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Effect of Different Preparation Methods on Crosslink density and Mechanical Properties of Carrageenan filled Natural Rubber (NR) Latex Films

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Abstract

This research discussed the influenced of different preparation methods of Carrageenan fillers as new natural biodegradable additives in Natural Rubber (NR) latex compound. NR latex compounds with addition of 2 phr Carrageenan fillers was prepared through normal pre-vulcanization method which the NR latex compound was subjected to 70°C denoted as Method 1. The preparation of NR latex compounds with 2 phr Carrageenan fillers without temperature is denoted as Method 2. The unfilled NR Latex films also was prepared as a control through Method 1. The crosslink density and mechanical properties of NR Latex films were investigated via swelling test and mechanical testing (tensile and tear) respectively. The swelling test results shows that Method 2 have highest crosslink density where the crosslink density and mechanical properties via Method 1 shows a decreased value. This may contribute from the hydration of carrageenan at temperature of 40°C-70°C. The experimental results indicate that the addition of carrageenan with elimination of pre-vulcanization step is mainly responsible for the enhancement of crosslink density and mechanical properties compared to Method 1. Method 2 gives higher crosslink density, tear strength and lower modulus as evaluated from the mechanical properties. Carrageenan can be added as natural filler in NR Latex films with gives better interaction between rubber matrix and fillers with softer NR latex films which required in NR latex products especially gloves.

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1. Introduction

Natural Rubber (NR) Latex is a natural commodity resource that has tremendous economic and strategic importance. The attractive properties of NR Latex includes its excellent elasticity (ability to stretch many times from its original length without creating holes or breaches), flexibility, have antivirus protection and biodegradable¹. These excellent properties offers NR Latex as a versatile material in different products applications such as dipped goods², extruded threads³, blood transfusion tubing catheters⁴ and adhesives³. Despite its good performance, significant research is directed at using biodegradable fillers such as starch⁵, banana fibers⁶, oil palm⁷ and chitosan⁸ to place common filler used such as carbon black, silica and synthetic fibers. The addition of biodegradable fillers offers a solution to waste disposal problem, which affected human health and the quality of our environment⁹. The biodegradable fillers are chosen because they are readily available at low cost, abundant and have good intrinsic properties with NR Latex products.

Carrageenan is a natural water-soluble sulfated anionic polysaccharide extracted from edible red seaweed of Rhodophyceae class¹⁰⁻¹². For centuries, carrageenan was used extensively in the food industry and other products such as thickening agent, stabilizer and emulsifier¹³. It also often used in dairy based foods like ice cream, yogurt and etc. For non-food items, carrageenan was used in toothpaste and soap, color binding, bio-fuel, pharmaceutical industry and paper^{10,14,15}. There are three main categories of carrageenan: kappa, iota and lambda. Kappa carrageenan forms strong and rigid gels when combined with potassium ions in the mixture while Iota carrageenan forms weak and elastic gels. On the other hand, lambda carrageenan is a non-gelling type which forms thick viscous solution^{10,14,15}. Utilization of carrageenan as a hydrogel received a great attention and used in wide applications including biomedical, pharmaceutical, cosmetics, paints and agriculture fields^{16,17}. Despite the efforts made in these fields, there are many studies reported on the incorporation of carrageenan with biopolymer¹⁸. In this study, newly developed material using NR Latex and carrageenan fillers was prepared to investigate the compatibility between the matrix and the filler. The effect of pre-vulcanization on the crosslink density and mechanical properties of NR Latex films with addition of carrageenan was analyzed.

2. Experimental

2.1 Materials

Refined carrageenan ($\leq 53 \mu\text{m}$) samples was obtained from Faculty of Science and Natural Resources, Universiti Malaysia Sabah. Commercial High ammonia (HA) Natural Rubber (NR) Latex with 60% dry rubber content (DRC) and 1100.5 sec mechanical stability time (MST) was used. All compounding ingredients include sulphur, zinc oxide (ZnO) zinc diethyldithiocarbamate (ZDEC) and antioxidant were in dispersion form, while potassium hydroxide (KOH) in solution form. All ingredient and NR Latex were purchased from ZARM Scientific and Supplies (Malaysia) Sdn. Bhd were commercial chemicals and used without further purification.

2.2 Preparation of pre-vulcanized NR Latex films

The pre-vulcanized NR Latex films were prepared by dry coagulant dipping process. The carrageenan was mixed with water under high stirring speed (400 rpm) prior to addition to NR Latex compounds. The NR Latex compound was prepared by compounding the ingredients as shown in Table 1, in reaction flask. KOH solution was added first before other ingredient followed by carrageenan solution to the NR Latex compound. The compound was mixed for 2 hour at 200 rpm in room temperature (ca. 28-30 °C) prior to pre-vulcanization at 70 ± 1 °C (Method 1)¹⁹. A chloroform number test was used to determine the degree of pre-vulcanization of the compound. The pre-vulcanization was stopped at chloroform number 3 after which the NR Latex compound was allowed to cool and mature under room temperature for 24 hours. For Method 2, the typical pre-vulcanization process was eliminated. The compound was mixed for 2 hours at 200 rpm at room temperature (ca. 28-30 °C) before left for 24 hours maturation process under room temperature.

The NR Latex films were prepared by coagulant dipping using 10% calcium nitrate as the coagulant. Cleaned and dried aluminum plate was dipped in the coagulant for 20 seconds followed by drying in the oven at 100°C for 15

minutes. The dried aluminum plates were then cooled under room temperature for 5 min and dipped into the NR Latex tank for 10 seconds dwell time. After that, the aluminum plates were withdrawn and dried in the oven at 100°C for 30 minutes. The dried NR Latex films were then stripped from the aluminum plates and stored in the desiccators before further tests. The control NR Latex film (without carrageenan) was also prepared without carrageenan based on pre-vulcanization process (Method 1) as a comparison.

2.3 Swelling Equilibrium Test

The swelling test was carried out according to ASTM D 471 where a test pieces weighing about 0.2 g were cut from NR Latex films. The sample was then immersed in toluene for 48 hours at 40°C with a replacement of toluene after the first 24 hours of soaking. The swollen sample was then wiped with a tissue paper and weighed. Then the sample was dried in an oven at 60°C until constant weight was achieved. Swelling index and cross link density was calculated using Flory-Rehner equation²⁰.

Table 1. Formulation for NR Latex films.

Total solid content (TSC)	Ingredients	Parts by weight (phr*)
60 %	NR Latex	100
10 %	KOH	1.0
55 %	ZDEC	1.0
50 %	ZnO	1.0
50 %	Antioxidant	1.0
50 %	Sulphur	1.5
100 %	Carrageenan	2.0

*phr-part per hundred rubber

2.4 Tensile and tear properties

The tensile test was done according to ASTM D 412-92. The test was performed to determine the capability of a material to resist the deformation during stretched. The important data obtained from tensile test were modulus at 100% elongation (M100), modulus at 300% elongation (M300), tensile strength and elongation at break. Test samples with the thickness of 0.15 mm + 0.05 mm were prepared in dumbbell shape. The measurements were carried out using tensometer Universal Testing Machine (Model Instron 3366, Norwood, MA, US) with a crosshead speed of 500mm/min and the data was recorded. The tear strength of NR Latex films was measured using tensometer Universal Testing Machine (Model Instron 3366, Norwood, MA, US), according to ASTM D 624. The samples were cut into crescent shape (die type C) and the thickness of samples was measured before tear test (0.15 + 0.05 mm). The crosshead speed for tear test was set at 500 mm/min and performed under room temperature. Five samples were prepared and the average values were calculated.

2.5 Scanning electron microscopy (SEM)

The fractured surfaces from the tensile test pieces of NR Latex films were coated with chromium using an EmitechK575X sputter coater (Emitech, Houston,TX) for 30 seconds. The coated surfaces were scanned using a ZEISS SUPRA 35 VP (Oberkochen, Germany) scanning electron microscopy (SEM) with 1000x magnification. The voltage acceleration was set at 5 kV.

2.6 Particle size analysis

A Malvern Mastersizer 2000 (Malvern Instruments, Worcestershire, UK) was used to analyze the sub-sampled powder by laser diffraction. The samples were dispersed in 0.1% Tween 80 in water (Sigma-Aldrich, A5376, Dorset, UK) using a Hydro 2000SM cell. Powder was added to the cell until a laser obscuration of 3% was reached. The laser diffraction measurements were used to generate volume distribution plots of particle size and obtain the volume median particle diameter, $d(0,5)$.

3. Results and discussion

3.1 Effect of carrageenan loading on the swelling index of NR Latex films

The swelling data was used to determine the cross-link density of the NR Latex films. Table 1 shows the swelling index and cross link density value of NR Latex films for control, Method 1 and Method 2 respectively. The addition of 2 phr carrageenan as filler in NR Latex films has decreased the value of swelling index which is 329.01% for Method 1 and 323.59 % for Method 2 compared to control 337.26%. It was found that the swelling index of Method 1, where the compound already exposed to 70°C temperature in the pre-vulcanization step was slightly higher (1.6%) than Method 2. This is possibly due to hydration of carrageenan at temperature of 40°C-70°C¹⁵. Furthermore, it was expected that gelation has occurred upon cooling at temperature below 40-50°C¹⁵. This gelation produced an amorphous region in NR Latex films that tends to absorb more toluene during swelling test. This result was also supported by crosslink density value.

Crosslink density of the unfilled NR Latex films is strongly depending on the number of crosslinking formation in rubber network. The results showed cross-link density for filled NR Latex films increased compared to unfilled NR latex films. Carrageenan is a high-molecular-weight linear hydrophilic polysaccharide comprising repeating disaccharide units of galactose and 3, 6-anhydrogalactose (3, 6 AG), joined by alternating α -(1,3) and β -(1,4) glycosidic links. This could increase the tendency for physical entanglement between carrageenan and NR Latex polymer chains. The molecular entanglement between rubber and filler are able to overcome disadvantages of poor adhesion between rubber and filler. This physical entanglement could resist the polymer chain mobility, thus reduced penetration of solvents into the samples²¹. Thus resultant the low swelling index and cross-link density for filled NR Latex films.

Table 2. Swelling index and crosslink density of NR Latex films

Testing	Control	Method 1	Method 2
Swelling Index (%)	337.26	329.01	323.59
Crosslink Density ($2Mc^{-1} \times 10^{-5}$)	7.8	7.98	8.55

3.2 Effect of carrageenan loading on the mechanical properties of NR Latex films

Table 3 shows the mechanical properties for unfilled and filled NR Latex films for Method 1 and Method 2 respectively. Tensile strength (27.28 MPa) for the control NR Latex films was initially high which contributed from the stereo-regularity of *cis*-1,4 polyisoprene in NR Latex which allows a rapid crystallization when the samples stretched more than 300% of its original length, which also called stress induced crystallization²². In the presence of carrageenan in NR Latex films, the decreased in tensile strength, Method 1 (6.54MPa) and, method 2(17.88MPa) is observed. It is also found that tensile strength for Method 1 decreased dramatically (76%) compared to control NR Latex films. The filled NR Latex films have lower tensile strength compared to control NR Latex films. This is due to the inefficient transfer of load from the latex rubber matrix to the carrageenan powder. This may due to the size

and geometrical factor of the filler as shown in SEM images in Figure 1, whereby the irregular shaped fillers tend to decrease the strength composite film due to the inability of the fillers to support the stress transferred from the matrix²³. Agglomeration and large particle size filler provides a smaller surfaces area, which gives rise to a weaker interaction between the filler and the rubber matrix²³. SEM observation of the carrageenan particles (Fig. 1) revealed that they had these characteristics. Whereas Fig. 2 showed the particle size distributions of carrageenan powder with particle size d(0.1), 9.41 μm , d(0.5) 53.32 μm and d(0.9) 146 μm . The mean particle size was at d(0.5). This proven carrageenan has a large particle size. Fig. 3(a) and 3(b) shows the SEM images of fracture surface for control and NR Latex films prepared by Method 1, respectively. There is a gap and no filler-rubber interaction between carrageenan and rubber matrix (Fig. 3(b)), which resulted in lower value of tensile strength¹⁸.

Incorporation of carrageenan as filler in NR Latex does not greatly influence the tensile modulus, stress at 100% elongation (M100) and stress at 300% elongation (M300) (Table 3) of NR Latex films. However, the tensile modulus for Method 2 showed higher (63%) value than filled NR Latex films prepared with Method 1. Tensile modulus for Method 1 lower than Method 2. This is due to higher crosslink density of Method 2. High crosslink results a rigid and stiffer film²⁴. However, the lower value of tensile modulus was due to the softening effect of the latex films by the addition of 2 phr carrageenan. The amount of carrageenan was so little to give the significant effect to the tensile modulus of NR Latex films. This finding was the opposite of the reported observation by Premalal and co worker²⁴ where tensile modulus increased with the addition of filler. This finding was important especially in the latex glove industry where stronger and softer gloves can be produced without addition of chemicals ingredients such as softener²⁵.

The elongation at break (EB) of samples using Method 1 (928 %) and method 2 (1168%) showed a decreased trend when the carrageenan was added in NR Latex films. The addition of carrageenan filler in NR Latex films produced a stiffer material that reduced the EB of the NR Latex films. The addition of carrageenan had restricted the flexibility of the rubber chain and cause the film to break at lower force.

Table 3. Tensile properties and tear strength of NR Latex films

Properties	Control	Method 1	Method 2
M ₁₀₀ (MPa)	1.072	0.494	0.71
M ₃₀₀ (MPa)	4.497	1.06	1.374
Tensile strength (MPa)	27.28	6.54	17.88
Elongation at Break (%)	1258	928	1168
Tear Strength (N/mm)	44.66	33.88	61.39

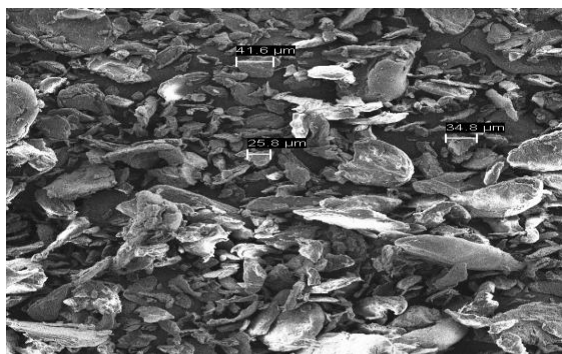


Fig. 1. SEM image of carrageenan particles at 100x mag.

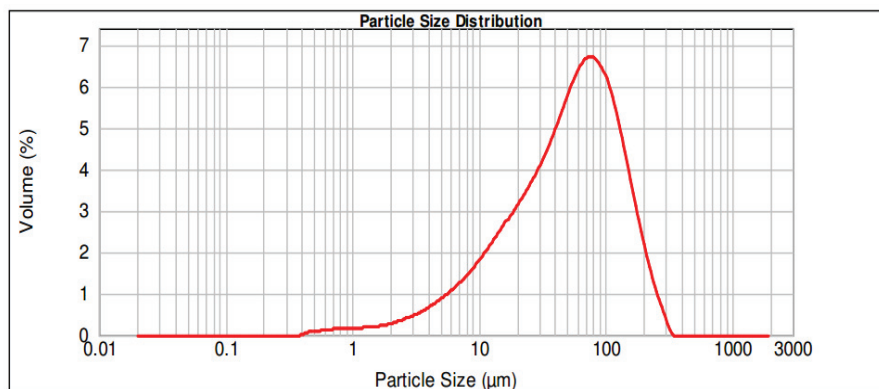


Fig. 2. Particle size distribution of carrageenan

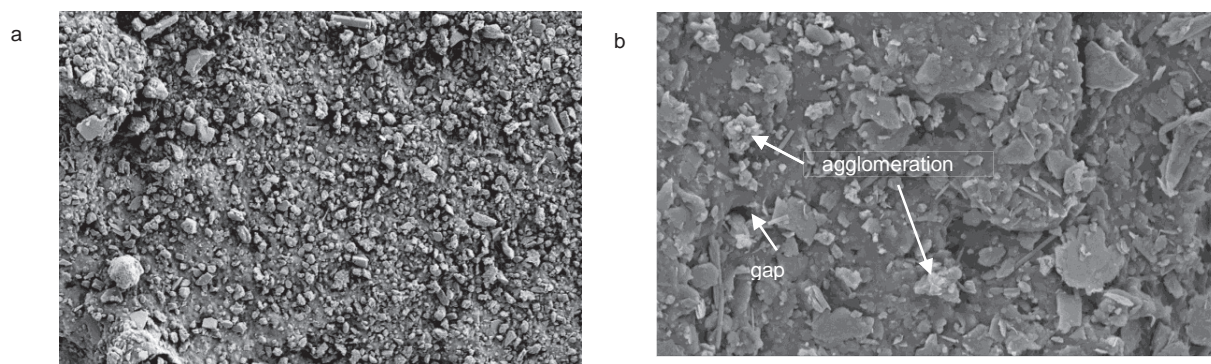


Fig. 3. SEM images of tensile fractured surfaces of NRL film (a) control and (b) Method 1 at 1000K mag

For tear strength (Table 3), the incorporation of carrageenan showed the significant increment of NR Latex films via Method 2, 61.39 N/mm compared to the control, 44.66 N/mm. It was observed during the tear test for control sample, the crack propagated straight across the tear specimen because there was nothing to divert the crack. Typically, addition of fillers improves tear strength due to the ability of fillers to deviates cracks²⁵. Sample prepared using Method 1, showed the lowest tear strength due to the amorphous region by gelation of the hydration carrageenan as discussed in previous. It was expected that the crack propagation occurred at the amorphous region in the NRL films. This region acted as crack propagation during tear measurement.

4. Conclusions

As the conclusion, incorporating carrageenan via Method 1 and Method 2 increased crosslink density and tear strength, but decreased in tensile properties. Meanwhile Method 2 showed better result than Method in swelling and mechanical properties. This is attributed by the elimination of pre-vulcanization step in Method 2, whereby the heating of compound to the gelation temperature of filler do not occurred. The studies on different method of produced NR Latex films conclude that, the effect of particle size, hydration and gelation process plays an important role towards the NR Latex films properties.

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References

1. Peter SJ. Rubber processing: An introduction .2001.Canada: Hanser Gardner Publications Inc.
2. Pendle, T. Dipping with natural rubber latex. in: Malaysian Rubber Producers' Research Association, Malaysian Research and Development Board, Brickendonbury, UK; 1995:1–33
3. Blackley DC. Latex thread. in: *Polymer Latices*. 2nd ed. London: Chapman and Hall; 1997: vol 3.Miscellaneous applications of latices. Chap 23, p. 544-552.
4. Lawrence, E. L. and I. G. Turner. 2005. Materials for urinary catheters: A review of their history and development in the UK. *Medical engineering & physics*. 27(6):443–53.
5. Afiq MM, Azura AR. Effect of sago starch loadings on soil decomposition of natural rubber latex (NRL) composite films mechanical properties, *International Biodeterioration & Biodegradation*, 2013; 85: 139-149.
6. Merlini C, Soldi V, Barra GMO. Influence of fiber surface treatment and length on physico-chemical properties of short random banana fiber-reinforced castor oil polyurethane composites, *Polymer Testing* , 2011; 30: 833-840.
7. Ooi, Zhong Xian, Hanafi Ismail, and Azhar Abu Bakar. 2013. Optimisation of oil palm ash as reinforcement in natural rubber vulcanisation: a comparison between silica and carbon black fillers. *Polymer Testing* , 32:625–30.
8. Rao V, John J. Mechanical properties of thermoplastic elastomeric blends of chitosan and natural rubber latex, *Journal of Applied Polymer Science*, 2008; 107:2217-2223.
9. Ikram A. Environment-Friendly Natural Rubber Glove, *Malaysian Rubber Board*, September 1999.
10. Necas J, Bartosikova L. Carrageenan: a review, *Veterinarni Medicina* , 2013; 58: 187-205.
11. Mustapha S, Chandar H, Abidin ZZ, Saghravani R, Harun MY. Production of semi-refined carrageenan from *Eucheuma cottonii*, *Journal of Scientific & Industrial Research* , 2011;70: 865-870.
12. Azizi R, Farahnaky A. Ultrasound assisted cold gelation of kappa carrageenan dispersions, *Carbohydrate Polymers*, 2013; 95: 522-529.
13. Wüstenberg, T., 2015. General Overview of Food Hydrocolloids. , pp.1–68.
14. Glicksman, M., 1987. Utilization of seaweed hydrocolloids in the food industry. *Hydrobiologia*, 151-152, pp.31–47.
15. Blakemore WR, Harpell AR. Carrageenan: Food Stabilisers, Thickeners and Gelling Agents,(2010). Blackwell Publishing.
16. Campo VL, Kawano DF, da Silva Jr DB, Carvalho I. Carrageenans: biological properties, chemical modifications and structural analysis – a review , *Carbohydrate Polymers* ,2009; 77:167-180.
17. Sukhlaaied W, Riyajah W. Synthesis and properties of carrageenan grafted copolymer with poly (vinyl alcohol), *Carbohydrate Polymers*, 2013; 98: 677-685.
18. Sadeghi M, Ghasemi N, Kazemi M. Synthesis and Swelling Behavior of Carrageenans-Graft-Poly(Sodium Acrylate)/Kaolin Superabsorbent Hydrogel, Composites,*World Apply Science Journal* , 2012; 16: 113-118.
19. Claramma, N. M. and N. M. Mathew. 1997. "Effect of Temperature on Sulfur Prevulcanization of Natural Rubber Latex." *Journal of Applied Polymer Science* 65(10):1913–20
20. Blackey, D.C, *Polymer Latices: Science and Technology*, 2nd Ed. Vol. 2(1997). New York: Springer. vol 1,Fundamental Principle
21. Nah, C., Lim, J. Y., Sengupta, R., Cho, B. H. and Gent, A. N. (2011). Slipping of carbon nanotubes in a rubber matrix, *Polymer International*, 60, pp. 42-44
22. Chenal, J. M., Gauthier, C., Chazeau, L., Guy, L. and Bomal, Y. (2007). Parameters governing strain induced crystallization in filled natural rubber, *Polymer*, 48, 23, pp. 6893-6901
23. Ismail H, Shaari SM, Othman N. The effect of chitosan loading on the curing characteristics, mechanical and morphological properties of chitosan filled natural rubber (NR), epoxidised natural rubber (ENR) and styrenebutadiene rubber (SBR) compounds, *Polymer Testing*, 2011; 30: 784-790
24. Premalal, H.G.B., Ismail, H. & Baharin, A., 2002. Comparison of the mechanical properties of rice husk powder filled polypropylene composites with talc filled polypropylene composites. *Polymer Testing*, 21(7), pp.833–839.
25. Siti Nuraya AS ,Baharin A, Azura AR, Mas Rosemal Hakim MH, Mazlan I, Adnan M, and Nooraziah AA. Reinforcement of prevulcanized natural rubber latex films by banana stem powder and comparison with silica and calcium carbonate, *J. Rubb. Res.* 2012;12:124-140.