Swelling Resistance and Tensile Strength of Natural Rubber (NR) and Carboxylated Nitrile-Butadiene Rubber (XNBR) Latex Blends

S.Azemi[1], M.Y. Amir[2], A.R. Ruhida[*]

[1]Polymer Department, Faculty of Applied Sciences
Universiti Teknologi MARA (UiTM)
40450 Shah Alam, Selangor,
Malaysia

[2]Lembaga Getah Malaysia
145, Jalan Ampang
50250 Selangor
Malaysia
*ruhida@lgm.gov.my

Abstract:

Natural rubber (NR) latex glove possesses superior mechanical properties compared to many synthetic glove, but it has a relatively poor oil swelling resistance and this limit the application in food handling industry, especially for food containing oils and fats. In this study, differently sulphur content crosslinked NR latex and NR blended with compounded carboxylated nitrile (XNBR) latex to improve the films' oil swelling resistance. The tensile properties of NR latex film and NR:XNBR latex film was evaluated before and after exposure to cooking oil. As expected, the increasing the XNBR content improved swelling resistance due to increase in the polarity, which reduced the oil mass uptake and decreased the diffusion coefficient. The results indicated that the optimum blend at a ratio 80 part NR to 20 part XNBR with 1.5 pphr sulphur content gave the optimum acceptable swelling resistance and tensile properties.

1. Introduction

Natural rubber (NR) is a non-polar rubber that has excellent mechanical properties but relatively poor swelling resistance [1] and thus limits its applications particularly in the fast-food industry. In order to improve the swelling resistance, one can use nitrile rubber (NBR), since it is polar in nature. The carboxylated NBR has a good swelling resistance as compared to NR latex but the former is more expensive than a latter. For this reason, XNBR latex is blended with NR latex in order to optimize the swelling resistance and cost. Besides that, the swelling resistance of NR latex film can be increased to a limited extent by increasing the crosslink concentration of the latex film [1].

Although XNBR is more expensive than NR but blending these two rubbers together is one of the best solutions to gain a good mechanical properties and swelling resistance [2]. *K. Vivayganathan* has found that by blending NR with XNBR could improve mechanical properties and oil resistance [3]. This paper describes the preparation of NR latex film at different crosslink concentration and blends NR with XNBR at 80:20, 50:50 and 20:80 ratios at 1.5 pphr and 2.0 pphr sulphur content. The experiment involves the measurement of mass uptake of cooking oil and diffusion coefficient of cooking oil through NR and NR: XNBR vulcanisate films and the reduction of tensile property of NR and NR: XNBR after exposure to cooking oil. The effect of crosslink concentrations and carboxylated nitrile (XNBR) content on swelling resistance and tensile property of NR and NR blends with XNBR latex at certain ratio vulcanisates films were studied in order to determine the optimum level of blend ratio of NR and XNBR latex films that produce an acceptable swelling resistance.

2. Experimental Method

2.1 Materials

The high ammoniated (HA) latex (Lee Rubber, Malaysia) and XNBR with acrylonitrile content of 46% (Synthomer 6311, Malaysia) were used in this study. Sulphur dispersion is used as a crosslink agent and cooking oil was used as a swelling agent.

2.2 Preparation of NR latex film

The NR latex films were prepared from latex mixes with varying amount of sulphur as shown in Table 1 [6]. The NR latex compound were diluted to 40% total solid content and stirred for one hour. Then the compound was left for maturation at least 24 hours at room temperature (28ºC). After maturation, the latex compound was stirred for one hour and allowed to stand at room temperature for at least one hour before dipping process. The NR latex films were prepared by dipping calcium nitrate coagulated glass plate into the prepared latex mixes. The latex film was leached in distilled water at 70˚C for one minute before drying at 70˚C for 20 minutes and curing at 110°C for 15 minutes. Cornstarch was used for stripping purposes.

Table 1. Formulation for NR latex compounding (Part Per hundred Rubber)

Ingredients	**1**	**2**	**3**	**4**	**5**	**6**	**7**
60% HA latex concentrate	100	100	100	100	100	100	100
50% Sulphur dispersion	0.2	0.6	1.0	1.5	2.0	2.5	3.0
33.3% ZDBC	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50% Zinc oxide	0.2	0.2	0.2	0.2	0.2	0.2	0.2

2.3 Preparation of NR: XNBR Latex Blends

The blends of NR: XNBR were prepared at 80:20, 20:80, and 50:50 ratios. Firstly, the XNBR latex was compounded with 0.5 phr ZnO and adjusted to pH 10 with 5% potassium hydroxide (KOH) before blending with natural rubber compound. Then the NR compound was prepared by adding the ingredients as shown in Table 2 and Table 3. The NR and XNBR compounds were then allowed to stand overnight separately before blending and dipping process as described elsewhere [3].

Table 2. Formulation for XNBR compounding before blending with NR latex

Ingredients	pphr	
46% XNBR	100	100
50% ZnO	0.5	0.5

Table 3. Formulation for NR latex compounding at two different sulphur content before blending with XNBR compounding

Ingredients	1	2
60% NR latex	100	100
10% KOH	0.1	0.1
20% Potassium laurate	0.5	0.5
50% Sulphur	1.5	2.0
33.3% ZBuD	1	1
50% ZnO	0.5	0.5
33.3% Wingstay L	0.5	0.5

2.4 Swelling Measurement

2.4.1 Crosslink concentration and mass uptake of cooking oil

Circular shaped samples (diameter at 23 mm) were cut from NR latex and NR:XNBR vulcanized latex film at various crosslink concentration and the thickness of the samples was measured with accuracy of ±0.01mm. Initial weight the cut film was taken before immersed into swelling agent (cooking oil) at room temperature. The swollen sample was blotted with filter paper to remove the excess oil on the surface and edges of the sample. Then the sample was re-weighed on the electronic balance and re-immersed into cooking oil. The procedure was continued until the equilibrium oil uptake was achieved. The results of these experiments were expressed as mass-uptake of oil per unit area of the samples, [4] (g mm^{-2}) and calculated base on the following equation (1);

$$\text{Mass uptake} = \frac{W_1 - W_0}{A_o} \ (\text{g mm}^{-2}) \quad \ldots.(1)$$

W_0 and W_1 are the weights of the sample before and after swelling, respectively. A_o is the surface area of the sample.

The crosslink concentration of NR latex film was determined by using the equilibrium volume swelling method based on Flory-Rehner equilibrium swelling equation as stated in equation (2) below [9]:

$$-\ln(1 - v_r) - v_r - \chi (v_r)^2 = 2\rho V_o (ŋ)_{phy} v_r^{1/3} \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Where, $(ŋ)_{phy}$ is manifested crosslink concentration , V_o is molar volume of toluene.
For toluene, V_o is 103.11 cm^3 , □□□□□□□□□□□□□□□□□□□□□ □□□□ χ is 0.37 (Higgin rubber-solvent interaction parameter) [10] and ρ is density of rubber hydrocarbon (0.919 g/cm^3)

2.4.2 Diffusion coefficient (D) of cooking oil

The diffusion coefficient , D of cooking oil through NR and NR:XNBR latex films at various crosslink concentration and at 1.5 pphr sulphur content were evaluated from the plotted graph of mass uptake against square root of time . The diffusion coefficient is calculated according to the equation (3) below:

$$\frac{M_t}{M_x} = \frac{2}{l} (D.t/\pi)^{1/2} \quad \ldots\ldots(3)$$

Where, M_x is the amount of oil absorbed at infinite time, M_t is the total amount of liquid which as crossed unit area of the boundary interface at time t in second and l is a half thickness of the sample film. The diffusion coefficient, D can be obtained from the initial slope of the graph of M_t against square root time together with equilibrium concentration of oil in rubber [4].

2.5 Tensile Strength of NR and NR:XNBR Latex Films Before and After Exposure to Cooking Oil

NR and NR:XNBR latex films were cut into a dumbbell shape before immersed in glass tube containing 70 ml cooking oil for three days. Tensile properties were measured on that particular day by using a tensile machine (Instron 5565) with crosshead speed at 500 mm/min. All sample dimensions were measured according to ASTM D 412 [5]

3. Results and Discussion

3.1 Relationship between Sulphur Content and Crosslink Concentration

Figure 1 shows relationship between sulphur content and crosslink concentration. The crosslink concentration increases almost linearly with sulphur content, hence the higher the sulphur used, the more crosslink formed in the network. The coefficient of correlation, R equal to 0.9297 is good indicating very good correlation between crosslink concentration and sulphur content.

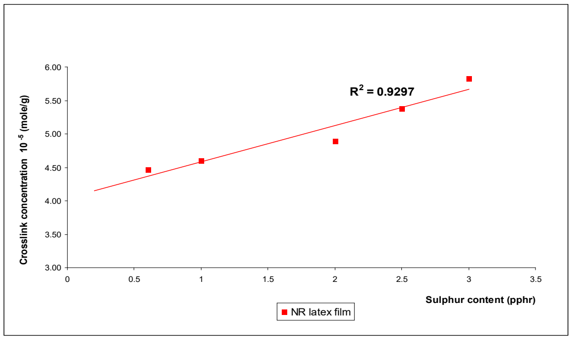

Figure 1: The crosslink concentration of NR latex films at different sulphur content.

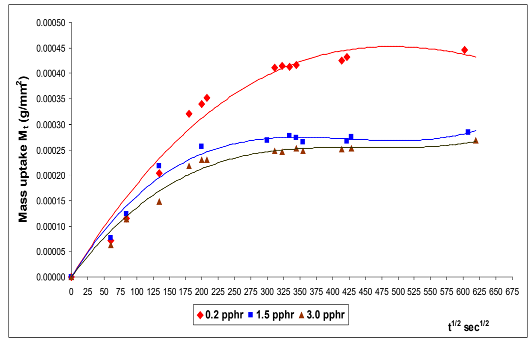

Figure 2: Mass uptake (g/mm^2) of cooking oil against square root of time through NR latex film at 0.2 pphr, 1.5 pphr and 3.0 pphr sulphur content.

3.2 The Mass Uptake of Cooking Oil through NR Latex Film and NR: XNBR Latex Film

The results of mass uptake of cooking oil on the NR latex films at different sulphur content are shown in Figure 2. There are two important observations here. First at particular sulphur content the mass uptake increased progressively with time since mass uptake is controlled by diffusion process, so the longer time more oil diffuses into a rubber matrix. Second at a particular time, the mass uptake decreased as the sulphur content increased. This is attributed to the increase in the crosslink concentration as the sulphur content increased. The increased in the crosslink concentration retard the diffusion rate of the cooking oil by providing physical barriers against the oil transport. Table 4 and Table 5 show the mass uptake of cooking oil at equilibrium state on the NR latex film at various crosslink concentration and NR: XNBR vulcanised latex at different blend ratio at 1.5 pphr sulphur content. The equilibrium state may be depending on the crosslink concentration of the film samples.

Table 4. The mass uptake of cooking oil (M_x) at equilibrium state on NR latex film at various crosslink concentration

Sulphur Content (pphr)	M_x x 10^{-4} (g/mm^2)
0.2	4.15
0.6	3.65
1.0	3.10
1.5	2.80
2.0	2.75
2.5	2.65
3.0	2.55

Table 5. The mass-uptake of cooking oil at equilibrium state on NR:XNBR latex with 1.5 pphr sulphur content at different blends ratio

NR:XNBR Blend ratio	M_x x 10^{-4} (g/mm^2)
80:20	2.13
50:50	1.56
20:80	0.71

Figure 3 compares the mass uptake of natural rubber latex film and NR: XNBR blend latex film at the same sulphur level. Although the sulphur level is the same, but the crosslink concentration may not necessarily be equal because the chemistry of vulcanisation of the blend is different from that of natural rubber. The most important point is that effect of blending NR with XNBR has reduced the mass uptake substantially. The effect of increasing polarity of the latex is more effective means of improving the swelling resistance towards cooking oil than by increasing the crosslink concentration.

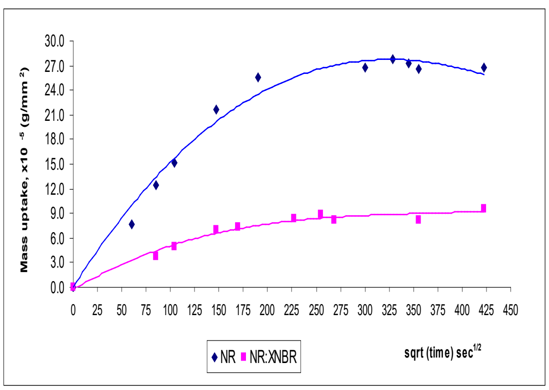

Figure 3: The mass-uptake of cooking oil on the NR latex film and NR: XNBR blend latex film at 50:50 ratio with 1.5 pphr sulphur content .

Figure 4 shows a large effect of acrylonitrile level on swelling resistance of NR: XNBR blends vulcanisate latex films. It is well established that the swelling resistance of NBR is dependant on the acrylonitrile content [8] .The acrylonitrile content influences the films strength, oil resistance and mechanical properties. [6,7]. There is a steady decrease in the mass uptake of cooking oil of the NR: XNBR vulcanised blends on increasing the nitrile component in the blends. However, there was a slight effect of mass uptake of cooking oil when the sulphur content was increased from 1.5 to 2 pphr. This indicates that effect of polarity outweighs the effect of crosslink concentration.

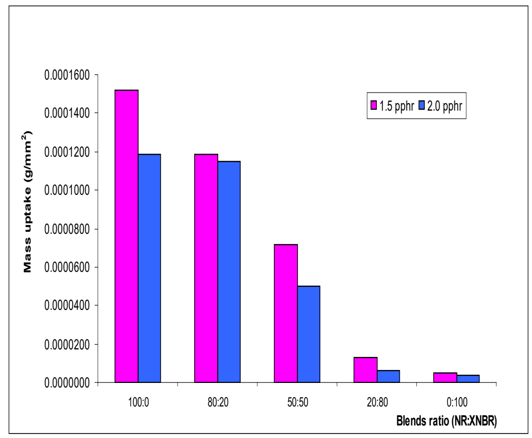

Figure 4: The mass uptake of swelling agent at different NR: XNBR latex films at different blends ratio after exposure to cooking oil.

3.3 Diffusion coefficient, D through the NR Latex Film and NR: XNBR Vulcanised Latex Film

The diffusion coefficient was calculated once the equilibrium state has been reached. Table 6 and Table 7 show the diffusion coefficient of oil through NR latex films at various crosslink concentration and NR: XNBR latex at different blends ratio respectively. The results of the absorption rate ($M_t/t^{1/2}$) and diffusion coefficient, D decreases as the crosslink concentration increased. This might be attributed to retarding effect on the diffusion rate since high number of crosslinks provides more physical barriers than that of lower crosslink concentration. The effect of crosslinking is to restrict the mobility of rubber molecules so the diffusion coefficient is reduced. In the case of NR:XNBR latex at different blends ratio, once the content of XNBR increases the diffusion coefficient, D decreases. These indicate that the polarity component in XNBR provides chemical resistance toward oil [6].

Table 6. Diffusion coefficient, D of NR latex at different crosslink concentration.

Sulphur Content (pphr)	$(M_t/t^{1/2})$ (g/mm^{2}sec$^{1/2}$) x10^{-6}	Diffusion Coeficient D, (m^2/sec)
0.2	1.88	4.14
0.6	1.58	3.53
1.0	1.68	3.62
1.5	1.56	3.81
2.0	1.29	3.36
2.5	1.25	3.18
3.0	1.18	3.06

Table 7. Diffusion coefficient, D of NR:XNBR latex at different blends ratio with 1.5 pphr sulphur content.

NR:XNBR Blends ratio	$(M_t/t^{1/2})$ (g/mm^{2}sec$^{1/2}$) x10^{-6}	Diffusion Coefficient D, (m^2/sec) x 10^{-13}
80:20	1.19	2.98
50:50	1.56	1.10
20:80	0.23	0.95

3.3 Tensile Properties of NR Latex Film and NR: XNBR Vulcanised Latex Film

The result on Figure 5 shows the tensile strength of NR latex before and after exposure to cooking oil against at various crosslink concentration. It can be seen that the tensile strength increases progressively up to 4.6 x 10^{-5} mole crosslinks per gram. At low crosslink concentration, the number of chain segments is low and thus unable to support high tensile force. It is easier for the rubber to react to deformation stress by viscous flow than by crystallization. Thus the stress is dissipated before it is sufficiently high to effect reorientation and crystallization. As more crosslinks are introduced and crosslink concentration increases, the network can support large stresses and viscous flow no longer feasible. Consequently, the chain molecules are reoriented to effect crystallization which enhances tensile strength. Then, at crosslink value greater than 4.6 x 10^{-5} mole crosslinks per gram, tensile strength begin to decrease with increasing crosslink concentrations. The reason is due to the shortening of chain segments and tightening of the network which imposes restrictions on re-orientation of molecules. Consequently the degree of crystallinity reduces and hence tensile strength decreases.

However, after the NR latex film was exposed to cooking oil for three days, the tensile strength and modulus of NR latex film decreased drastically. The tensile strength of NR latex film is gradually decreased after 4.6 x 10^{-5} mole crosslinks per gram. This is because in part oil that absorbed into the rubber matrix reduces hysteresis (energy dissipation), and in part the oil softens the rubber matrix and hence not strong enough to resist high stress and break easily.

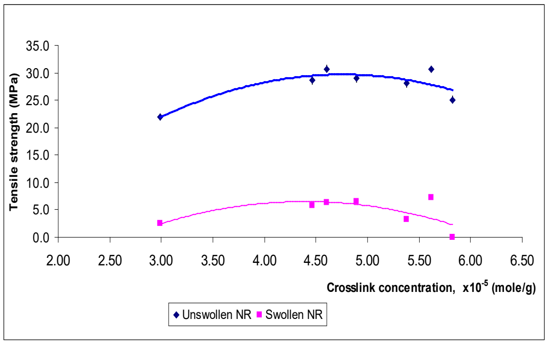

Figure 5: Tensile strength of unswollen and swollen NR latex films at various crosslink concentration.

The effect of blend ratio on tensile strength of the latex film containing of 1.5 pphr and 2.0 pphr of sulphur respectively, before and after exposure in cooking oil for three days as shown in Figures 6 and 7. There is a general trend where the tensile strength of rubber blend decreases as NR component decreases to 50 per cent. Below 50 per cent, the tensile strength increases again.

After exposure in cooking oil, the tensile strength of NR latex film decreased. This is due to poor swelling resistance of NR. However, when the two rubbers are blended, the low tensile strength with decreasing NR content might be associated with uneven distribution of crosslink in the two rubber phases and sulphur prefers to go into NBR phase because of the polar nature sulphur and NBR [11,12]. The crosslink concentration in NR phase is lower than XNBR phase. As a consequence, the NR phase is unable to strain-crystallize to it fullest because the crosslink concentration is too low to support high stresses to cause reorientation and molecular allignment necessary for crystallization. The lower crosslink concentration in the NR phase is also responsible for the very low tensile strength after exposure to oil. The NR phase is highly swollen because of its non-polar nature as well as its low crosslink concentration. Thus, the highly swollen NR phase provides sites for failure initiation. As the XNBR content increases more than 50 per cent, tensile strength increases again since the NR component which acts as failure initiation becoming low.

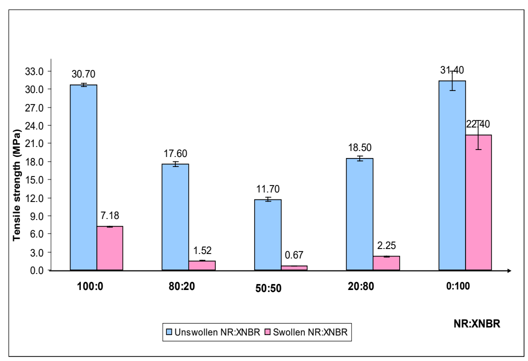

Figure 6: Tensile strength of unswollen and swollen NR: XNBR latex film at different blends ratio at 1.5 pphr sulphur content.

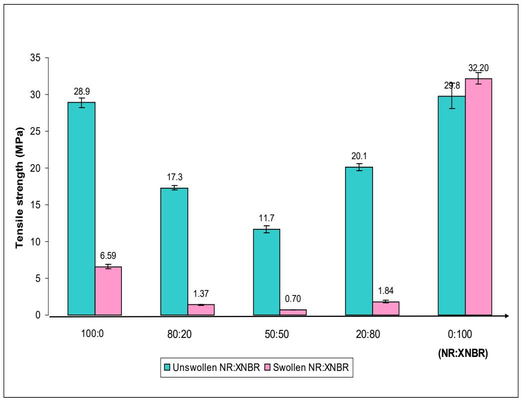

Figure 7: Tensile strength of unswollen and swollen NR:XNBR latex film at different blends ratio at 2.0 pphr sulphur content.

4. Conclusion

The swelling resistance of NR latex films improved with crosslink concentrations. It is found that the diffusion coefficient decreased by about 26 per cent, as the crosslink concentration increased by a factor of 1.9. Blending NR with XNBR, the swelling resistance improved substantially. Blend at ratio 80 part NR to 20 part XNBR with 1.5 pphr sulphur content gave oil absorption rate 1.3 times slower compared to NR latex film with similar sulphur content. However, the tensile strength reduction of NR latex film and NR blend (80:20) with 1.5 pphr sulphur content was 77 per cent and 91 percent respectively. Considering the cost reduction and swelling resistance, the optimum acceptable of physical properties concluded at 80:20 (NR: XNBR) blend ratio.

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