Effects of Prevulcanization Time of Natural Rubber on Kenaf Filled Natural Rubber Foam

A F Abdul Karim¹, H Ismail¹ and Z Mohamad Ariff¹
¹School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang

E-mail: ihanafi@usm.my, profhanafi@gmail.com

Abstract. The objective of this study was to determine the effects of prevulcanization time of natural rubber latex (NRL) on properties of kenaf filled natural rubber latex foam (NRLF). The prevulcanization time of NRL was set at 24 hours. The tensile properties, compression set and morphological properties of kenaf filled NRLF after 24 hours of prevulcanization time were compared with samples without prevulcanized. The tensile strength and modulus at 100% elongation (M100) of prevulcanized samples was higher but lower in elongation at break as compared with without prevulcanized samples. The results from thermal gravimetric analysis (TGA) revealed that the thermal stability of prevulcanized samples was higher than without prevulcanized samples. The prevulcanized samples found to have higher elasticity compared with without prevulcanized samples based compression set test. The morpholgy of both samples were also compared using scanning electron microscope (SEM). From the micrograph of SEM, it was found that prevulcanized kenaf filled NRLF samples show better interfacial bonding compared with kenaf filled NRLF without prevulcanized. This proved that prevulcanized natural rubber latex enhanced the properties of kenaf filled NRLF.

1. Introduction
The advantages of prevulcanized latex such as high crosslink density and high tensile strength make them dominant in various application including glove, catheters, toy balloons, marking rings, pillow and mattresses [1]. Actually the researchers found that prevulcanized latex was generally not suitable for foam products due to inherently poor gel strength [2]. But nowadays, with some modification of the formulation, the prevulcanized latex could now be used sucessfully for making a foam products such as pillow and mattresses [2]. Therefore, a precise determination of prevulcanized NRL is necessary to ensure the production of final products having optimum performance with competitive cost. In addition, a good understanding factors that affect the prevulcanized NRL is crucial to predict the optimum properties of the final products [3].

Nowadays, the interest of using renewable resources such as bio fiber (as banana, sisal, hemp, jute, pineapple, bamboo, cotton, coconut, rice husk, and kenaf) in polymer matrix has attract the attention of the worldwide [4,5,6]. This was due to the various properties offered by natural fiber such as light weight, renewability, low cost and environmental friendly which suits to various application [7, 8]. In this study, the well-known bio filler in Malaysia which is kenaf was used as bio fillers in NRLF. Kenaf is single, straight and without branch, grows quickly, rising to four to five meter tall in a four to five month growing season, and 25-35 mm in original diameter [9, 10]. Kenaf fibers was extracted from kenaf's bast to get a kenaf fiber in order to use in various application such as in polymeric composites
The compatibility between kenaf and the matrix, structure and surface of kenaf fiber can be improved by chemical or physical treatment on kenaf fibre [12]. In this study, the tensile properties, thermal, compression set, and morphological properties of kenaf-filled NRLF were investigated using a standard methods.

2. Experimental procedures

2.1. Materials and formulation

The formulation used in this study are shown in Table 1. Natural rubber latex (Low Ammonia (LATZ) type) and other chemicals such as sulphur, antioxidant, potassium oleate, Zinc diethyldithiocarbamate (ZDEC) and Zinc 2-mercaptobenzhiozolate (ZMBT) were all purchased from Zarm Scientific & Supplies Sdn. Bhd, Malaysia. Kenaf fiber supplied by National Kenaf and Tobacco Board were grounded and sieve to acquire a kenaf powder.

| Ingredients         | Total solid content (%) | Formulation (pphr) |
|---------------------|-------------------------|---------------------|
| LA Latex            | 60                      | 100                 |
| Sulphur             | 50                      | 2.2                 |
| Antioxidant         | 50                      | 1                   |
| Potassium oleate    | 20                      | 4.5                 |
| ZDEC                | 50                      | 0.9                 |
| ZMBT                | 50                      | 0.9                 |
| Kenaf powder (~300µm)| 25                      | 0/1/3/5/7           |

Table 1. Formulation of kenaf filled NRLF.

Table 2 shows the ingredients used for gelling process. All the chemicals was purchased from Zarm Scientific & Supplies Sdn. Bhd, Malaysia.

| Ingredients           | Total solid content (%) | Formulation (pphr) |
|-----------------------|-------------------------|---------------------|
| Zinc Oxide (ZnO)      | 50                      | 3                   |
| Diphenyl guanidine (DPG)| 40                      | 0.3                 |
| Sodium silicofluoride(SSF)| 25                      | 1.2                 |

Table 2. Gelling agents of kenaf-filled NRLF.

2.2. Sample preparation

First, LATZ latex was measured and filtered according to the required amount followed by stirred the latex using a mechanical stirrer for about 15 minutes at 10 rpm. After that, sulphur and antioxidant were added and stirred at 10 rpm. After 30 minutes, ZMBT and ZDEC were slowly added to the mixture and continued stirred about 1 hour. After 1 hour, potassium oleate soap and a predetermined volume of kenaf powder were added to the compound slowly and the NRLF compound was then prevulcanized for 24, 48 and 72 hours at room temperature with a continuous stirring speed of 6 rpm. After the prevulcanization process, the NRLF compound was beaten intensively and foamed using the stand mixer (KENWOOD, kMix) until the volume was increased up to three times of the initial volume. The compound was beating time of about 5 minutes at maximum speed and once the desired volume obtained, the foaming speed was lowered to obtained fine and even foam. Next, the gelling agent was prepared according to formulation in Table 2. DPG together with zinc oxide (ZnO) were added to the foam and beating was continued for another 1 minutes. Then, SSF was added and the foam was beaten for 45 minutes. Finally, the un-gelled foam was quickly poured into the desired aluminum mould and allowed to gel for 3 minutes at ambient temperature. Gelled foam was then cured in an oven at 105 °C for two hours. Once the foam has cured, the foam was stripped from the mould and washed thoroughly with de-ionized water to remove potassium oleate soap and excessive...
non-reacted materials. After washing, the cured NRLF was evenly dried in a hot air oven at 80 °C for 8 hours.

2.3. Measurement of tensile properties
The tensile test kenaf filled NRLF with and without prevulcanized samples was performed by using universal testing machine Instron 3366 according to ISO 48. Dumbbell-shaped of kenaf filled NRLF in the formed of sheet were cut by using Wallace die cutter. The test was performed at ambient temperature with a crosshead speed of 500 mm/min. Five samples of each kenaf loading for prevulcanized and without prevulcanized were tested, and the averages were reported. Tensile properties such as tensile strength, tensile modulus and elongation at break were obtained from this test.

2.4. Compression set
Compression set properties of kenaf filled NRLF with and without prevulcanized was performed according to ASTM D3574. Samples used were in regular shape of 50 mm x 50 mm x 25 mm with parallel top and bottom surface and essentially perpendicular sides. Three specimens per samples were tested. Specimens were placed in test apparatus and deflected to 75 ± 1 % of its original thickness. Within 15 minutes, deflected specimens and the apparatus were placed in mechanically convicted air oven overnight with test temperature of 70 ± 2 °C. Specimens were immediately removed from apparatus and measured after 30 minutes recovery. Compression properties such as constant deflection compression set were obtained from this testing.

2.5. Thermogravimetric analysis (TGA)
TGA of the samples was conducted by using Perkin Elmer Pyris 6 testing instrument (USA). Both samples with and without prevulcanized of the kenaf filled NRLF were tested at a heating rate of 20 °C/min from 30 to 600 °C under nitrogen gas conditions. The TGA and DTG values of kenaf filled NRLF were recorded.

2.6. Scanning electron microscopy
Surface morphology of prevulcanized and without prevulcanized kenaf filled NRLF was studied by using scanning electron microscope (Hitachi, TM1000). The foam surfaces were mounted on aluminum stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging and poor image resolution during examination. The morphology of the bot samples with and without prevulcanized of kenaf filled NRLF were observed.

3. Results and discussions
3.1. Tensile properties
Table 3 shows the tensile strength, elongation at break and modulus at 100% (M100) of NRLF with and without prevulcanized. Both samples of kenaf-filled NRLF show decrement in tensile strength as the kenaf loading increased. Tensile strength of without prevulcanized samples decreased from 0.48 MPa (for the 0 phr kenaf loading) to 0.22 MPa (sample with 7 phr kenaf loading) while samples of prevulcanized NRLF decreased from 0.71 MPa to 0.26 MPa. As can be seen in the resules, kenaf-filled NRLF with prevulcanized NRL have higher tensile strength as compared with samples without prevulcanized. This enhancement was due to the increased in crosslink density in prevulcanized samples hence reduced the breakage of the samples in an applied stress during tensile test.

From the results, increment in filler loading cause reduction in the elongation at break for both groups of samples, with and without prevulcanized. For samples with prevulcanized, the elongation at break was lower than the elongation at break for samples without prevulcanized. The elongation at break for samples without prevulcanized reduced from 441.70% to 282.68% while samples with prevulcanized reduced from 367.52% to 279.01% with respect to the comparison between samples with zero kenaf loading and those of having 7 phr kenaf loading. As mentioned before, prevulcanized
latex tend to have more crosslinking chain network. This resulted of good stress propagation and improved the tensile strength but made the samples more brittle. Therefore, the samples are more likely to fail at lower strain instead of experiencing higher elongation.

The M100 increased with increased of kenaf loading for both samples, with and without prevulcanized NRL. At similar kenaf loading, sample with prevulcanized exhibited the high value of M100 as compared with samples without prevulcanized. The M100 for sample without prevulcanized increased from 0.21 MPa to 0.28 MPa while M100 for sample with prevulcanized increased from 0.25 MPa to 0.31 MPa. The used of prevulcanized NRL in the kenaf-filled NRLF give a positive effect on the M100 due to the elasticity of foam was reduced, resulting in more stiff and rigid foam. The increasing trend in M100 was observed as a consequent of the elasticity of the foam was reduced, resulting in stiffer, more rigid foam. This decreased its resistance to breakage [11].

Table 3. Tensile strength, elongation at break and modulus at 100% (M100) of NRLF with and without prevulcanized.

| Sample | Tensile strength (MPa) | Elongation at break(%) | M(100)(MPa) |
|--------|------------------------|------------------------|-------------|
|        | Without prevul. | With prevul. | Without prevul. | With prevul. | Without prevul. | With prevul. |
| 0 phr  | 0.48  | 0.71   | 441.70  | 365.50  | 0.21  | 0.25   |
| 1 phr  | 0.42  | 0.43   | 367.52  | 340.72  | 0.24  | 0.25   |
| 3 phr  | 0.38  | 0.40   | 365.15  | 388.91  | 0.26  | 0.27   |
| 5 phr  | 0.23  | 0.37   | 332.70  | 300.30  | 0.27  | 0.28   |
| 7 phr  | 0.22  | 0.26   | 282.68  | 279.01  | 0.28  | 0.31   |

3.2. Thermo Gravimetric Analysis (TGA)

Figure 1 show the results of thermal stability for control and kenaf filled NRLF with prevulcanized NRL. The weight loss of the kenaf-filled NRLF with increasing temperature under a nitrogen environment was measured, and graphs of the weight loss and derivative thermogravimetric (DTG) as a function of the temperature were plotted. Decomposition of the cellulose in the kenaf occurred at lower temperatures [12]. Increasing the amount of kenaf caused the decomposition of cellulose to occur at lower temperatures. As shown in Figure 1, control and kenaf-filled NRLF experienced weight loss from 259 to 588 °C which can be related to the decomposition of natural rubber and the cellulose of kenaf. Higher char residue was produced by the kenaf filled NRLF at 7 phr kenaf loading as compared to the other loading. The thermal stability of the polymer was enhanced by increasing the amount of char residue formed, as char hinders diffusion of volatile decomposition products [13]. Hence by increasing the amount of kenaf at a certain loading, the thermal stability of the kenaf-filled NRLF was increased.

Table 4 shows the temperature at 50% weight loss (°C), the maximum weight loss (%) and the final char residue (%) for prevulcanized and without prevulcanized samples. Prevulcanized samples have lower weight loss and high char residue compared with samples without prevulcanized. It is due to the high crosslink structure inside prevulcanized samples that restrict the chain mobility of rubber chain. Therefore, high energy needed to break the crosslinking for prevulcanized samples. In addition, high char residue was also contribute to hinder the diffusion of volatile materials as mention before. Hence, prevulcanized samples have high thermal stability compared with without prevulcanized samples.

3.3. Compression set

The compression set is the measure of the elastic behavior of the materials. Figure 2 shows constant deflection compression set, C(t) of kenaf filled NRLF with and without prevulcanized. From Figure 2 the 0 phr kenaf loading (control) for both samples has the lowest compression set indicates the high elasticity of the samples compared with other samples. The compression set increases with increase in kenaf loading which indicates the lower elasticity of kenaf filled NRLF. This is due to the non-elastic
deformation of the hard phase of which more kenaf is present led to slower recovery and may explain the higher compression set observed after 30 min relaxation. Meanwhile, prevulcanized samples have lower compression set compared with without prevulcanized samples. This was due to the better filler matrix interaction and high crosslink density of NRL for prevulcanized samples.

![Figure 1. TGA of control and kenaf-Filled NRLF with prevulcanized at different filler loading.](image)

**Table 4.** Thermal stability parameters of prevulcanized and without prevulcanized kenaf filled NRLF.

| Sample | Without prevul. | With Prevul. | Without prevul. | With Prevul. | Without prevul. | With Prevul. |
|--------|-----------------|--------------|-----------------|--------------|-----------------|--------------|
| 0 phr  | 398             | 411          | 94.9            | 90.2         | 4.5             | 9.4          |
| 1 phr  | 378             | 413          | 95.3            | 88.6         | 4.7             | 11.2         |
| 3 phr  | 374             | 416          | 95.5            | 86.2         | 5.3             | 13.6         |
| 7 phr  | 374             | 414          | 95.6            | 87.2         | 5.8             | 12.5         |

![Figure 2. Constant deflection compression set, Ct of samples with and without prevulcanized kenaf filled NRLF.](image)
3.4 Scanning electron microscopy (SEM)

Figure 3 (a) and Figure 3 (b) show the filler-matrix interaction of kenaf filled NRLF with and without prevulcanized at 7 phr kenaf loading. Sample without prevulcanized shows weak interfacial adhesion while sample with prevulcanized NRL shows good filler-matrix interaction at interfacial bonding. This is an indication that prevulcanized NRL was able to increase the adhesion at the filler-matrix interfacial which resulted in increased tensile strength as well as the modulus of kenaf filled NRLF. During prevulcanization process, better filler dispersion occurred due to adequate time and forced during prevulcanization process hence give small size of pores and well distribution of pores as shown in.

![Micrograph of kenaf in kenaf filled NRLF without prevulcanized at 7 phr](imagea)

![Micrograph of kenaf in kenaf filled NRLF with prevulcanized at 7 phr](imageb)

**Figure 3.** (a) Micrograph of kenaf in kenaf filled NRLF without prevulcanized at 7 phr; (b) Micrograph of kenaf in kenaf filled NRLF with prevulcanized at 7 phr.

4. Conclusions

By using the optimum prevulcanization time (24 hours), it was found that the tensile strength and M100 of prevulcanized samples of kenaf filled NRLF were higher while the elongation at break lower compared with without prevulcanized samples. The thermal stability was higher for prevulcanized kenaf filled NRLF compared with without prevulcanized. The results of compression set shows that samples with prevulcanized have higher elasticity compared with without prevulcanized. From the micrograph of SEM, it was observed that sample without prevulcanized shows weak interfacial bonding between filler and matrix but samples with prevulcanized shows better interaction and good interfacial bonding between filler and matrix.

5. References

[1] Sasidharan K K, Shiny P, Gopalakrishnan K S, George K E and Rani J 2004 *Journal of Applied Polymer Science* **94** 1164 –1174
[2] Blackley D C 1997 *Polymer Latices: Science and technology Volume 2: Types of latices* Netherlands Springer Netherlands
[3] Porter M, Rosemaze K and Sapi'ai A R 1992 *Journal of Natural Rubber Resources* **7(2)** 85 - 101
[4] Dahham O S, Noriman N Z, Mohd Kahar A W, Ismail H and Sam S T 2015 *Journal of Applied Science and Agriculture* **10(5)** 33-39
[5] Han S O, Karevan M, Sim N I, Bhuiyan M A, Jang Y H, Ghaffar J and Kalaitzidou K 2012 *Journal of Materials Science* **47** 3535-43
[6] Ismail H, Nasaruddin M N and Rozman H D 1999 *European Polymer Journals* **35**(8) 1429-37
[7] Muniandy K, Ismail H and Othman N 2012 *BioResources* **7** 841-858
[8] Rozman H D, Tay G S, Kumar R N, Ismail H and MohdIshak Z A 1999 *Polymer-Plastics Technology and Engineering* **38**(5) 997-1011
[9] Salman S D, Leman Z, Sultan M T, Ishak M R and Cardona F 2015 *BioResources* **10**(4)
[10] Fiore V, Di Bella G and Valenza A 2015 Composites: Part B 68 14-21
[11] Ismail H and Haw F S 2008 Journal of applied polymer science 110(5) 2867-76
[12] Akhtar M N, Sulong A B, Fadzly Radzi M K, Ismail N F, Razab M R, Muhamad N and Khane M A 2016 Progress in Natural Science: Materials International 26(6) 657–664
[13] Abdullah N and Hashim A Y M 2014 Developments within the Glove Industry 14(1) 16-20

Acknowledgements
The author would like to gratefully acknowledge the Fundamental Research Grant, FRGS (Grant Number 203.PBAHAN.6071375) and MyBrain15 of Ministry of Higher Education Malaysia for the financial assistance.