve of loading and unloading of the SD coating with 5 wt. % of dammar (SD5). At the maximum load of 5 mN, the maximum penetration depth (h_{max}) of 4000.0 nm is obtained. The asymptotic slope of load curve is proportional to the modulus of elasticity of SD5. The unloading curve shows linear relationship and it is almost equal to the loading curve with a small hysteresis. This shows the SD5 coating layer has a high modulus of elasticity.

For the coating material containing 10 wt.% of dammar (SD10 sample) the load-indentation graph is shown in Table 1(b). At the end of the creep, the maximum penetration depth (h_{max}) of 850 nm is obtained with maximum load bearing equal to 5 mN. The large hysteresis between loading and unloading curve observed indicating low modulus of elasticity in SD10 as compared to SD5. Oliver and Phar did the same evaluation technique in determining the elastic property of coating using indentation method [7].

Table 1. Conventional load-displacement curve resulting from indentation of SD film with a 20 μm radius spherical indenter

(a) SD5wt%	(b) SD10wt%	(c) SD15wt%
		
(d) SD 20wt%	(e) SD25wt%	(f) SD30wt%
		
(g) SD35wt%	(h) SD40wt%	(i) SD45wt%
		

In Table 1(c) the maximum depth of penetration of 1300 nm is obtained for the sample coated with SD coating having 15 wt. % of dammar (SD15). Even though SD is a soft coating material but SD15 can bear maximum loading of 20.0 mN. From Table 1(c), a large hysteresis can be seen and this reveals a low value of modulus elasticity for SD15 coating. The unloading curve in both SD10 and SD15 show non-linear relationship.

In the SD20 sample, Table 1(d) the maximum penetration depth is 5600 nm. There is a large hysteresis between load and unload curve. Since the coating is very soft, the diamond tip moved independently and it is clearly seen that at the upper part of the unloading curve the SD20 behave completely plastic.

Table 1(e) and (f) depict the load indentation for sample SD25 and SD30 respectively. In Table 1(e), the curve of penetrating load is less steep as compared to unloading curve with maximum depth measurement of 2850.0 nm in SD25. The indenter tip was hold at 2.8 mN and it continued penetrating deeper into the sample independently prior to the unloading stage. In the SD30 sample, the maximum penetration depth is 3000 nm with maximum load bearing of 5.0 mN. Large hysteresis between load and unload curve can be seen in both SD25 and SD30. This means that the modulus of elasticity of the coating is very low.

The unload curve of SD35 shows non-linear relationship and the slope is less steep as shown in Table 1(g). The maximum load bearing of 5.0 mN is achieved with maximum penetration of 1060 nm. The asymptotic slope of load curve is proportional to the modulus of elasticity of SD35. The upper part of the loading and unloading curve indicates the elastic behavior of SD 35. Elastic-plastic behavior of SD35 was observed. The unloading curve is almost similar to the load curve with a small hysteresis. This shows that the SD35 coating layer have a high modulus of elasticity [7, 9].

Similarly, the curve of loading and unloading of SD40 is less steep. The maximum load bearing of 5.0 mN with maximum penetration depth of 1300.0 nm can be seen from Table 3.1(h). The asymptotic slope of load curve is proportional to the modulus of elasticity of SD40. The unloading curve is almost equal to the load curve with a small hysteresis. This indicates that SD40 coating layer have a high modulus of elasticity. Similar technique was employed and reported in the literatures. Based on Hertzian model, the effective sharp indenter can perform half space and geometrically well-defined in analysis of elastically-plastically behavior in a coating materials [7].

In SD45, the maximum load bearing of 9.0 mN was achieved with the maximum penetration depth of 2900.0 nm. The tip was hold forseveral seconds but it continues moving deeper into the sample before unloading. The unloading curve is extremely steep as compared to the loading curve. This shows that SD45 coating layer does not behave elastically. This could be due to the chemical reaction occurring between silicone resin and dammar resin where the silicone resin’s free bonding are fully occupied with dammar complex molecule as polymer has an alcohol fragments in their end group [8].

3.2 Stiffness of Silicone–Dammar (SD)

Nano-indentation curve was used to extract mechanical properties of the SD coatings. Stiffness is one of the properties and it is a reflection of flexibility and elasticity. From the load-unload data, the stiffness of the SD samples are calculated using the Equation 3.3 and results are tabulated in Table 2 below.

Table 2. Stiffness Data for Varied Compositions of Silicone-Dammar, SD

SD (%WT)	Load (N)	h max (m)	Hi (m)	Dh (m)	stiffness (N/m)
SD0	5.00E-03	3.60E-06	3.20E-06	4.00E-07	1.25E+04
SD5	5.00E-03	4.00E-06	3.50E-06	5.00E-07	1.00E+04
SD10	5.00E-03	8.50E-07	8.00E-07	5.00E-08	1.00E+05
SD15	2.00E-02	1.30E-06	1.00E-06	3.00E-07	6.67E+04
SD20	5.10E-06	5.60E-06	3.00E-06	2.60E-06	1.96E+00
SD25	3.00E-03	2.85E-06	2.60E-06	2.50E-07	1.20E+04
SD30	5.00E-03	3.00E-06	2.25E-06	7.50E-07	6.67E+03
SD35	4.50E-03	1.06E-06	8.10E-08	9.82E-07	4.58E+03
SD40	5.00E-03	1.30E-06	9.50E-07	3.50E-07	1.43E+04
SD45	9.00E-03	2.90E-05	2.80E-06	2.62E-05	3.44E+02

Figure 2 portrays the stiffness profile of varied compositions of SD. It was found that SD10 have highest value of stiffness with 1.00E+05 N/m. The lowest stiffness belongs to SD45 at 3.44E+02 N/m. Other compositions of SD showed stiffness in the range of log of 3 and 4. From the literature, it is known that for soft coating surfaces the apparent spring constant cannot go beyond the maximum value of 50 N/m [9, 10].

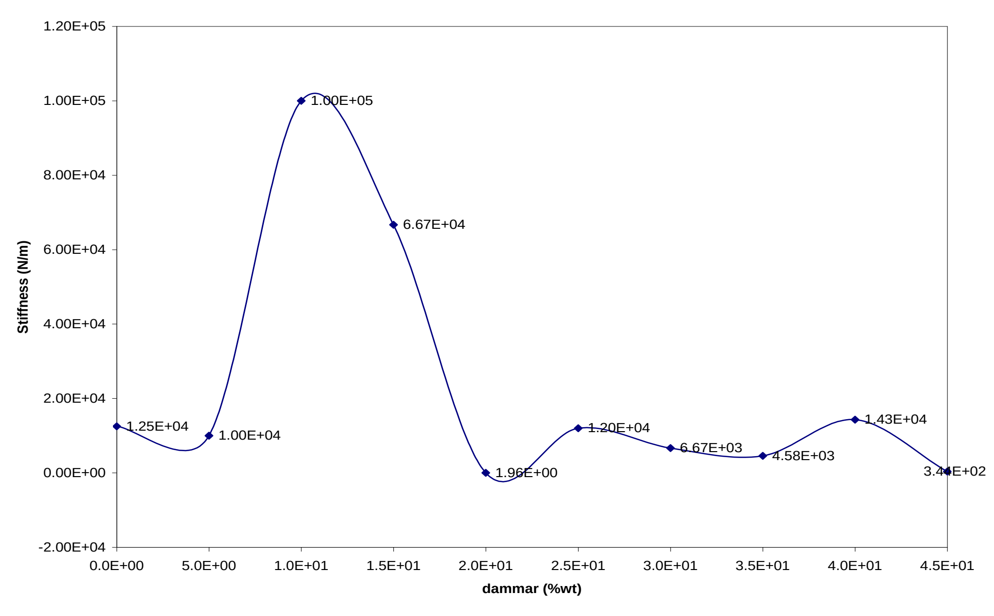


Figure 2. Stiffness Profile of Varied Compositions of Silicone-Dammar

3.3 Hardness Measurement

In the indentation test, the hardness measurement provides information about the micro-mechanical properties of different phases in material and their volume distributions. Table 3 below shows the hardness value of different compositions of dammar in the modified silicone

– dammar thin film and the variation of the hardness with composition of dammar is depicted in Figure 3

Table 3. Hardness Data for Varied Silicone-Dammar, SD

SD	Load, P	Hardness, H (Pa)
SD0	5.00E-03	2.687
SD5	5.00E-03	4.132
SD10	5.00E-03	28.533
SD15	2.00E-02	1.624
SD20	5.00E-03	3.414
SD25	3.00E-03	4.869
SD30	5.00E-03	15.229
SD35	4.50E-03	25.680
SD40	5.00E-03	18.625
SD45	9.00E-03	4.545

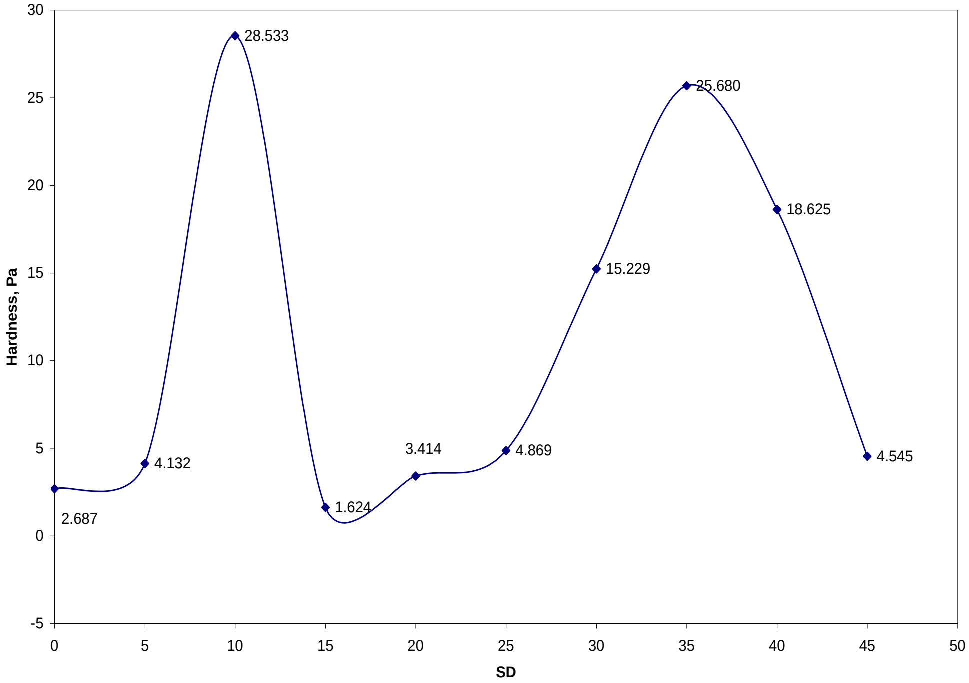


Figure 3. Hardness Test Value for Modified Silicone-Dammar thin Film

Referring to Figure 3 a small hardness value of 2.687 Pa for pure silicone which is due to its extremely flexible properties, followed by 4.132 Pa for the coating mixed with 5 wt% of Dammar. The coating become harder with hardness value of 28.533 Pa when 10 wt% of dammar is added to the coating. When the composition of dammar is increased to 15 wt%, the cured coated films become soft again with hardness value is 1.624 Pa.

The hardness value of 3.414 Pa belong to 20 wt% of dammar indicates that it is amorphous and soft in nature, hence the SD coating mixture become more flexible when spin coated onto aluminum substrate. The cured sample becomes harder again gradually proportionate with

Dammar addition and the SD35 exhibits the second hardest value at 25.680 Pa after SD10. This could be due to amorphous networks of dammar and silicone resin, which made the SD coating becoming harder and more brittle. Further addition of Dammar resulted in lower hardness value of SD coating. From the literature, the hardness measurement also portray the amorphous nature of polymers when the modulus of cured thin coating at range of (3.5 ± 0.5) Pa [11].

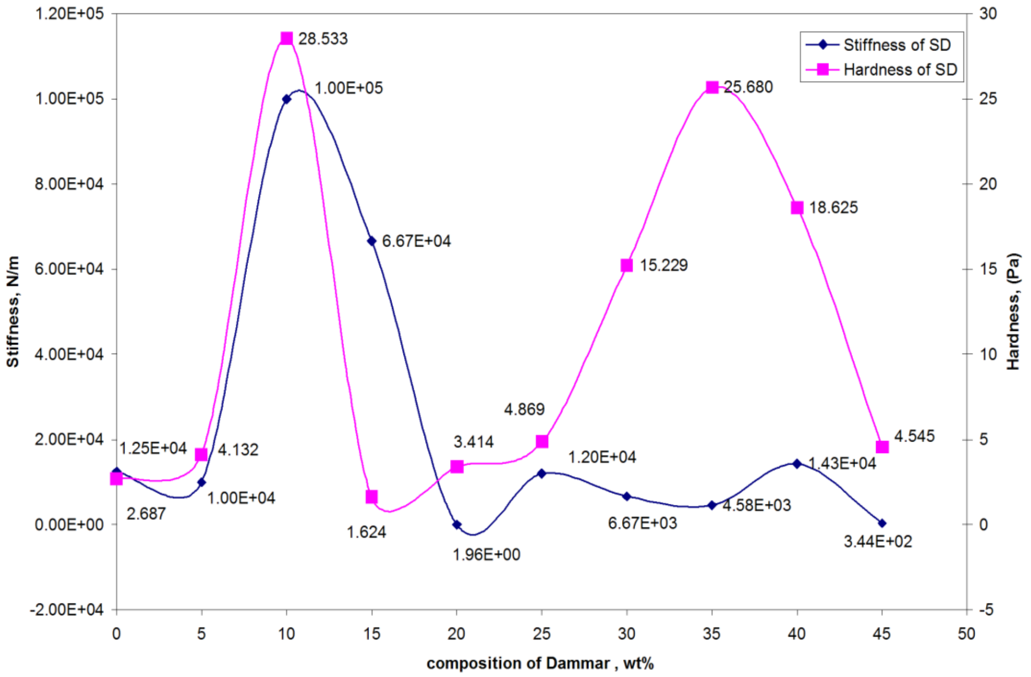


Figure 4. Comparison of Hardness and Stiffness Test Value for Modified Silicone-Dammar thin Film

3.4 Reduced Modulus (Er) of SD Coating

Generally, there are three different types of stress-strain behaviour in polymer materials. They were categorized under brittle, plastic and elastic polymer. For brittle polymer, much fracture happened while it is elastically deformed. Plastic materials such as metallic material initially undergo elastic deformation, followed by yielding and a region of plastic deformation. A totally elastic polymer or rubber-like elasticity, a large recoverable strain produced at low stress level called elastomers.

In this experiment, the reduced modulus (Er) of SD coating materials with various wt% of dammar was calculated using Equation 3.3 and Table 4 shows the values of Er and Hardness for respective SD coating materials. Figure 3.5 shows the composition of dammar dependence on the Reduced Modulus, Er and the hardness of SD. Result shows that SD have reduced modulus, Er in the range of 4.6E+0 to 4.5E+1 MPa, excepts for SD20 the obtained reduced modulus is 1.15E-3 MPa. M. Wang *et. al* reveal a reduced elastic modulus of polymeric thin films at a value of 3.5 ± 0.5 GPa [12].

Table 4. Hardness and Reduced Modulus for Varied Composition of Silicone-Dammar, SD

SD	Load, P	hardness, H (Pa)	reduced modulus, Er (MPa)
SD0	5.00E-03	2.687	5.76E+00
SD5	5.00E-03	4.132	7.08E+00
SD10	5.00E-03	28.533	4.89E+02
SD15	2.00E-02	1.624	4.64E+00
SD20	5.00E-03	3.414	1.15E-03
SD25	3.00E-03	4.869	1.67E+01
SD30	5.00E-03	15.229	1.74E+01
SD35	4.50E-03	25.680	2.24E+01
SD40	5.00E-03	18.625	4.56E+01
SD45	9.00E-03	4.545	1.49E-01

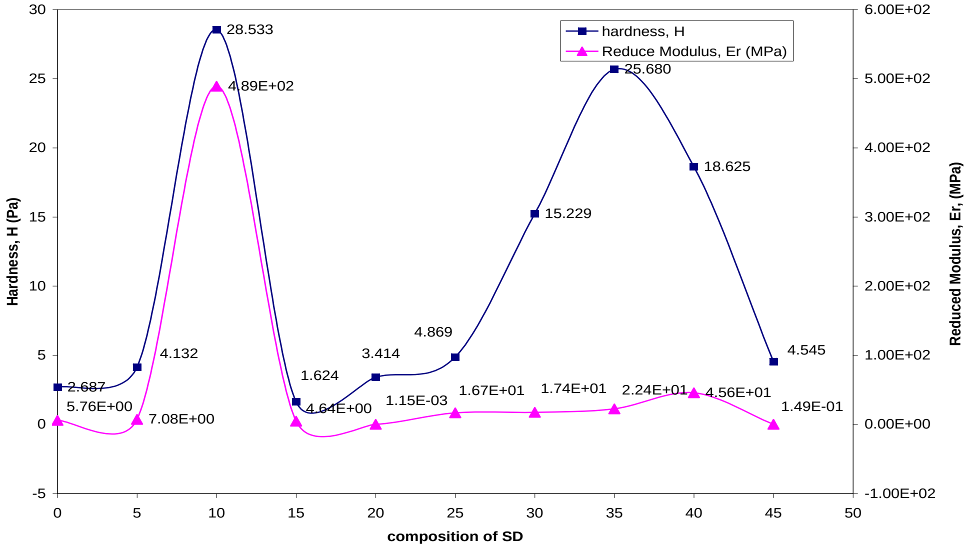


Figure 5. Comparison between Hardness and Reduced Modulus Curve of Modified Silicone-Dammar Thin Film

It can be seen that as the hardness of the SD sample increase the reduced modulus of SD increases together with dammar content until they reach the maximum at 10 wt% of dammar. However, both the hardness and Er decrease when the dammar content is increase to 15 wt. The hardness and Er values increase again when more than 15 wt% of dammar is added and the trend continues until the composition of dammar is increased to 25 wt% for SD25 sample. Although the hardness of the samples increases, the values of the modulus remain almost constant with further addition of dammar (SD30 and SD35). Finally, the decrease in the values of Er and hardness is observed when more than 40 wt% of dammar is added into the SD.

4. Conclusion

Nano-indentation provides valuable information about materials being investigated especially in surface monitoring. Load – displacement curves that presented by nano-indentation instrument portray the material behaviors which could be elastic, plastic or brittle. In this experimental work, pure silicone coating shows low modulus of elasticity with stiffness of 1.25 x 10^4 N/m. It is confirmed that silicone is a soft coat when the calculated hardness and reduced modulus obtained was 2.687 Pa and 5.76 MPa respectively.

The addition of dammar helped to improve the elastic behavior of SD. In SD coated samples with varied compositions of dammar, most of the samples show low modulus of elasticity with different penetration depths. However, load – unload curve of SD5 shows high modulus of elasticity while SD35 and SD40 show an elastically-plastically behavior.

Results showed that dammar influenced the SD material's parameter; hardness, stiffness and the reduced modulus Er. SD10 represents the hardest coat with hardness of 28.533 Pa and maximum stiffness of 1.0 x 10^5 N/m. Highest reduced modulus Er of 4.89E+02 MPa is obtained for SD10. This indicates that SD coating tightly buckles its molecules from being tear off and that 10wt% of dammar is sufficient to make SD coating becomes harder with higher reduced modulus Er than the pure silicone. It can be concluded that the addition of dammar enhanced the mechanical properties of SD with optima composition of 10 wt. % of dammar in SD10 sample.

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