

Natural Latex Foam

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Abstract: *The work presented in this paper describes an alternative compounding formulation for natural rubber (NR) latex foam. This novel formula is designed to address the environmental control and health issues typically associated with NR latex products. The NR latex foam produced was shown to have ultra-low protein allergenicity (Type I) and chemical sensitivity (Type IV). The physical properties of the NR latex foam were typical of normal NR latex foams. Images obtained by Scanning Electron Microscopy (SEM) demonstrate that the foam has an open-cell structure. Soil burial was utilised to demonstrate the biodegradability of the foam product, and the resulting degraded area of the cell wall confirmed that natural degradation was occurring.*

Keywords: NR latex foam, alternative compounding formulation, biodegradable

1. INTRODUCTION

Natural rubber (NR) latex is a natural commodity that has tremendous economic and strategic importance. Among the applications of NR latex is the production of dipped goods, extruded threads, adhesives, carpet-backing and moulded foams.^{1,2} This is primarily because of the unique characteristics of NR latex, such as high strength, flexibility and elasticity.^{3,4} Most NR latex products are derived via a sulphur vulcanisation system, which achieves the desired physical properties for the product application. There are alternative methods to vulcanisation, such as radiation and peroxide curing systems, but these methods have not gained industry acceptance because of inconsistency in the mass production practices of these latex products.¹ However, there are claims of a peroxide system, appropriate for prevulcanised latex, for producing latex products with improved physical properties.^{5,6} The claims assert that products made from peroxide prevulcanised latex tend to have low levels of chemical sanitizers, nitrosamines, nitrosatable amines, non-cytotoxicity and a relatively low level of extractable protein, compared to products made from normal NR latex. Furthermore, products made from the peroxide vulcanisation system can be regarded as environmentally friendly due to the absence of heavy metals and toxic chemicals.

To date, there are no published reports on the application of peroxide prevulcanised latex for NR latex foam products. The main drawback is that the low wet-gel strength of peroxide prevulcanised latex contributes to foam collapse upon deformation and fracture upon tearing. Thus, the present study will demonstrate a practical application of the peroxide curing system for NR latex to make latex foam. Without altering the normal production process of NR latex foam, this method offers an alternative curing system for the NR latex foam industry.

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

The ingredients for the NR latex foam mixture used in this study are shown in Table 1. The industry standard NR latex, t-butyl hydroperoxide and hydroxyacetone were obtained commercially. Solid materials, such as sulphur, zinc diethyldithiocarbamate, zinc dibutyldithiocarbamate, zinc oxide, diphenyl guanidine, sodium silicofluoride, and an antioxidant were prepared in dispersion form by ball-milling for 72 hours. Liquid materials, specifically, potassium oleate and Irganox[®] 1520 [Ciba-Geigy (M) Sdn. Bhd., Selangor, Malaysia], were prepared in emulsion form by continuously stirring in warm water at 60°C to 70°C until completely dissolved.

Table 1: NR latex compounding formulation used in the study.

NR Latex Compound A		
Ingredient	TSC %	pphr
High-ammonia NR latex	60	100
t-butyl hydroperoxide solution	69	0.9
Hydroxyacetone solution	85	0.4
Irganox [®] 1520 antioxidant emulsion	50	1.0
NR Latex Compound B		
Ingredient	TSC %	pphr
High ammonia NR latex	60	100
Sulphur dispersion	50	1.5
Zinc diethyldithiocarbamate dispersion	50	0.5
Zinc dibutyldithiocarbamate dispersion	50	0.5
Zinc oxide dispersion	50	0.3
Wing stay L [®] antioxidant dispersion	50	1.0

Note: TSC = total solid content

Two NR latex compounds, coded in this paper as A and B, were first matured at room temperature for 48 and 16 hours, respectively. Then, both compounds were mixed at a ratio of 70:30, respectively. After mixing the compounds, a foaming agent was added, and the mixture was slowly and continuously stirred for one hour. During the experiment, 2.0 pphr of potassium oleate emulsion (P.O.) was added to the latex mixture. The latex mixture was frothed using mechanical agitation until the desired foam density was achieved. Then, zinc oxide and a secondary gelling agent were added. The foam was stirred slowly until a fine foam structure was achieved.

The NR latex foam was moulded to a thickness of 25 mm and dried in an oven in air for one hour. The composition of the foaming and gelling agent used in the study is shown in Table 2, and the process flow diagram is illustrated in Figure 1.

Table 2: Composition of foaming and gelling agent used in the study.

Ingredient	TSC %	pphr
Mixture of compounded NR latex	58	100
P.O.	20	2.0
Diphenyl guanidine dispersion	25	1.0
Zinc oxide dispersion	50	2.5
Sodium silicofluoride dispersion	50	1.15

Note: TSC = total solid content

2.2. Determination of Physical Properties of NR Latex Foam

The determination of the physical properties of NR latex foam was performed in accordance to Malaysian Standards (MS) 679.

2.2.1 Hardness index

The indenter foot was first brought to the top surface of the test sample. Then, the test sample was indented at $40 \pm 1\%$ of the initial thickness. The corresponding force was recorded, in Newtons, as the hardness index.

2.2.2 Accelerated ageing test

The accelerated ageing test was carried out similarly to the hardness index test. However, the sample was subjected to ageing for 22 hours at 100°C before testing. The difference between the hardness indexes before and after ageing was expressed as percentage of hardness change due to ageing.

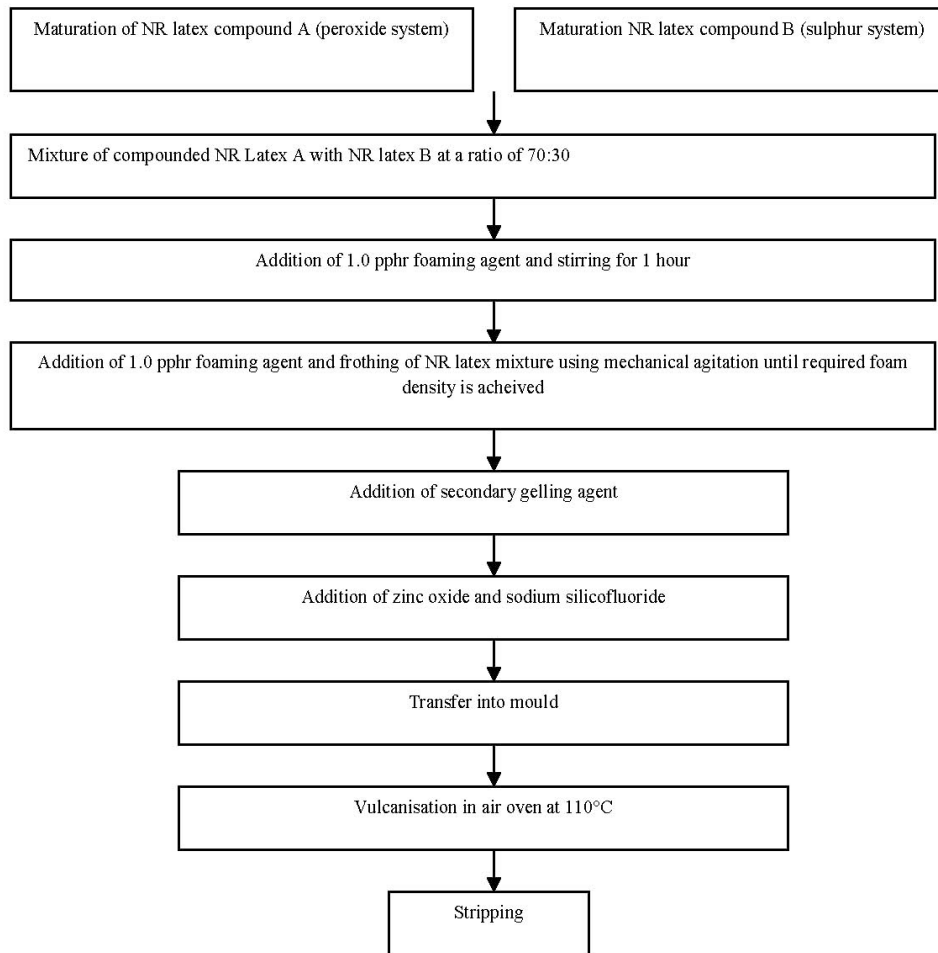


Figure 1: The process flow for preparing foam.

2.2.3 Compression set

The sample was placed between the plates of the compression device and compressed to 50% of its original thickness. The compression was maintained for 72 hours at $23\pm 2^\circ\text{C}$. Next, the compression was released, and the test sample was allowed to rest for 30 minutes at room temperature before the final thickness was measured.

2.2.4 Elongation at break

A gauge length of 25 mm was marked on the test piece, and it was then fastened into the clamps of the testing machine. After that, the sample was pulled

at a constant rate of 500 ± 50 mm/min until the sample broke. Elongation at the break, expressed as the percentage of the original gauge length, is given by the formula:

$$\text{Elongation at break (\%)} = \frac{\text{Length at break} - \text{Initial gauge length}}{\text{Initial gauge length}} \times 100 \quad (1)$$

2.2.5 Foam density

Density of the foam is calculated from the mass and volume of the sample. The density is calculated in grams per cubic centimetre as follows:

$$\text{Density} = M/V \quad (2)$$

where M is the mass of the foam latex in grams, and V is the volume of the container in cm^3 .

2.3 Tests on the Allergenicity of the NR Latex Foam

The adverse reaction associated with the use of NR latex products has become a focal point. Therefore, evaluation of toxicity and allergic potential of NR latex foam was investigated.

2.3.1 Extractable residual chemicals

The chemical residue of NRL foam was determined in accordance to ASTM D1140.^{7–10} The chemical residue was extracted using an azeotropic mixture (AM) at a ratio of 1:10 (1 g to 10 mL). The AM containing the extracted residual chemicals was collected and dried. The dried residue was then re-dissolved in 5.0 mL of chloroform and mixed equally with a copper sulphate solution (1 M). The copper complex formed⁷ was quantified by high-performance liquid chromatography (HPLC) equipped with a C_{18} -bonded reversed phase column (3.9 micron, 150 mm) with detection at a UV-wavelength set at 279 nm. The gradient mobile phase used was acetonitrile and water at a ratio of 90:10 (v/v) with 1.0 mL/min flow rate.

2.3.2 Extractable protein

A test specimen measuring 7×7 cm was extracted with phosphate-buffered saline (0.025 M) (1 g/5 mL) at 25°C for 2 hours. The total extractable protein was determined following the protocols drafted in ASTM D5712-95 and ASTM D5712-99.^{10, 11–13}

2.4 Morphology Study and the Evaluation of the Biodegradability of NR Latex Foam

Due to the increase in public concern over preserving the quality of the environment, this paper undertakes an intensive study of the biodegradability of the designed product. Surface morphology analysis upon disposal was studied.

2.4.1 Scanning Electron Microscope (SEM) imaging

The test sample was cut and placed onto the specimen stub with double-sided carbon tape. The specimen was then prepared for examination by evaporative coating of an ultra-thin layer of gold under high vacuum. This provides a conductive layer that permits SEM examinations. The JOEL SEN 5300 (Bruker AXS, Singapore) was operated at 10 kV with a 10 mm working distance.

2.4.2 Number of cells per unit volume

An SEM micrograph of NR latex foam was obtained. In this study, the number of cells per unit volume of latex foam was determined from equation (3)¹⁴,

$$N = \frac{6}{\pi d^3} \left(\frac{\rho_{rubber}}{\rho_{foam}} - 1 \right) \quad (3)$$

where N = number of cells per unit volume, d = average cell diameter, ρ_{rubber} = density of the solid rubber and ρ_{foam} = density of the rubber foam.

2.4.3 Biodegradability study

Testing of the biodegradability of NR latex foam was conducted in a time-course experiment under environmental fate conditions. The test pieces were placed in nylon mesh bags (38 μm pore size) and then buried in an unspecified clay-type soil. The samples were retrieved from the soil in 1 month intervals, washed in running water and dried prior to weighing. The weight-loss percentage was used to determine the biodegradability of the NR latex. Additionally, the physical changes of the NR latex foam structure due to the degradation were visualised using SEM.

2.5 Determination of Crosslink Density of Latex Film Using Stress-strain Measurement

The test sample was cast into films. The cast films were then subjected to a stress-strain C_1 - C_2 measurement using an Instron 5500 (Mecomb, Selangor Malaysia) machine. The sample was pulled at 25 mm/min, and the gauge length of the strip was approximately 100 mm. The procedure for best fit was to select 8 points along the film in equally-spaced increments of 1/(extension ratio). The Mooney-Rivlin equation is as follow:

$$L = 2A_0 (\lambda - \lambda^{-2}) (C_1 + C_2/\lambda^{-1}) \quad (4)$$

The cross-sectional area, A_0 , of the test piece was calculated from the density, mass and length of the specimen. The stress-strain data were plotted using a computer programme that was written for the Mooney-Rivlin equation. The C_1 and C_2 values were taken from the intercept and the slope of the curve, respectively. The total physical crosslink density (n_{phys}) is derived from the C_1 value, where C_1 and C_2 represent the elasticity of the film. An intensive investigation was conducted to determine the total poly-sulphidic concentration, which is related to the strength of the film. To determine the concentration of poly-sulphidic crosslinking, the test sample was first subjected to a chemical probe treatment. The chemical probe reagent [propane-2-thiol (0.4 M) and piperidine (0.4 M) in n-heptane] was used for selectively cleaving poly-sulphidic crosslinks, leaving just mono-sulphidic, di-sulphidic and carbon to carbon crosslinks in the test sample. The test specimen was then subjected to a stress-strain C_1 - C_2 measurement as described above. The total poly-sulphidic crosslink density was determined by taking the difference between the untreated and treated sample. Details of the technique have been described elsewhere in literature.^{15,16}

3. RESULTS AND DISCUSSION

3.1 Physical Properties of NR Latex Foam

In this study, the NR latex mixture was frothed to produce NR latex foam with the target foam density ranging from 0.8 g/cm³ to 0.14 g/cm³, which is considered firm NR latex foam. The presence of P.O. in the latex mixture as a foaming agent, as well as a foam stabiliser, is important because it reduces the surface tension during whipping of the NR latex mixture to introduce air. However, during the frothing process, the normal practice is to prevent the foam volume from exceeding seven times the initial volume of the NR latex mixture to avoid cracks and cavities in the final product. In this study, a 0.13 g/cm³ foam density was achieved, and thin (25 mm thick) moulded NR latex foam was

obtained as the product. Table 3 shows the physical properties of the NR latex foam produced in the study.

As expected, the NR latex foam produced in this study retained adequate physical properties of standard NR latex foam. It is well known that the indentation index expresses the hardness of NR latex foam. Hence, the NR latex foam was designated as medium-hardness latex foam. After ageing, the hardness of the foam increased by 2.28%. The elongation at break was comparable with normal NR latex foam. Also, the compression set percentage values are acceptable for normal foam products. However, with our novel mixture of the sulphur and peroxide latex systems, we observed the foam exhibit the memory property for a short period before slowly recovering to its initial form, without damaging the foam structure, as is indicated in Figure 2.

Table 3: Physical properties of the NR latex foam.

Test	Value	MS 679 Requirement
Indentation index (N)	136	Soft 100< Medium 101–170 Hard >170
Ageing (%)	2.28	±20%
Elongation at break (%)	300	Min 150
Compression set (%)	3.87	Max 6%
Foam density (g/cm ³)	0.13	

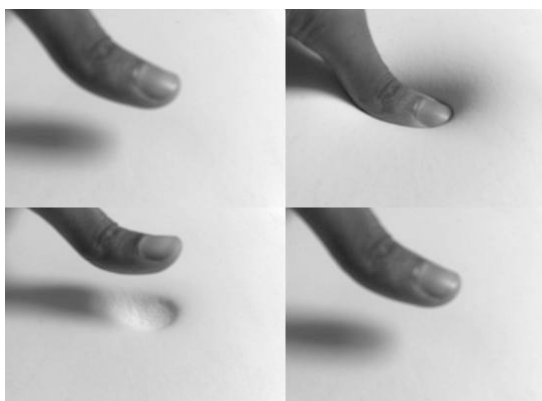


Figure 2: The slow recovery behaviour of NR latex foam: A-before compression; B-compression; C-release; D-recovery.

We conclude from this observation that the ability of NR latex foam to recover from deformation opens up a possibility for new applications of latex foam based on products made from this NR latex foam type. For example, this NR latex foam can be employed in orthopaedic applications, which usually utilise synthetic memory foam, for which this memory characteristic will allow the release of surface pressure by contouring to the shape of the body.

3.2 Allergens Level of NR Latex Foam

Our NR latex foam exhibited ultra-low allergenicity in both common NR latex allergy, specifically protein allergy (Type I), and chemical sensitivity (Type IV). The results are given in Table 4. During the production of NR latex foam, it undergoes many washing processes; therefore, it is reasonably expected that NR latex foam will not contain many residual materials, as they are washed away during processing. This is an advantage for NR-based foam over its synthetic counterpart in the green movement.

Table 4: Cytotoxicity and allergenicity level of NR latex foam.

Test	Value
Type I allergy ($\mu\text{g/g}$)	36.94
Type IV allergy ($\mu\text{g/g}$)	LOD*

Note: *LOD = under limit of detection

3.3 Surface Morphology and Biodegradability Study of NR Latex Foam

SEM images indicate that the foam structure (Fig. 3) is made of continuous interconnecting open cells. From the SEM micrograph, a qualitative measurement of the foam cell size could be obtained. Table 5 shows the average cell diameter and number of cells per unit volume of the NR latex foam.

The average cell size of the foam was 300 μm in diameter, and the number of cells per unit volume was $3.86 \times 10^4 \text{ cm}^{-3}$. However, it should be noted that the cell size and number of cells is proportional to the density of the foam. Extending the frothing process may result in decreasing the foam density; hence, increasing the number of foam cells per unit volume. The SEM micrograph (Fig. 4) of latex foam that was allowed to degrade in soil showed physical breakdown, distinguished by a degraded area on the cell wall, due to biodegradation activities during soil burial. The biodegradability of the NR latex foam was further supported by investigating the weight loss percentage over time. The increase in the weight loss percentage over one month intervals further confirmed that the NR latex foam is a biodegradable material (Fig. 5).

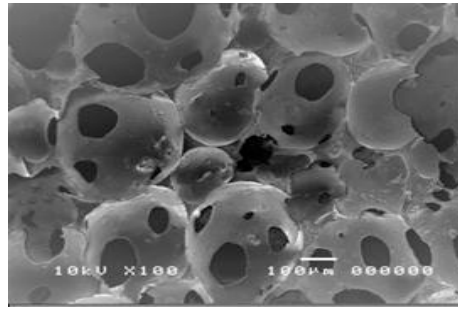


Figure 3: Micrograph of the NR latex foam cell structure.

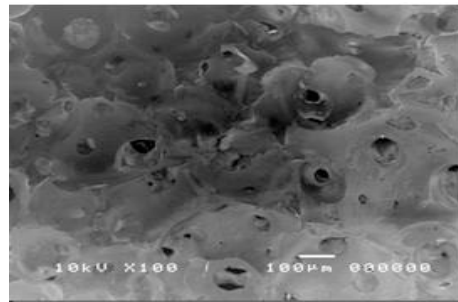


Figure 4: Effect of degradation on NR latex foam cell structure.

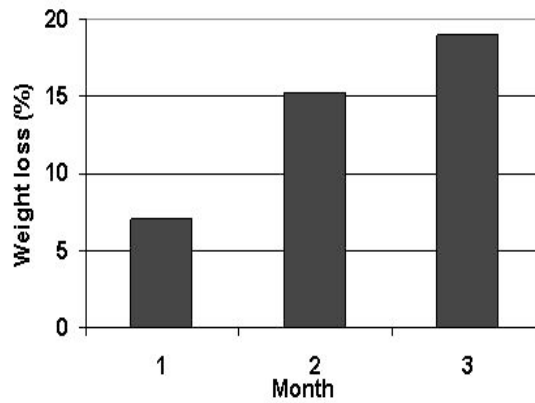


Figure 5: Weight loss percent of NR latex foam during 3-month soil burial.

Table 5: NR latex foam cell structure.

Test	Value
Average cell diameter (μm)	300
Number of cells per unit volume (cm^{-3})	3.86×10^4

3.4 Determination of Crosslink Density and Poly-sulphidic Crosslink Concentration

Table 6 shows the value of stress-strain C_1 and C_2 and total physical crosslinks (n_{phys}). The presence of peroxide vulcanised latex in the latex compound of this study gives the film the unique physical characteristic of less poly-sulphidic crosslinking, which is generally known to be thermally unstable. Application of this NR latex type as a substitute for NR latex foam shows good ageing resistance and compression set but slow recovery after compression. The actual reason for this behaviour is not clear; therefore, further investigation of the mechanism of the vulcanisation system of the latex mixture is needed.

Table 6: C_1 and C_2 and physical crosslinks concentration.

Sample	C_1 value	C_2 value	n_{phys} (mmol / 100 g rubber)	Percentage of reduce (%)
NR latex film before treatment	1073	1703	4.94	
NR latex film after treatment	707	979	3.23	57.5

4. CONCLUSION

In this study, an alternative NR latex foam vulcanising system for producing safe NR latex foam was designed. The unique and excellent properties of the NR latex foam were developed through the art of the NR latex vulcanisation system. In general, the NR latex foam formulation used in the study is a mixture of the sulphur and peroxide vulcanisation systems. The compounded NR latex was frothed and processed into thin NR latex foam at laboratory scale. Minimising the usage of hazardous chemicals in the vulcanisation system produces NR latex foam with ultra-low allergenicity in both Type I and Type IV. In addition, the release to the effluent of potential eco-toxins from foam processing could be minimised. It was also determined that the physical properties of the fabricated NR latex foam retained adequate NR latex foam characteristics, for example, hardness, age hardening percentage, elongation at break, and compression set. Images obtained from SEM demonstrated that the foam has a continuous interconnecting open-cell structure. Biodegradability of the NR latex foam was monitored by the weight loss percentage upon soil burial. The biodegradability of NR latex foam was further supported by the degraded area of the cell structure, visualised by SEM. The fabricated NR latex foam from this study is expected to not only fulfil the desirable properties of NR latex foam, but also to be the green alternative to latex foam products typically made from synthetic latex foam. Knowledge gained in this study is important to branding and

marketing NR latex foam with a conceptually green image and environmental advantages relative to synthetic foam.

5. ACKNOWLEDGMENT

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