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Degradation of blending vulcanized natural rubber and nitril rubber (NR/NBR) by dimethyl ether through variation of elastomer ratio

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Abstract. Dimethyl ether can cause degradation of the rubber material seal in some applications. In order to use of natural rubber in industry, research about a blending of natural rubber (NR) and nitrile rubber (NBR) to produce rubber to meet the standard seal material application were conducted. This study will observe the degradation mechanisms that occur in the blending natural rubber and nitrile rubber (NR/NBR) by dimethyl ether. Nitrile rubber types used in this study is medium quality nitrile rubber with 33% of acrylonitrile content (NBR33). The observed parameters are percent change in mass, mechanical properties and surface morphology. This study is limited to see the effect of variation vulcanized blending ratio (NR/NBR33) against to swelling. The increase of nitrile rubber (NBR33) ratio of blending rubber vulcanized can reduce the tensile strength and elongation. The best elastomer variation was obtained after comparing with the standard feasibility material of seal is rubber vulcanized blending (NR/NBR33) with ratio 40:60 NR: NBR.

1. Introduction

Dimethyl ether is a simple compound of ether which is able to substitute fossil energy and has meets the criteria as high energy [1]. Moreover, dimethyl ether is categorized as hydrocarbon compound which is interconnected with rubber seals and gaskets, so that makes it the cause of leakage [2]. Such interaction is referred to as polymer degradation. When the polymer is exposed to the liquid, the form of the degradation is swelling and dissolution [3]. The type of rubber widely used in order to overcome such problem is nitrile rubber (NBR) with its resistance to swelling degradation. In order to increase the consumption of natural rubber in automotive industry, especially in Indonesia, the research about natural rubber blending by utilizing its superior properties in the application of seal in machine parts are continuously performed.

The required physical properties are a rubber material compound which is resistant to swelling degradation and has good mechanical strength. Such properties are obtainable from natural rubber (NR) and nitrile rubber (NBR) materials. Natural rubber has good mechanical strength, while nitrile rubber is resistance to oil exposure. Both elastomers are able to be combined in order to obtain the best properties. However, the blending between natural rubber and nitrile rubber (NR/NBR) is not easy due to the significant level of polarity and solubility. Saputra and Johan (2016) has been conducted degradation characteristics of vulcanized natural rubber research by using minarex-B plasticizer [4]. Therefore, this study also can be developed to the vulcanized natural rubber research by replacing minarex-B with soybean oil as a plasticizer.

The objective of this study is to obtain the blending ratio (NR/NBR) used for rubber vulcanization. While, the type of NBR used is nitrile rubber containing 33% of acrylonitrile, Krynac 33.45F (NBR 33). The content of acrylonitrile determines the difficulty level of blending and oil resistance level.

Therefore, this study is to find out the leverage of blending ratio (NR/NBR) to the swelling degradation by dimethyl ether and its mechanical as well as morphological characteristics.

2. Materials and methods

The experiment is divided into: the synthesis of vulcanized natural rubber and nitrile rubber (NR/NBR26) as well as mechanical and morphological characterization.

Synthesis of vulcanized natural rubber and nitrile rubber has a purpose to produce the rubber product that will tested in this research. The synthesis of vulcanized rubber blending consists of 5 variations of NR/NBR ratio. They are (75: 25), (60: 30), (50: 50), (40: 60), (25: 75) of NR/NBR ratio. The study of elastomer mixture technique does a concern on consideration of typical behaviour from elastomer mixture and the combination of these properties in vulcanized process [5]. First step is preparation the equipment such as setting up the open mill, press moulding and rheometer. The material used in this synthesis process is natural rubber (NR), nitrile rubber (NBR33), anti-degradation, accelerator, activator, sulphur, carbon black and soybean oil. Natural rubber (NR) and nitrile rubber (NBR33) were masticated by the open mill equipment for 5-10 minutes. After the mastication process, the vulcanization material was mixed into the open mill until got the homogeneous mixture. Then, the rubber product was cooled for a day. A piece of the rubber product was used for determining time of vulcanization in rheometer and then put the rubber product in press moulding equipment. After that, the vulcanization process with vulcanization temperature and time that displayed in rheometer were conducted. The rubber product was cooled for more or less one hour. All procedure was repeated with different ratio natural rubber (NR) and Nitrile Rubber (NBR33).

The procedure of swelling of the blending vulcanization degradation test (NR/NBR33) is based on ISO 1817:2005. The first step of this test is to stick the rubber product into copper rod and it must be in perpendicular position between rod and the rubber product and then put them into pressure vessel and the PTFE insulate tape was installed in every channel of pressure vessel. Then the channel was closed tightly for avoiding the leakage. After that, the pressure vessel was cooled by putting it into plastic jar that filled with ice cubes and salt. The pressure vessel was connected with 50 kg gas cylinder that filled with dimethyl ether. The valve was opened slowly for 15 minutes and then was closed. The dimethyl ether was changed into liquid phase. For 7 days, the sample product was immersed in pressure vessel. The sample of rubber was put and dried for characterization steps. The procedure above was repeated with different ratio natural rubber (NR) and Nitrile Rubber (NBR33).

The other procedures are mechanical and morphology characterization. Mechanical characterization was conducted before and after swelling of blending vulcanization degradation test. There are 4 types of mechanical test. First the percentage of mass changing is measured by electronic mass balance, then maximum tensile and elongation strength were tested based on ISO 37:2005. The hardness characterization was tested with hardness testing machine (ISO 48:2010) and the compression set was tested based on ASTM D395 standard [6]. To observe the morphology of material, scanning electron microscopy (SEM) was used.

For calculate the percentage of mass changing is used the equation (1) as shown as below and m symbol is stated as sample rubber mass [7].

$$\%\boldsymbol{\Delta m} = \frac{m_{beforeimmerse} - m_{afterimmerse}}{m_{beforeimmerse}} X\ 100 \quad (1)$$

Calculated data for tensile strength is maximum tensile force from blending vulcanized material (NR/NBR26) while retraction. The strength of tensile force can be calculated with the equation (2).

$$\boldsymbol{\sigma} = \frac{F_{maxsimum}}{A} \quad (2)$$

The following variable is stated as σ = tensile strength (Mpa), F = Maximum Tensile force (Newton), and A = Area of tensile (m^2).

The value of blending vulcanized sample length (l) was measured before and after elongation. The equation (3) shows the percentage of maximum elongation

$$\% \Delta l = \frac{l_{beforeelongation} - l_{afterelongation}}{l_{beforeelongation}} X100\ \% \qquad (3)$$

The calculated data for the Compression Set value is the value of the initial thickness and the final thickness of the rubber compound sample. In order to calculate compression set, the equation 4 is used as shown as below

$$C_B = \left[\frac{t_o - t_i}{t_o - t_n}\right] X100\ \% \qquad (4)$$

The following variable is stated asC_B= compression set percentage, t_o = sample thickness before experiment, t_i = sample thickness after experiment and t_n= spacers thickness

3. Result and discussion

3.1 The result of physical characteristic change

The result is the physical characteristic change of the sample rubber; such as percentage of mass change, tensile strength change, elongation change, and hardness change. The percentage data of mass change is obtained from the mass calculation of the sample before and after immersion. The mass change value of each sample due to the DME immersion is displayed in Table 1.

The process of partial dissolution occurs with a decrease in rubber mass, while the swelling process is seen with the addition of rubber mass. The Table 2 is the value of the physical characteristic change of the sample rubber. The elongation value is in association with the tensile strength value which is the percentage change in accordance with the result of tensile strength test until. The elongation value of rubber samples decreases due to the immersion of dimethyl ether; such decrease tends to subside as the addition of nitrile rubber ratio into the rubber mixture. In addition to the elongation value, tensile strength value can also be obtained from tensiometer.

In Table 2, it shows that the tensile strength value of each sample changes. After immersion, the increase of nitrile rubber composition is able to reduce tensile strength. However, the tensile strength will increase after immersion in sample F and G of 75% and 100% of nitrile rubber content. Furthermore, the rubber sample is subjected to hardness test as also shown in Table 2. The hardness value is prone to increasing along with the addition of nitrile rubber composition (NBR33) within the rubber mixture. Nitrile rubber generally improves the physical properties of the mixed samples after dimethyl ether immersion.

3.2 Measurement of mass change

The presence of swelling and partial dissolution phenomena can be seen from the percentage mass change of the samples before and after dimethyl ether immersion. The mass change can be seen in Figure 1 with the positive value indicating mass addition is called swelling and negative value showing mass decrease is called partial dissolution.

Table 1. Percentage of mass changing of vulcanized rubber mixture (NR/NBR33) by DME.

Sample	Ratio (%)		Treatment	Mass Change, %
	NR	NBR		
A	100	0	After (direct)	10.94
			After (+ 3 hours)	-7.55
B	75	25	After (direct)	13.18
			After (+ 3 hours)	-5.69

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C	60	40	After (direct)	6.71
			After (+ 3 hours)	-6.44
D	50	50	After (direct)	14.56
			After (+ 3 hours)	-4.50
E	40	60	After (direct)	11.52
			After (+ 3 hours)	-4.43
F	25	75	After (direct)	10.10
			After (+ 3 hours)	-4.27
G	0	100	After (direct)	11.10
			After (+ 3 hours)	-3,10

Table 2. Elongation, tensile strength and hardness of vulcanized rubber mixture (NR/NBR33).

Sample	Ratio, %		Treatment (Before/After immersion)	Elongation (%)	Tensile Strength, (Mpa)	Hardness, Shore A
	NR	NBR				
A	100	0	Before	590	16,7	60
			After	400	9,7	60
B	75	25	Before	560	16,3	65
			After	500	13,2	65
C	60	40	Before	570	16,5	67
			After	510	15,1	70
D	50	50	Before	550	16,3	67
			After	560	15,7	68
E	40	60	Before	540	15,8	67
			After	580	15,7	69
F	25	75	Before	580	17,3	67
			After	570	18,6	70
G	0	100	Before	520	15,9	64
			After	530	20,3	70

The result also shows that the swelling process occurs when DME fills the crack in the rubber sample which then extracts the soybean oil compound out of the rubber sample. The principle of this process is that similarity in terms of chemical structure will facilitate the occurrence of swelling and partial dissolution which is known as “like dissolves like” [3]. Soybean oil which contains most of the unsaturated fatty acid, when in large amount, is dissolved more easily into the DME which a polar compound is. It is also asserted that if more oil is used in the rubber vulcanizing formula, the oil extraction is greater [4]. Such process is unavoidable despite the presence of synthetic rubber (NBR33) within the rubber formula. Figure 1 informs that the presence of NBR makes the vulcanized rubber mixture is relatively resistant to soybean oil extraction. Further impact due to DME immersion is the occurrence of degradation based on physical property changes.

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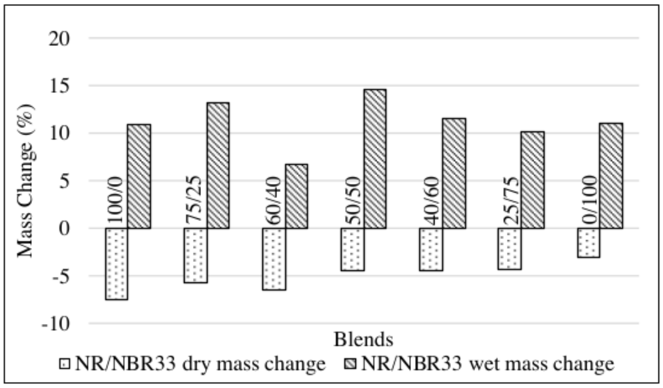

Figure 1. Percentage mass change of vulcanized rubber mixture (NR/NBR33).

3.3 Tensile properties change

The change of tensile strength value as a result of immersion is an indicator that the degradation mechanism due to the partial dissolution. Physical property degradation will occur if the rubber sample in the test is deteriorated. The change in tensile strength is shown in Figure 2. In the samples, natural rubber (NR) content is lower the tensile strength value. This is due to the fact that the absorption of DME makes the carbon black filler distribution become uneven within the vulcanized rubber. Carbon black distribution can be seen from SEM morphology test. Tensile strength value decrease approaching 50% is also predicted as a result of devulcanization, the breaking of cross linking bond of sulphur between natural rubber molecules. On the other hand, devulcanization phenomenon does not occur on natural rubber (NR) sample based on FTIR test; there is no change in the composition of the double bond number [9]. From Figure 2, it can be concluded that nitrile rubber prevents degradation as a result of swelling and partial dissolution phenomena by raising the value of tensile strength after DME immersion.

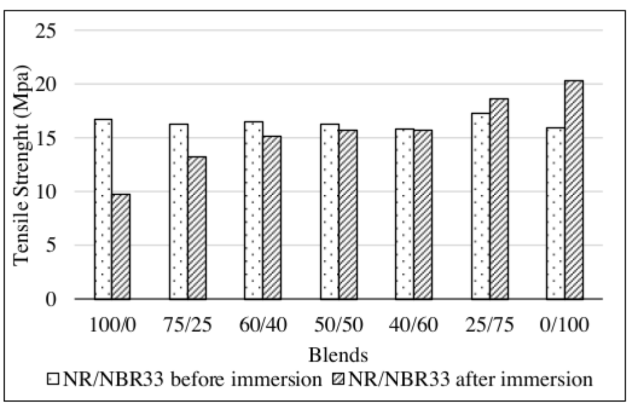

Figure 2. Tensile strength of vulcanized rubber mixture (NR/NBR33).

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The elongation value will be associated with the tensile strength value. The elongation value is obtained after maximum tensile strength value is reached until eventually rubber sample breaks. The elongation change of the rubber sample after immersion can be seen in Figure 3. The elongation value in Figure 3 is similar to Figure 1 in terms of increased elongation value along with the increase of nitrile rubber ratio (NBR33) in vulcanized rubber mixture.

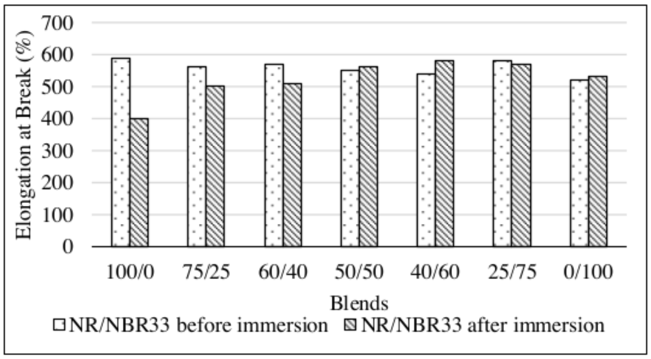


Figure 3. Elongation of vulcanized rubber mixture (NR/NBR33).

3.4 Hardness properties change

The presence of soybean oil is very influential on the hardness of rubber blends. Soy oil can act as a solvent or plasticizer. Plasticizer is an additive in rubber vulcanization that serves to increase the flexibility but reduces the hardness of a polymer [3]. Figure 4 shows a tendency to increase the value of violence with NBR33 contents increase. This was due to the blending of rubber to lose soybean oil after soaking. However, blends with higher NR is not affected by increased hardness values. It might be due to low compatibility between soybean oil and natural rubber. Figure 4 also informs about the hardness before immersion in NR / NBR mixtures is better if it is compared with pure natural rubber and pure nitrile rubber.

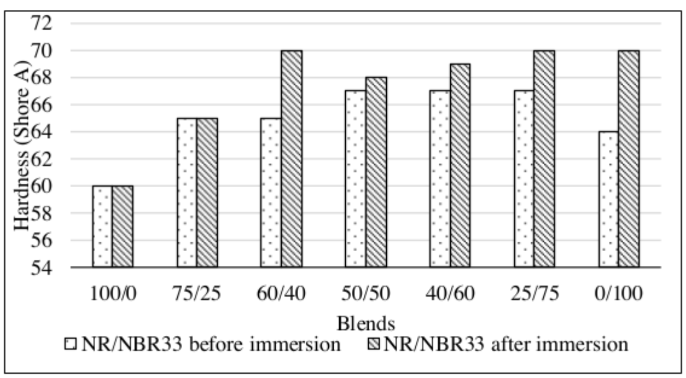


Figure 4. Hardness of vulcanized rubber mixture (NR/NBR33).

3.5 Compression set B properties change

Figure 5 informs that each blended sample has a similar compression set value before being immersed. This means that both NR and NBR resistance are relatively similar to plastic deformation. However, after the rubber blend is soaked, the compression set tends to rise with higher NBR33 to NR / NBR blends at 40/60 and drops back to pure NBR33. Figure 5 shows compression set NR / NBR33 blends at 40/60 and 50/50 tends to be lower. This was due to the lower compatibility of NR / NBR33 blends at those ratios than others. In addition, the lack of compatibility also affects the decreased tensile strength and elongation at break at the same blends before immersion that can be seen at Figure 2 and 3.

Thus, based on the physical properties, the increase of nitrile rubber ratio (NBR33) in rubber vulcanized mixture starting from 100% NR to 100% NBR33 can increase physical properties due to swelling and partial dissolution degradation which are % mass change, tensile strength, elongation and increase of hardness value. The best ratio of rubber vulcanized mixture (NR/NBR33) is 60: 40.

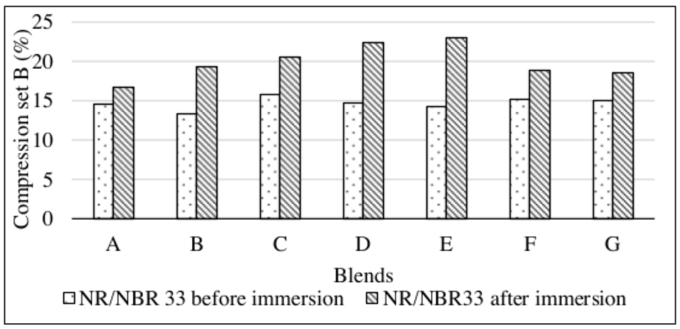


Figure 5. The compression set B change of NR/NBR33.

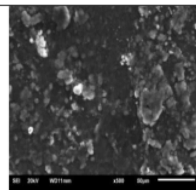
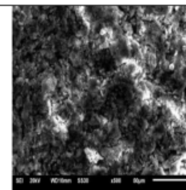
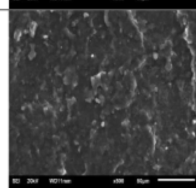
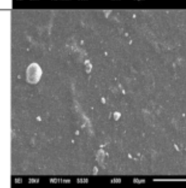
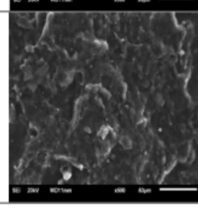
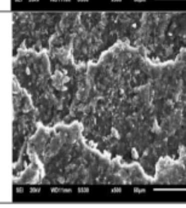
3.6 Morphology analytical (SEM)

Based on Table 3, it can be seen that pure NR before immersion has many white spots. The white spot shows uneven carbon blacks evenly distributed on the rubber molecule. This can facilitate the absorption of DME by filling an empty gap that is not filled with carbon black. While the SEM result of 50/50 NR/NBR33 before immersion shows the rougher surface due to low compatibility between NR and NBR33. Rough surfaces create an empty gap that can also facilitate DME absorption. On the other hand, pure NBR33 before immersion displays a smoother surface than others. NBR33 is very well tied to carbon black or plasticizer.

In compare to SEM result of after immersion condition, it shows failure distribution of carbon black on surface of pure NR, NR / NBR33 blends at 50/50 and pure NBR33 respectively after immersion by DME. According to pure NR, the surface of the visible rubber shrink was indicated with a rougher surface than pure NR before immersion. This was likely due to mass transfer of carbon black into the rubber due to absorption of DME. while picture 50/50 NR/NBR33 result does not look rough surface or white spot. The gap on the rubber surface was not visible, as if the rubber has a finer surface after immersion. It was possible that the bond between natural rubber and nitrile rubber prevents the presence of carbon black maldistribution. In pure NBR33 result, it was seen that nitrile rubber was not significantly altered by DME immersion. The pattern of the surface of nitrile rubber was similar to before immersion. The image proves that nitrile rubber was not easily affected by DME exposure.

Such phenomenon can be interpreted that based on SEM analysis carbon black is distributed more evenly on nitrile rubber (100% NBR33) than 100% NR before immersion, such that it has good physical properties and can prevent swelling and partial dissolution by dimethyl ether.

Table 3. SEM result of different ratio NR/NBR33 before and after immersion

Ratio (NR:NBR33)	Before Immersion	After Immersion
NR 100%		
NR/NBR33 50/50		
NBR33 100%		

4. Conclusion
The increase of nitrile rubber ratio (NBR33) in rubber vulcanized mixture starting from 100% NR to 100% NBR33 can increase physical properties due to swelling and partial dissolution degradation which are % mass change, tensile strength, elongation and increase of hardness value. The best ratio of rubber vulcanized mixture (NR/NBR33) is 60: 40 NR NBR33 and it based on changes in physical properties that meet standard criteria. Based on SEM analysis, the distribution of carbon black is more evenly in 100% NBR33 than 100% NR before immersion.

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