Moisture and Solvent Uptake in Various Types of Rubber

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***Abstract*— The moisture uptake in rubber is investigated by using the equilibrium weight content method. This method helps us to find out the maximum fluid that can be absorbed by the two rubber samples, which are natural rubber and silicone rubber. The differences in water content for both rubbers are given by their matrix composition. Silicone rubber show more resistance to fluid compared to natural rubber due to its complex helical shape. Ficks' Law was also used to know the diffusity, D of fluid in of each sample. From this study too, we could find out the behavior of rubbers in different environments as well. Distilled water, toluene, ethanol, triethyl amine and ethanol amine are used as sources of fluid. The samples exhibited various behaviours such as swelling and shrinking as a result. Natural rubber dissolved in toluene and triethyl amine. Overall, the study proved that silicone rubber is a better water resistant compared natural rubber and different solvent have different effect on rubbers.**

***Keywords*— Moisture uptake in rubber, rubbers' solvent, Fick's Law, water-swellable rubber, polymer**

I. INTRODUCTION

Rubber is a material that is critical to modern industrial civilization, with the applications are everywhere around us. However, rubber is probably are the least understood material that engineers use.

According to general beliefs, rubber is believed to be waterproof. However in contrary, rubber will absorb moisture until it is completely dispersed and saturation has been reached. Before synthetic rubber first discovered, natural rubber proved to be waterproof. The addition of different and new composites material may change the composition and matrix of the rubber. This is also afraid to cause the synthetic rubber to losses its original characteristics of natural rubber[1]. It is important to know whether a rubber is waterproof or how much moisture can they absorb in order to predict their long-term behaviour.

Polymer does not corrode via the same mechanisms as metals, when exposed to moisture, hazardous solvents, UV radiation. In spite of that, they have a tendency to undergo plasticization and degradation[3]. They also behave differently according to these environments. This results in deterioration of mechanical properties and reduction in the life of composite structures. Therefore, the transport behaviour of various organic solvents and gases through rubber, is of great technological importance and it plays a vital role in a variety of barrier applications[2].

It is shown through many studies and experiments before that different types of rubber has different maximum uptake of moisture. Pure rubber (latex) can only absorbs a relatively small amount of moisture. Purification of the commercial rubber hold the keys to prevention of rubber's water uptake. Vulcanized rubber shows the same relative characteristics of the original rubber it is made from [4].

In another experiment, Flushin had an objectives of finding out the absorption of fluid by rubber in connection with its use as a semipermeable membrane in osmosis determination. The results he obtained was somewhat similar to the experiment by Hancock. Flushin concluded that rubber can be classified is a comparatively inactive absorbent of fluid [5].

The swelling properties of filled natural rubber/linear low density polyethylene blends was investigated by Ahmad et al.[6] and was found that the swelling index decreased with increase in filler loading when immersed with various types of solvent[7] . For immiscible blends, the nature of the two blends involved and the interface affect the transport properties. Solvent resistant properties of nano-structured layered silicates filled blend of NR, and carboxylated styrene butadiene rubber (XSBR) were investigated by Stephan et al.[8].

According to Hopfenberg and Frish [9] (Hopfenberg HB, 1969), when the solvent penetrates into the solute, several transport mechanisms could occur. This could be shown in figure below:

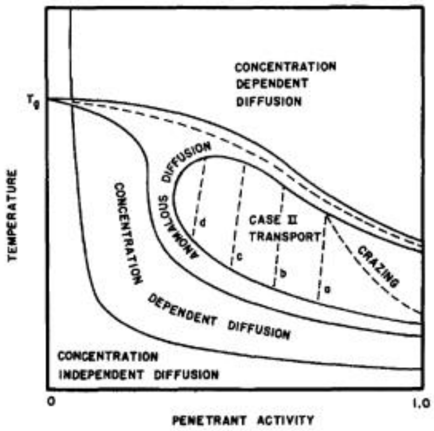


Figure 1: Relationship between environment temperature and penetration activity on the likelihood sorption transport in a solvent-solute system [9].

These are a few moisture absorption mechanisms and phenomena. One of them is concentration independent Fickian diffusion. According Fickian diffusion, the water is able diffuse into the materials through atomic motion[10]. Spherical water molecules can move randomly (Brownian motion) and fill in between the voids (sub-microscopic network and free volume) of the material network by concentration gradient[10].

Other than that, Non-Fickian or also known as anomalous are also one of the mechanism for fluid transport. Anomalies or non-fickian occurs when the moisture mobility and the stress relaxation rate in the polymer are almost similar to each other which usually happen below the glass transition temperature, Tg. The low crosslink density area surrounding the fibres that creates a preferential diffusion path for the water molecules is caused by non-Fickian response in composite materials[11].

Another mechanism of water uptake is called adsorption. The phenomenon of the adsorption can be described as that when the polar water molecules form an interaction with the polymer network. Then, the hydrogen bonds is formed with hydroxyl groups in the polymer chain. They are formed when inter-chain hydrogen bonding is modified. This subsequently interrupts the cross-linking in the polymer network, the intersegmental hydrogen bond length is therefore augmented. Anomalous diffusion is pmore noticeable in the polymer that displays large chain-chain interactions due to small size, regular spacing and polar nature of the hydroxyl side groups [12].

Hydrolysis is the chemical reaction to describe the binding of the water molecules to the rubber and polymer chains. In a rubber and polymer, the level of the hydrolysis depends on the number of the groups available in the polymer macromolecular chains that could react chemically with water molecules. Hydrolysis has the possibility to reduce the cohesive mechanics of the molecular network and increase the mobility of the molecules. Hydrolysis leads to the degradation of the molecular structure. This, as a result cause the polymer to loss its mechanical properties of the polymer[12]. In fact it is found out by Long and Thompson [11] that hydrogen bond is responsible for degrading the material properties.

In order to investigate the rate of moisture and solvent uptake in rubber, different factors should be taken into considerations. This is because different factors will affect every rubber's behavior and give different results in the rate of uptake. According to George and Thomas[13], these are a few factors that affect the transport degree in polymer and rubber.

The first factor is the nature of polymers. The nature of the polymer is the most factor for the moisture transport. According to George and Thomas [13], the diffusion of moisture is affected by the unoccupied volume within polymer and segmental mobility of the polymer chains directly

Another factor is the nature of cross-links. Through many studies that have been conducted, it is known that higher chain network flexibilities could enhance the maximum solvent uptake of the polymer and increasing the crosslink density could decrease the permeation rate [14]. According to, T. P. Mohan, Job Kuriakose and K. Kanny [8], water uptake of base rubber continuously reduces as nanoclay content increase in rubber matrix. Thus, the mechanical properties of base rubber is severely affected due to moisture uptake compared to nanoclay filled rubber composites.

The sizes and the shapes could also affect the moisture and fluid uptake in rubber. It was reported that when size of substances that penetrates the rubber surface increases, the diffusivity decreases . Besides, increasing the chain length of the penetrant was found to decrease the equilibrium penetrant uptake. In addition, some research works found that higher diffusion coefficients were attained in flattened or elongated molecules compared to spherical molecules or equal molecular volume [15].

Last but not least, the temperature is also one of the factor to consider when investigating the rate of moisture and solvent uptake in rubber. Lv et al. [16] revealed that high temperature has the ability to increase the molecular chain relaxation, decrease Tg and thus weakened the strength of the molecules' bonding. This caused space formation between molecules and enhanced water ingression. Water absorption and maximum moisture content were thus increased and the samples were attacked in a more aggressive way.

From the studies that have been done before, it can be said that different type of rubber has different maximum uptake of moisture. Amount of moisture absorbed by rubber has impact on its thermal stability and mechanical property. So as its electrical property. Thus, from this study, we need to find out the appropriate moisture uptake of rubber to determine the quality of them before they are turn into product.

II. METHODOLOGY

A. Materials

The most important materials that are required in this experiment is the rubber samples. Two samples of different types of rubbers which are silicone rubber and natural rubber are prepared specifically for this experiment. The two results obtained from the two rubbers can be compared. Thus, a clear conclusion on which type of rubber has the better resistant to moisture can be made. The samples is obtained from local rubber factory.

Other than rubber samples, various types of fluid of certain amount is also required as a medium of moisture for the samples. Five mediums from various chemical group are prepared which are distilled water, toluene solvent, ethanol solvent, triethyl amine and ethanol amine. Both samples will be immersed in the water bath. Finally, a few tissue paper also is needed to dry the samples

B. Process Methodology

The samples of silicone rubber and natural rubber is made by cutting them into the dimensions of 20 mm x 30 mm x 3 mm. The samples are weighed by using electronic balance with an accuracy level of 0.5 mg and the initial weights are recorded as $W_{o.}$

The five mediums are prepared in different closed containers and let at room temperature. All ten specimens is put in the mediums and are soaked throughout the experiment. The samples are taken out and dried using tisuue paper by blotting them lightly to remove the excess moisture content. The specimens are weighed at specific interval and the weight after drying is, W_t is recorded. The water and solvent content, Wc is calculated at every interval by using formula[8],[9]:-

$$Wc = \frac{(W_t - W_o)}{W_o} \quad (1)$$

Wc is meaured until the samples obtained equlibrium water uptake content which means there is no more uptake by the rubber samples. The water transmission rate (WTR) of each samples are also calculated by using the Eq.(2)[8]:-

$$WTR = \frac{Weight\ of\ equilibrium\ water\ content\ (g)}{TSA\ (m^2)\ x\ Time\ to\ reach\ equilibrium\ (days)} \quad (2)$$

where, the TSA is the total surafce area of the samples, considered as is exposed to water in all directions. The graph of moisture uptake against time, $\sqrt{t}$ is plotted. The WTR for both type of rubber is compared and analyzed.

The value of D for each sample or the diffusion coefficient of a solvent molecule through a polymer membrane is obtained by obeying the Fick's Second Law:-

$$D = \pi \left(\frac{M_t L}{M_E 4t}\right)^2 \quad (3)$$

Where D is the diffusivity, Mt is the weight of water content at time t, M_E is weight of samples at the equilibrium Wc, L is the sample thickness, and t is time in days.

III. RESULTS AND DISCUSSION

A. Moisture uptake in rubbers

From the results, it is shown that the water uptake for both types of rubber increases as function of time. Even with different environments surrounding the samples, the moisture uptake still showed the same phenomena. Figure 3 shows the water content,Wc vs √t for NR and silicone in all three medium. Throughout the experiment, the rubber samples are immersed in the distilled water which allow the water molecules to diffuse in and out of the rubbers' surface continuously. The movement of the fluid along the concentration gradient is known as molecular diffusion. As shown in Figure 5, the water molecules then move in-between the void of the rubbers' surface and fill them. When the voids are fully filled, there will be no more water uptake by the rubbers. That is when the equilibrium water uptake is achieved[16].

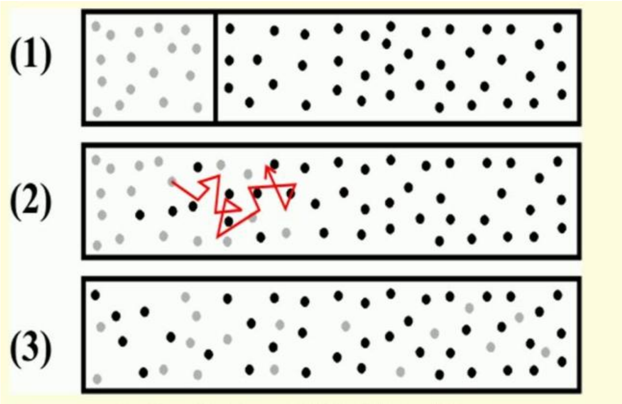
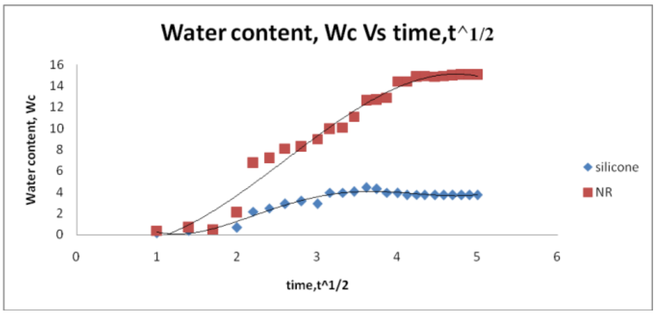
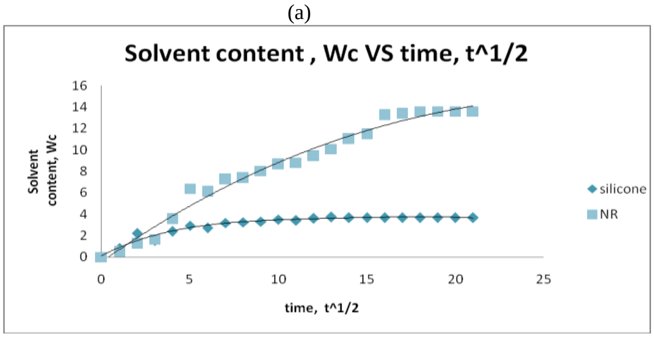


Fig 2 : (1) the initial region, high concentration of fluid (solvents) and low concentration of fluid in rubber. (2) the molecules moves from high to low region concentration and mixed together. (3) equilibrium state is achieved and no more movement between the region[16].

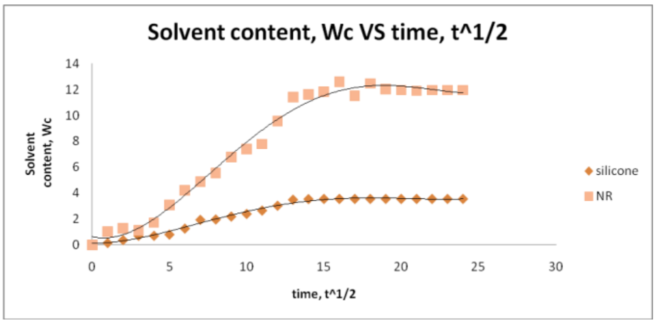
From the experiment, the results for water and solvent content in the rubber samples as shown in Figure 3.



(a)



(b)



(c)

Fig 3 : The Wc vs $\sqrt{t}$ graph for (a) distilled water (b) ethanol (c) ethanol amine showing the increase of Wc as the time increases.

B. Natural rubber(NR) Vs Silicone rubber (SR)

For every condition used in this experiment, it can be said that silicone rubber has a better resistance to moisture compared to natural rubber. This is due to its composition. As can be seen in Figure 4, their molecules are helical in shape and its intermolecular force is low. Furthermore, the methyl group located on the outside the coil structure gives them the freedom to move freely[17]. Thus, instead of altering the structure, the molecules move around when in contacts with the solvents and then go back to its original helical shape.

This is one of the characteristics that natural rubber lacks of. Its composition is loosely arranged making it easy for the fluid to penetrate them.

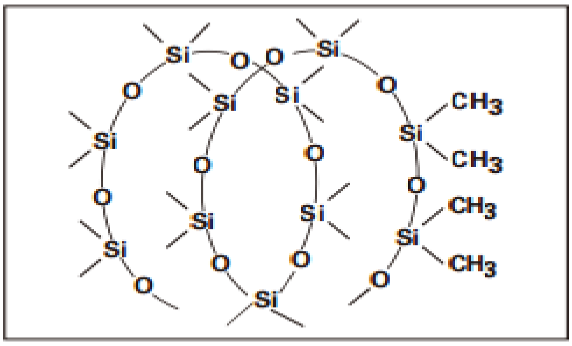


Fig 4 : The molecular structure of silicone rubber showing the methyl group that can move freely. This gives silicone the advantages of resistance to moisture.

As observed in Table 1, not only silicone rubber exhibited a lower equilibrium water content, but they also have a lower diffusion coefficient compared to natural rubber. The larger transmission rate indicated the fluid uptake in silicone rubber is higher making them reach the equilibrium faster. The slowest to reach equilibrium is the natural rubber sample with 25 days.

Both natural rubber and silicone are water-absorbing and fluid-absorbing polymers, also known as superabsorbent polymer (SAP). They bond with their respective aqueous solutions' molecule with hydrogen bond[18]. The total absorbency and swelling capacity are controlled by the type and degree of cross-linkers used to make the their structure. Low-density cross-linked SAPs such as natural rubber generally have a higher absorbent capacity and swell to a larger degree. Eventhough high cross-link density polymers such as silicone swells, they still exhibit lower absorbent capacity and swelling compared to low-density cross-linked polymers. Moreover, according to El-Sabbagh, S. H., et. el[19],

even a little increase in cross link density gives a better reinforcing effect of polar of the rubber matrix. This reinforcement, due to better
interaction between polymer and clay, reduces the penetration of solvent molecules. This, in return reduces the diffusivity of the rubber. The schematic in Fig. 5.4 a&b shows how forming of a network, and how at high concentration the clay agglomerates together, reducing the interaction between clay and polymer.

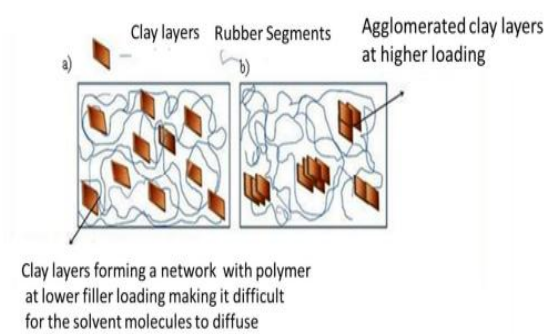


Figure 5 : Schematic showing the clay network a)at lower loading and b) aggregates at higher loading[19]

Table 1 : moisture uptake properties of rubber samples.

Type of rubber	Natural rubber			Silicone		
	Wc, %	WTR (g/mm^2.day)	D (10^{-3} mm^2/s)	Wc, %	WTR (g/mm^2. day)	D (10^{-3} mm^2/s)
Distilled Water	15.0	1.94	1.64	3.73	1.67	0.55
Ethanol	13.6	1.70	3.54	3.68	2.11	1.34
Ethanol Amine	11.9	1.44	2.99	3.35	2.06	2.95

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C. Effect of different solvents on rubbers' behaviour

Each sample is immersed in various types of medium and their behaviours are investigated. Their behaviours varies according to the particular mediums. While the samples in distilled water, ethanol solvent and ethanol amine only undergo swelling , the samples in toluene solvent and trietyhl amine showed an interesting behaviour. The natural rubber in both solvents swell and dissolved completely after a week. On the other hand, silicone rubbers swells enormously. However, when they are taken out from the solvents, they return back to their original volume.

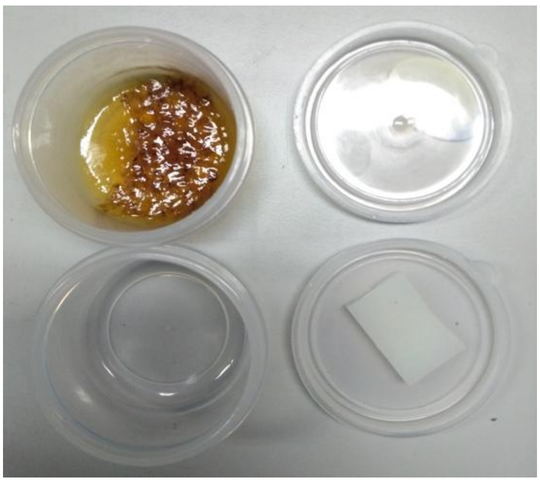

Figure 6 : Above, the natural rubber that has dissolves in toluene, Below, silicone rubber after it has been taken out from toluene.

Dissolution of polymers involves a slow process called salvation. The solvent molecules are absorbed on the surface of the polymer molecules, and then they diffuse into the bulk of the polymer resulting in an increase in the average dimension of the polymer molecule, a phenomenon known as swelling. This swollen polymer, if in a good solvent gradually disperses to yield a polymer solution[20].

A good solvent is one which is highly compatible with the polymer; the liquid-polymer interactions expand the polymer coil, from its unperturbed dimensions, in proportion to the extent of these interactions[20].

The forming of polymer solution can also be explained with the interaction of long chain molecules with liquids. For branched polymers (e.g natural rubber), usually will dissolve the polymer completely to form a homogenous solution while crosslinked polymers will only swell when in contact with the compatible liquids. When an amorphous polymer is mixed with a suitable solvent, it disperses in the solvent and behaves as if it is liquid[20].

Polar molecules have an uneven charge distribution. Chemical groups, such as alcohols, carboxylic acids, ketones, aldehydes, amides and nitriles, make a molecule more polar. Increasing solvent polarity typically decreases the extent of swelling; Indeed, many short-chain alcohols, including ethanol are compatible with natural rubber and silicone rubber[21].

Just like other studies that have been done before, this study could be used in the development of rubber industry as rubber is one of the most used material in the world. Rubber especially the one that is used for automotive tires are exposed to constantly severe wear and moisture environment. Due to this moisture and wear environments, rubber tires tend to lose its mechanical and thermal stability. Hence, this will affects their long-term performance. This necessitates a study on the improvement of this material in these environments.

There a few recommendations that can be done to contribute to the improvement. One of them is by using an appropriate concentration of the fluids. In another experiment that is done in this study, the natural rubber is immersed in diluted toluene with ratios of 1:10 and 1:20. In both medium, the natural rubber show swelling to average level instead of dissolving like in the previous experiment.

Addition of plasticisers in the polymer increases the segmental mobility and the penetration transport. As a result, the diffusion coefficient will increase and solubility coefficient will decrese[22]. Hence, polymer with lower plasticisers are preferred for uses in industries. Reinforcement could also improve the behavior of the rubber. Swelling is decreased with an increase of fibre content and addition of bonding agents[22]. Generally, increasing temperature decreases the solubility, increases diffusivity and increases moisture content because the increment in the driving forrce is greater than the 30 decrement in the solubility. Thus, whenever the application of rubber material involve temperature, use a polymer that can withstand high temperature.

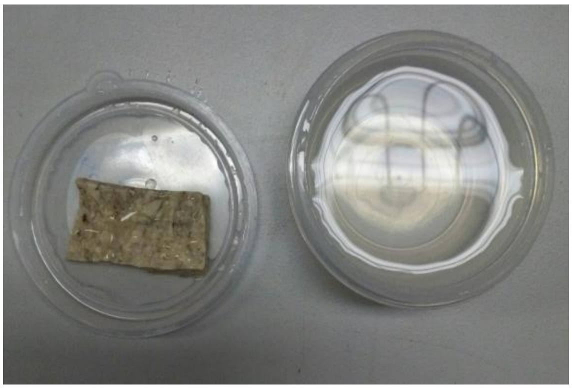

Figure 7 : Natural rubber in diluted toluene exhibit an average Swelling and does not dissolve in the solvent.

IV. CONCLUSION

The paper focuses on the moisture uptake in two rubber samples. They are natural rubber and silicone rubber. Diffusion take place in the medium using the concept of concentration gradient. Therefore, the fluid which is the high concentration region diffuse into the rubbers' composition which has lower concentration. The moisture uptake by the rubbers increased throughout the experiment. Moisture concentration gradient is weakened as the diffusion continues. When equilibrium is attained, the net diffusion is equal to zero.

From the calculation of the moisture uptake behavior (Wc, WTR, and D) it can be concluded that natural has lower water resistance to moisture. Higher water content, Wc showed that NR is more permeable to fluids surrounding them. This is supported by its high value of diffusion coefficient. On contrary, silicone rubber does absorb moisture and swell, but only at lower level.

A good solvent can dissolves a polymer completely and produce polymer solution. Thus, it is clear that toluene and triethyl amine are good solvents for natural rubber. In most application in the industry, this can be disadvantages as it can reduce its mechanical and thermal properties. Thus, to know which solvent is compatible with certain polymer, we can identify them according to a few aspects.

First, the crosslink of the rubber's composition plays an important role in determining the behavior of the rubber. Rubber with high density crosslink such as silicone has lower swelling. Then, the polarity of both rubbers' sample and the solvent also matters. The higher the polarity differences between the solvent and rubber, the lower the extent of swelling. Lastly, for certain solvents, their concentration can decrease the swelling because there are less molecules' attack on the rubber surface.

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