SPECIALTY NATURAL RUBBER LATEX FOAM: FOAMABILITY STUDY AND FABRICATION PROCESS

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ABSTRACT

Specialty natural rubber (SpNR) latex, namely, deproteinized natural rubber (DPNR) latex and epoxidized natural rubber (ENR) latex, has been produced to meet specific product's requirements. However, SpNR is normally used in the form of block rubber to manufacture dry rubber products such as tires and automotive parts. The applications of SpNR latex into latex foam products will be diversified. Findings indicate that foamability of SpNR latex is lower compared to normal latex (LATZ) but shows longer stability time after foamed. Findings also indicate that foam collapse and foam coagulate are two main challenges in the fabrication process of SpNR latex foam. Despite these challenges, SpNR latex foam can be fabricated at different density levels. During the foaming process, additional foaming agent is required to fabricate a SpNR latex foam, which is different from fabricating a normal NR latex foam, especially at low latex foam density. Consequently, a higher level of sodium silicofluoride, used as the gelling agent, is required to set the cell structure of the foam. Findings also indicate that foam density influenced the gelling time and volume shrinkage of the SpNR latex foam. An ideal compounding, foaming, and gelling formulation to fabricate SpNR latex foam via Dunlop batch foaming process has been developed. Morphological study showed that all latex foams are open-cell structure, with lower density foam exhibiting higher porosity and mean pore size. Comparison on hysteresis behavior between DPNR and ENR latex foam indicated that ENR latex foam exhibits higher hysteresis loss ratio compared to DPNR latex foam. [doi:10.5254/rct.21.78938]

INTRODUCTION

At present, microcellular polymers, which are also known as polymer foams, have received considerable attention among academia and industrial players due to their lower density and lighter weight, lower thermal conductivity, and higher load bearing strength per weight compared to normal non-cellular polymeric materials.[1–4] These properties are beneficial in numerous applications such as building and construction, packaging, furniture and bedding, footwear, sports and recreational, aeronautic, and automotive industries.[5,6] Furthermore, the porous structure of polymer foams makes them an excellent substitute for various functional materials that are used as barriers, such as thermal and sound barriers, impact absorbers, and vibration dampers.[7] The versatility and diverse applications of polymer foams have contributed to gradual world economic growth, and they were worth more than USD 100 billion in 2015, and are expected to increase up to USD 150 billion by 2025.[8]

Nevertheless, most of the polymer foam products available on the market are made from synthetic polymers (petrochemicals), which contribute to environmental and health issues and cause challenging waste management and disposal problems.[9,10] Therefore, many countries have implemented new legislation to restrict use of synthetic polymers in the products manufacturing process, and at the same time to promote use of "green materials."[11–13] Consequently, many related research studies have been carried out by numerous universities, government research institutes, and private companies to strike a balance between economic growth and well-being of the environment and society. A possible solution is to substitute synthetic polymers with natural polymers. However, substituting synthetic polymers with natural polymers is a great challenge.

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This is because most of the natural polymers are unable to comply with the foam product specifications and performances.[4,14,15]

Natural rubber (NR) latex is a high molecular weight hydrocarbon polymer of isoprene (C_5H_8), where one double bond unit exists for each C_5H_8 group.[16] NR latex occurs in the free-flowing milky cytoplasmic exudates of the commercial rubber trees known as *Hevea brasiliensis*. NR latex has become the material of choice for many thin-film products such as gloves, condoms, catheters, balloons, etc. due to its elasticity, durability, and naturally biodegradable properties.[17,18] Apart from thin films, NR latex also has been used to produce foam material known as latex foam. However, the application of latex foam is limited to bedding products such as mattresses and pillows.[16] The reason behind this is unclear, but it could be due to the lack of studies in this area.

Currently, there are two main types of NR latex that have been used to manufacture latex foam products, namely, high ammonia NR (HA) latex and low ammonia NR (LATZ) latex. However, there are also other forms of NR latex known as specialty NR (SpNR) latex, such as epoxidized NR (ENR) latex and deproteinized NR (DPNR) latex. SpNR latex is a modified NR latex produced to meet specific product requirements such as good wet-grip, high-damping, low creep, and low-stress relaxation as well as low extractable protein content.[19–24] Nevertheless, product applications of SpNR are relatively limited and normally used in the form of block rubber to manufacture dry rubber products such as tires and automotive parts.[19,25,26] To date, less information is reported concerning the use of SpNR in latex-based products. Application of SpNR latex in latex foam products is almost impossible due to their low total solid content (TSC) at 30%. This is because low TSC of latex leads to high volume shrinkage and variable physical properties, which is a great challenge in the latex foam products manufacturing process.[27]

To address this issue, the Malaysian Rubber Board (MRB) has developed a new generation of SpNR latex, where the TSC of SpNR latex has increased to 60% TSC through the ultrafiltration process using membrane separation technology.[28–30] The availability of SpNR latex with higher TSC has provided an opportunity to diversify the application of SpNR latex into latex foam products. It is well-known that the porous open-cell structure of foam materials is useful to absorb noise and minimize vibration transmission from one area to another.[31–35] Therefore, it is a great opportunity to use the SpNR latex foam for sound and vibration control applications such as acoustic foam material and seat cushions in the transportation industry. The advantage of using ENR latex is due to its high-damping property originated from the epoxy group in the rubber chains.[19–21,36] On the other hand, the advantage of using DPNR latex is due to its low protein content, which leads to hypoallergenic material and less smell of rubber.[22–24,37] However, there are a few challenges to develop latex foam from SpNR latex. First, physicochemical properties of SpNR latex are expected to differ from normal NR latex due to chemical reactions during the SpNR latex modification process. Second, there is a gap in knowledge on foamability and subsequence stability of SpNR latex. Therefore, the objectives of this study are to investigate foamability and stability of SpNR latex and to develop a compounding, foaming, and gelling formulation to fabricate a SpNR latex foam. Additionally, the physical properties of the fabricated SpNR latex foam material will be determined. Knowledge gained from this study is important to provide a method and formulation to fabricate SpNR latex foam, and their potential applications can be identified.

EXPERIMENTAL

MATERIAL PREPARATION AND COMPOSITION

In this work, both ENR and DPNR latex of 60% TSC were prepared from freshly tapped NR latex collected from MRB Plantation, Johor, Malaysia. All chemicals used were purchased from

Sigma-Aldrich (M) Sdn. Bhd., Selangor, Malaysia. In brief, ENR latex was prepared through in situ chemical reactions of hydrogen peroxide and formic acid, which substitutes the double bond structure to generate an epoxy group onto the rubber molecules. ENR latex was prepared in accordance with MRB standard process and formulation patented in PI2012004868[38] and PI2017700457,[39] respectively. The production of ENR latex involves heating of freshly tapped NR latex having TSC of 30%, with 2.0% non-ionic surfactant, 0.75 mol formic acid, and 1.00 mol hydrogen peroxide in a jacketed reactor. The NR latex mixture was heated at temperature of 45 °C for 1 h, 50 °C for another 3 h, and finally 60 °C for a further 21 h. This allows the epoxidation reactions to take place. Once the targeted epoxidation was achieved, the ENR latex was cooled down to room temperature and neutralized using ammonia to pH 7 to terminate the epoxidation reaction. Then, the ENR latex was subjected to a concentration process using an ultrafiltration membrane separation system to obtain ENR latex concentrate having a TSC content of approximately 60%. After that, the ENR latex was preserved using ammonia laurate to pH 10 to ensure stability of the material. On the other hand, DPNR latex was prepared in accordance with MRB standard process and formulation patented in PI2020004246.[40] In brief, the deproteinization was carried out via heat enzymatic hydrolysis reactions. The production of DPNR latex involves heating freshly tapped NR latex having TSC of 30% with 2.0% non-ionic surfactant, 0.15% alcalase, and 0.15% hydroxylamine neutral sulfate in a jacketed reactor. The NR latex mixture was heated to a temperature of 60 °C for 6 h to allow the heat enzymatic hydrolysis reactions to take place. After the completion of the heat enzymatic hydrolysis reactions, the reacted DPNR latex mixture was cooled down to room temperature. Then, the DPNR latex was pumped into the ultrafiltration membrane separation system to obtain DPNR latex concentrate having a TSC content of approximately 60%, similar to the ENR latex process. Finally, the DPNR latex was preserved with ammonium laurate and ammonia at levels of 0.1% and 0.4%, respectively. For comparative study, a commercial grade low ammonia NR latex (LATZ) purchased from Getahindus (M) Sdn. Bhd, Johor, Malaysia, was used as a control. The actual composition of LATZ is unknown, but it normally contains 0.2% ammonia, 0.013% tetramethyl thiuram disulfide (TMTD), 0.013% zinc oxide, and 0.05% lauric acid. LATZ was chosen as a control because LATZ is a commonly used NR latex for producing latex foam products such as mattresses and pillows.[41,42] Likewise, LATZ is the material of choice in the bedding industry due to its reduced ammonia content, which offers a safer manufacturing environment.

LATEX COMPOUNDING PROCESS

Table I shows the compounding formulation used in this work. The compounding formulation used in this study is a commonly used sulfur-vulcanized system.[42] All chemicals used for the compounding process were purchased from Alpha Nanotech Sdn. Bhd., Selangor, Malaysia. In this work, all vulcanizing agents were mixed first and allowed to activate at room temperature for 30 min. Sulfur and zinc diethyl dithiocarbamate (ZDEC) play the main role in the crosslinking of the rubber molecular chains to produce vulcanized latex foam material, while the presence of zinc 2-mercaptobenzothiazole (ZMBT) as a secondary accelerator helps to increase the compression modulus and reduce the compression set of the latex foam. However, small changes were made in this work, in which zinc oxide (ZnO) and zinc dibutyl dithiocarbamate (ZDBC) were used as part of the vulcanizing ingredients. Both chemicals were used to improve the prevulcanization process of the latex compound, which helps to accelerate the vulcanization process and to reduce the volume shrinkage of the end products. Upon compounding process, potassium oleate (PO) was added first into the latex, followed by a premix vulcanizing agent while the latex was being stirred at 100 rpm. The stirring process lasted for 2 h. Then, the speed of the stirrer was reduced to 45 rpm and the latex was allowed to mature at room temperature for 16 h.[43]

TABLE I
COMPOUNDING FORMULATION USED IN THIS STUDY

Ingredient	TSC (%)	Dry weight (phr)
Latex[a]	60	100
Potassium oleate	20	1.50
Sulfur dispersion	60	2.50
Zinc oxide (ZnO) dispersion	60	0.15
Zinc diethyl dithiocarbamate (ZDEC) dispersion	50	0.75
Zinc dibutyl dithiocarbamate (ZDBC) dispersion	50	0.25
Zinc 2-mercaptobenzothiazole (ZMBT) dispersion	50	1.0
Antioxidant dispersion (Wing stay-L)	50	1.0

[a] LATZ, ENR, and DPNR latex; phr = parts per hundred rubber.

FOAMABILITY AND STABILITY STUDY

This study was conducted to quantify the foamability and subsequence stability of SpNR latex foam over time. Foamability is the ability of the latex to change from colloid/liquid phase into latex foam phase when it is subjected to a constant rate of mechanical rotating motion. On the other hand, stability refers to the durability of the latex foam to retain the foam-cell structure before drainage (a tendency of the latex foam to change back into liquid phase). In this work, a FoamScan® analyzer from Teclis, France, was used.

Figure 1 shows the instrument configuration. To the best of our knowledge, study on the foamability and stability of NR latex using a FoamScan® analyzer has not yet been established; thus experimental parameters were set in this particular study. In this work, 60 mL of latex was injected into a glass tube with an inner diameter of 35 mm. Latex foam was generated through a whipping process using a high-speed rotary spin located at the bottom of the tube. A constant rate of 1000 rpm was set to foam the latex, under a controlled temperature of 25 °C. The latex foaming process stopped automatically when the foaming time reached 600 s. Then, the latex foam stability was observed for another 600 s. An integrated camera was used to capture images of the foam microscopically throughout the experiment. Foamability and stability of the latex was quantified in terms of volume expansion and foam decays, respectively. The foaming process latex foam using a FoamScan® analyzer was slightly different compared to the actual foaming process using Kenwood mixer, especially the design of the rotary blade and the speed of the whipping process. Nevertheless, a FoamScan® analyzer is the only instrument available that allows researchers to visualize the
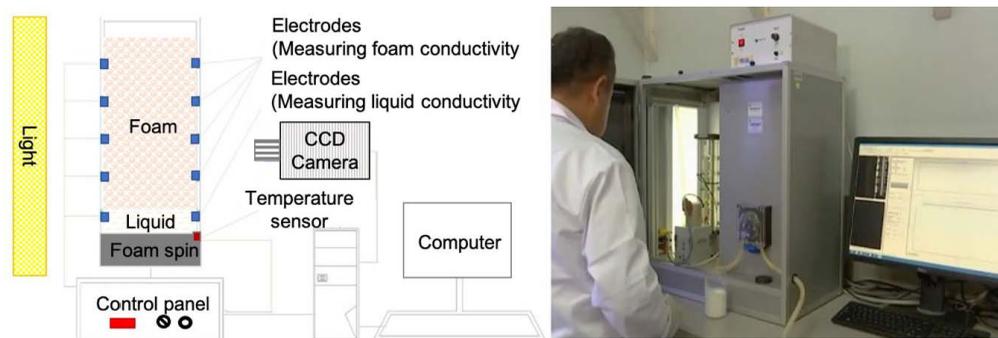

FIG. 1. — FoamScan® analyzer configuration.

FIG. 2. — The different stages involved in the fabrication of NR latex foam using the Dunlop batch foaming process.

microscopic transition of latex from liquid phase into foam phase, thus allowing further study on foamability and subsequence stability of the SpNR latex foam.

FOAMING, GELLING, AND FABRICATION PROCESS

The fabrication of latex foam in this work is similar to the conventional Dunlop batch foaming process,[42,43] which involves compounding, foaming, gelling, molding, vulcanizing, washing, and drying process (Figure 2). Table II shows the gelling formulation used in this study. In this work, the maturated latex compound was weighted accordingly and poured into a Kenwood mixer. Mechanical agitation was applied, where the Kenwood mixer stirrer rotated in a planetary motion at high speed. This whipping action resulted in air entrapped inside the latex compound. In this study, three wet density levels of latex foam, namely, high-density (0.16 g/cm^3) (HD), medium-density (0.12 g/cm^3) (MD), and low-density (0.09 g/cm^3) (LD) were prepared. This was achieved by controlling the weight of the latex and the volume expansion of

TABLE II
GELLING FORMULATION USED IN THIS STUDY

Ingredient	TSC (%)	Dry weight (phr)	Wet weight (g)		
			HD	MD	LD
Latex[a]	60	100	1000	750	500
Diphenyl guanidine dispersion	40	0.3	4.5	3.5	2.5
Zinc oxide dispersion	60	5	50	37.5	25
Sodium silicofluoride dispersion	50	0.4–1.3[b]			

[a] LATZ, ENR, and DPNR latex.
[b] Variable in this study; depending on the type of latex, alkalinity and the density levels.

the latex foam during the foaming process. In this work, the targeted volume of the latex foam is 5500 mL; therefore, the latex foam was whipped until it reached a level of volume marked at the bowl. This may require a duration of 5 to 6 min. Additionally, during the foaming process, a latex foam sample was taken out from the bowl mixer and poured into a 50 mL beaker to determine the wet density of the latex foam.

The foaming behavior of each type of latex examined in this study was elucidated, and the actual dosage of gelling ingredients for each type of latex at the targeted three density levels was determined. In this work, the latex foam that had been whipped to the targeted density levels was refined by slowing down the rotation speed from 400 rpm to 140 rpm and allowed the foam to be continuously stirred for another 2 min to refine the foam-cell structure. During the refining stage, all large bubbles were eliminated, resulting in a more uniform foam-cell size. Then, gelling ingredients listed in Table II were added. Zinc oxide (ZnO) dispersion was added first, followed by the addition of diphenyl guanidine (DPG) dispersion. DPG is a secondary delayed-gelling agent, which also act as a secondary accelerator during the vulcanization process.[42] After that, a gelling agent was added.

Sodium silicofluoride (SSF) dispersion in combination with ZnO dispersion is the primary gelling agent used in the NR latex foam industry. Although SSF is usually prepared at 50% TSC, in this study, it is proposed that diluting the SSF to 20% TSC prior to addition to the latex foam prevents sudden gelation of the latex foam. According to Blackley,[42] when pH value drops, the zinc complexes will react with soap (potassium oleate) to form zinc soap gradually, and therefore removes the protective layer of the foam-cell. At this point, SSF is added and gradually hydrolyzed so that the latex foam can be gradually gelled. The actual dosage of SSF may vary depending on the type of latex, alkalinity, amount of soap used, the density levels, and the speed of gelation required. Therefore, the dosage of SSF required for each type of latex and density levels were determined experimentally. In this work, SSF was diluted first to 20% TSC prior to addition into latex foam. Consequently, a glass electrode of a pH meter model HANNA Instruments 2210 was placed into the latex foam. A pH meter accurately measured the pH change in the latex during the gelation process. The methodology is based on the direct determination of hydrogen ion concentration in the solution. Normally, NR latex foam is gel at pH 8.5.[27,42] In this study, the effect of SSF levels on gelling time and pH values were investigated.

After a suitable level of SSF was added, the latex foam was poured into a square shape mold of $200 \times 200 \times 40$ mm (length $\times$ width $\times$ height). In this work, the latex foam was allowed to gel and rest at room temperature for 5 min before being transferred into a hot air oven at a temperature of 100 °C and vulcanized for 60 min. Vulcanization is a chemical reaction that gives the latex foam its final fixed and elastic shape. After vulcanization, the mold is opened, and the vulcanized latex foam was peeled out from the mold and then subjected to a washing process to remove excessive soap, extractable proteins, and residual chemicals. The washing operation is not critical, but this process is important to ensure that elasticity is retained and to counter ageing due to chemical residues. A typical process involves soaking the latex foam in warm water (45 °C) and then squeezing out the water through squeeze rollers. Then, the latex foam is subjected to a drying process. All samples were kept dry at room temperature before being subjected to testing.

DETERMINATION OF WET FOAM DENSITY

During the foaming process, the latex foam sample was taken out from the bowl mixer and poured into a 50 mL beaker to determine the wet density of the latex foam, to ensure each batch of latex achieved the targeted latex foam wet density. The wet density was calculated in accordance with Eq. 1.

$$\text{Wet density} = \frac{\text{Mass of the sample (g)}}{\text{Volume of the beaker (cm}^3)} \qquad (1)$$

DETERMINATION DRY DENSITY

During the foaming process, approximately 250 mL of latex foam was poured into a 250 mL square container. Then, the latex foam sample was subjected to a similar fabrication process. The dry density of the latex foam was determined in accordance with Eq. 2.

$$\text{Dry density} = \frac{\text{Mass of the specimen (g)}}{\text{Volume of the specimen (cm}^3)} \qquad (2)$$

DETERMINATION OF VOLUME SHRINKAGE

Volume shrinkage is an important property in latex foam technology as it determines the size of the finished latex foam products. Volume shrinkage was calculated as a percentage and measured from the difference in dimension between the mold and the fabricated foam (Eq. 3).[27]

$$\text{Volume shrinkage} = \frac{\text{Mold size (cm}^3) - \text{Latex foam size (cm}^3)}{\text{Mold size (cm}^3)} \times 100\% \qquad (3)$$

MORPHOLOGICAL STRUCTURE STUDY

Scanning electron microscopy (SEM) was used to visualize the morphological structure of the foam samples. A test portion of 5 mm × 5 mm × 5 mm (L × W × H) from the samples was cut and attached to a specimen stub using a carbon double-sided tape. The specimen was coated with an ultra-thin layer of platinum under a high vacuum evaporate process before visualizing under SEM operated at 15 kV. The SEM images were captured at 40× magnification. Images obtained from SEM were then analyzed using ImageJ software to quantify the porosity and pore size of the latex foams.

STRESS–STRAIN COMPRESSION TEST

A compression test is normally used to determine the compressive strength and energy absorption of a material.[44] In this work, DPNR latex foam prepared at dimension of 200 mm × 200 mm × 40 mm (length × width × height) was used. On the other hand, for PUF and CMF, foam samples cut at dimension of 200 mm × 200 mm × 50 mm (length × width × height) were used. The test was carried out using a 25 kN servo-hydraulic MTS Multi-Axis testing machine. The test was carried out at room temperature ($\sim$25 °C). The loading and unloading process was set to run for five cycles at a rate of 0.2 Hz. Each sample was compressed up to 50% from its original height using a square platen. An assumption was made that during the loading and unloading process of the tests, there was no separation between the platen and the foam samples. The load (compression stress) and displacement behavior for each specimen is digitally recorded throughout the test.

RESULTS AND DISCUSSION

EFFECT OF COMPOUNDING ON VISCOSITY AND PH VALUE OF LATEX

Table III shows the effect of compounding on viscosity and pH value of the latexes. It is clear that pH value of all latexes was decreased, while the viscosity was increased. The decreased pH

TABLE III
EFFECT OF COMPOUNDING ON VISCOSITY AND pH VALUE OF LATEX EXAMINED IN THIS STUDY

Stage of latex	LATZ pH/viscosity	ENR pH/viscosity	DPNR pH/viscosity
Latex concentrate	9.70/70	9.50/500	9.61/115
Compounded latex	9.46/135	9.20/500	9.35/175

value could be due to the evaporation of ammonia from the latex during overnight maturation process. On the other hand, the increased viscosity of the latex could be due to the chemical reactions of the vulcanizing ingredients. The viscosity of prevulcanized NR latex could be correlated to the colloidal stability of the material, which many factors depend on, such as prevulcanization temperature and time, the amount and type of stabilizers, and the dosage of vulcanizing ingredients, as well as the TSC and particle size of the latex itself. Previous study[45] indicated that the prevulcanization process has little effect on the viscosity of the latex compound. Contradictorily, another study[46] stated that the viscosity of NR latex increases due to the thickening effect resulting from the chemical reaction between soaps (in this case potassium oleate) and ZnO in the presence of ammonia in the latex system. This was further supported by Mathew and Varghese,[47] since the soluble soaps converted into insoluble material due to reaction with ZnO, thus increasing the viscosity. Further to that, the presence of ZMBT as a secondary accelerator also can cause latex thickening (increase in viscosity) because ZMBT is slightly acidic and thus neutralizes alkali in the latex system.[48]

FOAMABILITY AND STABILITY STUDY

Figure 3 shows that the foam volume of all latexes gradually increased with time due to the mechanical agitation process. In this experiment, the agitation process was automatically stopped after 600 s to elucidate the foamability of each latex. Apparently, all latexes could be foamed.

However, the foamability of each latex differs. The study found that the LATZ, DPNR and ENR latex was foamed from 60 mL to 200 mL, 160 mL and 140 mL latex foam respectively. This indicates that LATZ latex exhibits the highest foamability followed by DPNR and ENR latex. According to Sun et al.,[49] the thicker the liquid, the slower the growth speed, in other words the slower the transition of the material from a liquid phase to a foam phase. Therefore, the foamability of each NR latex examined in this study might be influenced by the viscosity of the latex, where higher viscosity led to decreased foamability of the latex. This correlates with viscosity results shown in Table III where the viscosity of ENR latex is the highest, followed by DPNR and LATZ latex. Figure 3 also shows that ENR latex foam is more stable compared to DPNR and LATZ latex foam, where the foam is retained at a similar foam volume for 80 s before drainage. The stability of foam material is normally measured starting from decaying until half of its original volume is reached. Nevertheless, in this study, all latex foams are considered stable because the drainage volume over time is less than 15%.

Figure 4 shows foaming images of the latex foams that were captured by an integrated camera. The gray area represents gas-phase encapsulated by latex film, while the darker area is the latex phase. The images show that at 300 s, all latex foams were still at the foaming stage. LATZ exhibits the highest number of bigger foam-cell size, followed by DPNR and ENR latex foam. This correlates with Figure 3, where LATZ shows the fastest foam growth compared to DPNR and ENR latex foam.

After the mechanical agitation automatically stopped at 600 s, the foam-cell size of each latex was visually compared. Assessing from the liquid film thickness (dark area) and foam-cell size,
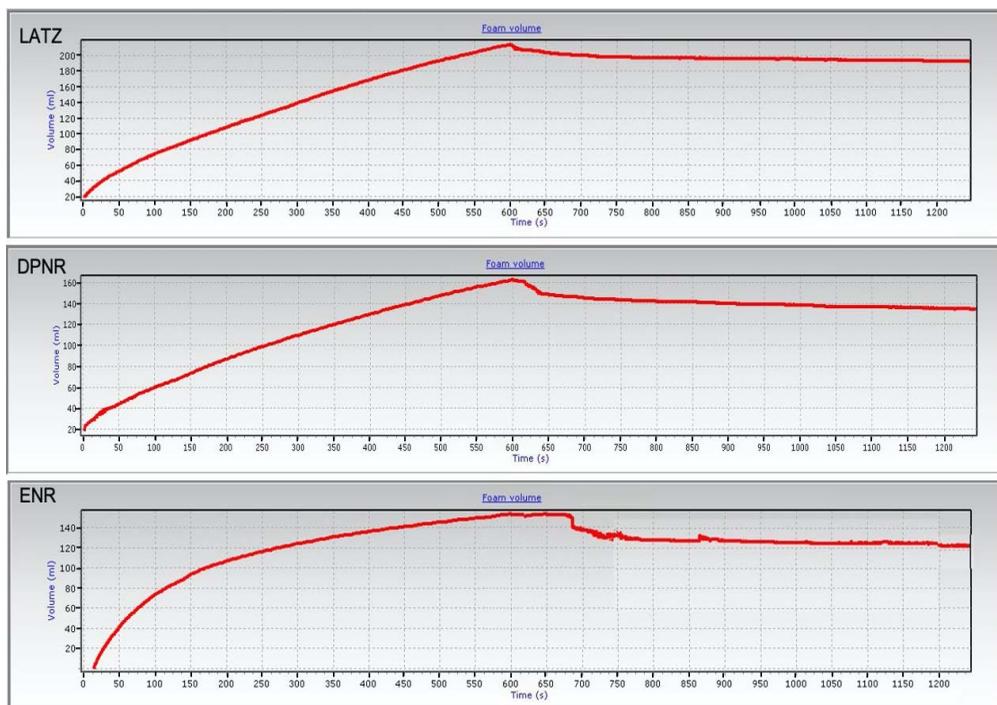
FIG. 3. — Foam volume versus time for LATZ, DPNR, and ENR.

LATZ and DPNR latex exhibit a moderately even liquid film thickness but unequal foam-cell size, thus the foam-cell structure of LATZ and DPNR latex is categorized as polynomial foams.[49] On the other hand, the liquid film thickness for ENR latex foam varies, and smaller foam-cell structure could be observed. This study assumed that addition of extra foaming agent in the latex system
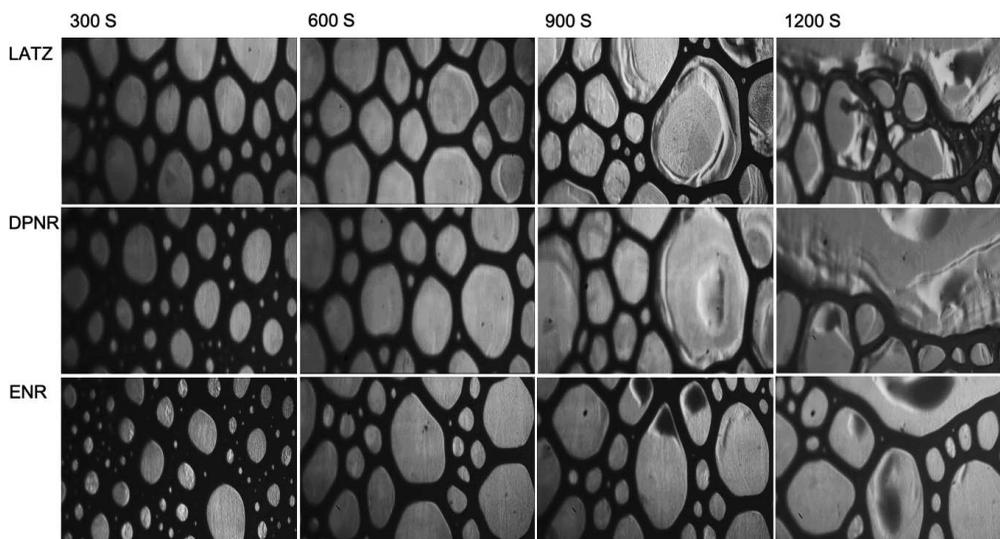

FIG. 4. — Foamability and stability study of latex.

could increase the foamability of the latex, thus a uniform liquid film thickness and foam-cell size of the latex foam could be obtained.

Figure 4 also demonstrates the foam-cell structure started to collapse after 900 s. This is due to the pressure difference between foam-cells and the gravitational force that causes the liquid film to drain out of the foam. This phenomenon has been explained by Sun et al.[49] where a pressure difference between smaller and bigger foam-cells has driven gas molecules trapped in the smaller foam-cells to diffuse into bigger foam-cells through liquid film. Gas molecules diffuse from smaller foam-cells into bigger foam-cells because the pressure in the smaller foam-cells is higher than the bigger foam-cells. Therefore the bigger foam-cells continue to grow bigger, eventually the liquid film ruptured and the foams collapse. Nevertheless, different types of latex might have different foam stability. Figure 4 shows that after 900 s foam-cell structure of ENR latex is more stable compared to LATZ and DPNR latex foam. The reason behind this phenomenon is unclear, but it is possibly due to the physiochemical properties (i.e., total solid content, dry rubber content, mechanical stability time, viscosity) of each latex. Previous study[50] revealed that the presence of non-ionic surfactant in the ENR latex system contributes to a high stability of the material. Additionally, the presence of non-ionic surfactant in the ENR latex system was observed to increase the viscosity of the latex. Previous studies[51] noted that the viscosity of a liquid affects its foam stability, where higher viscosity exhibits higher fluid flow resistance, consequently reducing the foam drainage tendency. Thus, the foam produced from higher viscosity is more stable. Table III indicated that each latex has different viscosity, and ENR latex shows the highest viscosity, followed by DPNR and LATZ latex. Therefore, ENR latex foam demonstrates a stable foam compared to LATZ and DPNR latex foam. This phenomenon can be observed in Figure 3 and microscopically visualized in Figure 4. Nevertheless, the viscosity of each latex is influenced by the composition of the latex system, where both DPNR and ENR latex contain non-ionic surfactant to stabilize and preserve the latex from coagulation after the modification process. Further to that, as indicated in Figure 3, the volume expansion of ENR latex foam is lower compared to LATZ latex foam and DPNR latex foam. However, at 1200 s all latex foams were observed to collapse.

PRELIMINARY OBSERVATION AND STUDY ON FOAMING BEHAVIOR

First, we recall that the first step of the Dunlop batch foaming process is compounding of the latex with vulcanizing agent together with a stabilizer, which also acts as a foaming agent. The second step is foaming the latex, where the latex changes from the liquid phase into the latex foam phase. This is followed by the addition of gelling ingredients to set the foam-cell structure. To develop foaming and gelling formulation for fabricating SpNR latex foam, it is crucial to determine relevant parameters controlling foaming and gelling behaviors of SpNR latex. This study observed that foam collapses and foam coagulate are two main challenges in producing SpNR latex foam (Figure 5). It was noticed that there are few factors that lead to foam collapse, such as volume expansion too high, levels of gelling agent not being suitable, and latex foam too stable to be gel due to excessive stabilizer or surfactants. On the other hand, foam coagulate is mainly due to insufficient foam stabilizers and excessive gelling agent. This study also found that lower foam density requires additional PO to function as a foaming agent. However, the presence of a higher level of PO requires additional SSF to balance the gelling system. In a well-balanced latex foam foaming and gelling formulation, the latex foam required about 5 to 7 min to set, and this must be regarded as the upper limit of time that is available for transferring the latex foam from the bowl to the mold.[48] Normally, a secondary delayed-gelling agent such as DPG can be added to stabilize the foam-cell structure.[16] Nevertheless, many other factors might contribute to foam process failure such as viscosity, total solid content, chemical stability of the latex as well as the type of chemical stabilizer used in the latex system.[42]

FIG. 5. — Failure during foaming process. (a) Foam coagulate; (b) Foam collapse.

In addition to foam collapse and foam coagulate, surface defects such as wrinkles, rat holes, coarse structure, flow marks, and phase separation may occur if the gelling formulation is incorrect (Figure 6). Figure 6a shows surface wrinkles caused by an imbalance between zinc soap and acidic gelling agent, typically insufficient SSF. Figure 6b shows an example of phase separation, where the foam-cell size at the bottom part of the latex foam sample appeared to be smaller than the upper part.

According to Blackley,[42] phase separation is a consequence of foam drainage caused by long gelling time. This is a situation where the latex foam-cell structure slowly collapse due to the pressure difference between foam-cells and gravitational forces. Figure 6c demonstrates a thick layer of skin that appeared at the bottom part of the latex foam. This is because the liquid foam that has been drained back into the liquid phase coalesces to become latex film. To address these issues, additional SSF should be added to set the latex foam-cell or locking latex foam at a consistent foam-cell structure. However, it is important to keep in mind that too much SSF would cause the latex foam to coagulate in a very short period. Figure 6d demonstrates surface defects such as rat holes, coarse structure, and flow marks. This is a result of incorrect gelling system, where the gelling reaction occurred at low pH due to acidic gelling agent.[52] Therefore, determination of actual dosage of SSF is important, especially in this study when different types of latex are used.

FOAMING AND GELLING BEHAVIOR

Table IV shows the wet density of the latex foam produced in this study. For LATZ latex, the latex was foamed to the targeted volume expansion within 5 min. The targeted wet density of HD, MD, LD were achieved. For DPNR latex, it was observed that, for HD, the latex was foamed to the targeted volume expansion within 5 min. But, for MD and LD, the growth of the latex foam was found to be slightly slower, thus unable to reach the targeted volume expansion within 5 min. Although the foaming time has been extended to 8 min, the latex foam was still unable to reach the targeted volume expansion. The latex foam was observed to reach only three-quarters of the targeted volume expansion.

Therefore, in this work, an additional dosage of PO was added into the DPNR latex to improve its foamability. Thus, to produce MD and LD of DPNR latex foam, an additional 0.25
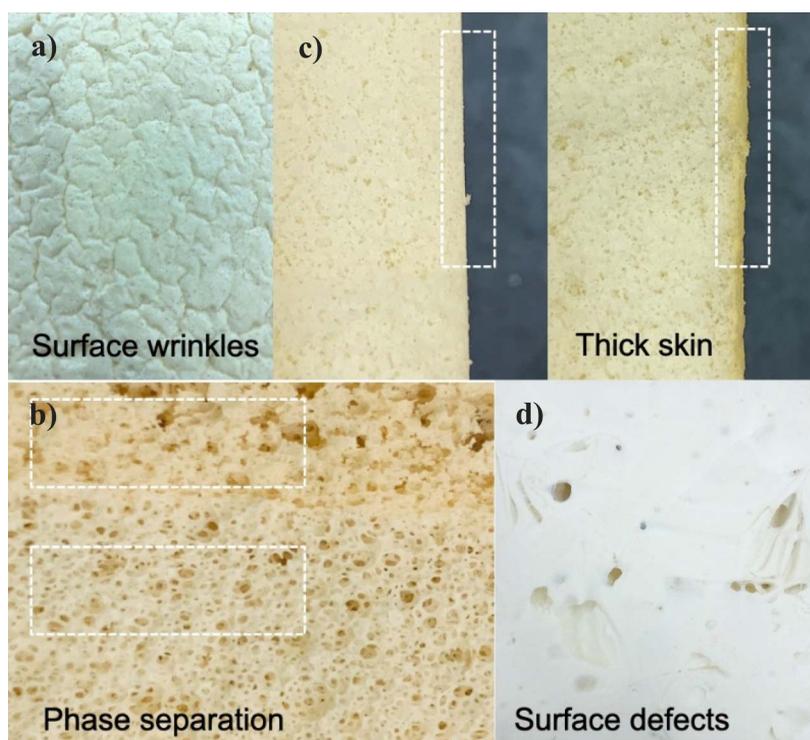
FIG. 6. — Latex foam failure. (a) Surface wrinkles; (b) Thick skin; (c) Phase separation; (d) Surface defects.

and 0.5 phr of PO was added, respectively. Similar to DPNR latex, ENR latex was unable to reach the targeted volume expansion within the targeted time. Therefore, additional 0.25, 0.5, and 0.75 phr of PO were added into the latex to produce HD, MD, and LD of ENR latex foam, respectively. This leads to the conclusion that the addition of extra PO as a foaming agent helped to improve the foamability of DPNR and ENR latex. Nevertheless, Table IV shows that the targeted wet density of ENR (LD) latex foam was found slightly higher than the targeted wet density. The reason behind this is still unclear and needs further investigation. After the latex foam achieved the desired degree of volume expansion, the speed of the foam mixer was reduced to refine the foam-cell structure. Then, ZnO and DPG were added. The latex foam was allowed to be continuously stirred for 1 min to ensure ZnO and DPG are well dispersed in the latex foam. Then, pH value of the latex foam was recorded.

TABLE IV
WET DENSITY OF THE LATEX FOAM

Parameters	LATZ Wet density (g/cm^3)	ENR Wet density (g/cm^3)	DPNR Wet density (g/cm^3)
HD	0.16	0.16	0.16
MD	0.12	0.12	0.12
LD	0.09	0.10	0.09

TABLE V
EFFECT OF COMPOUNDING AND DENSITY LEVELS ON pH VALUE OF LATEX FOAM

Stage of latex	LATZ (pH)	ENR (pH)	DPNR (pH)
Compounded latex	9.46	9.41	9.35
Latex foam + DPG + ZnO	$9.37^a/9.20^b/8.75^c$	$9.38^a/9.30^b/8.99^c$	$9.28^a/9.15^b/8.99^c$

[a] HD.
[b] MD.
[c] LD.

Table V shows that the pH value of the latex foam was reduced after the foaming process. The reduced pH value of the latex foam could be due to a chemical reaction between the ZnO+DPG and the latex and also due to the frothing process.

According to Madge,[52] during the foaming process, a certain amount of ammonia has been lost to the atmosphere, thus changing the acidity of the latex foam. Therefore, this study agreed with the report made by Madge.[52] Further to that, this study observed that the lower the density of the latex foam, the further the pH value was decreased. A similar trend was observed on each type of latex used in this study.

The latex foam fabrication process was continued by the addition of SSF as the gelling agent. In this work, the effects of SSF on pH value and gelling time of latex foam produced at different density levels were investigated. Figures 7, 8, and 9 show the results for LATZ, DPNR, and ENR latex foam, respectively. For LATZ, a gradual drop of pH value was observed after the addition of SSF. This study observed that a higher level of SSF leads to a bigger drop in pH value. However, this study also observed that the addition of 0.4 phr of SSF into LATZ (HD) latex foam is unable to gel the latex foam even after the latex foam was left to gel for 10 min.

Consequently, the latex foam tended to collapse. This indicates that 0.4 phr of SSF used is too low. Therefore, the level of SSF was increased. This study found that the addition of 0.5 and 0.6 phr of SSF was able to gel the latex foam within 5 and 4 min, respectively. Both samples were observed to gel at pH 8.6, almost similar to gelling pH value of 8.5 recorded by the previous study.[27] Comparison between 0.5 and 0.6 phr, gelling time 0.6 phr is slightly faster than 0.5 phr. According to a previous study,[52] in a well-balanced latex foam formulation, latex foam required about 5 to 7 min to set or completely gel. This is regarded as the time for transferring the latex foam from the bowl into the mold. Therefore, this study suggested that the best dosage of SSF for LATZ (HD) latex foam is 0.5 phr. Nevertheless, Figure 7 revealed that different density levels require a different dosage of SSF, where LATZ latex foam MD and LD requires 0.7 and 0.8 phr of SSF, respectively. Accordingly, the gelling time for MD and LD of LATZ latex foam was recorded at 5 and 6 min, respectively. On the other hand, the gelling pH for MD and LD of LATZ latex foam was recorded at pH 8.0 and 7.5. Generally, it can be observed that gelling time and gelling pH are influenced by the levels of SSF added. The level of SSF required depends on the density levels of the latex foam.

Figure 8 shows gradual drops of pH by time in each density level of DPNR latex foam after SSF was added, similar to the LATZ latex foam. Nevertheless, results showed in Figure 8 indicate that DPNR latex requires higher levels of SSF to reach gel state compared to LATZ latex foam.

For example, 0.5 phr SSF was required to gel LATZ (HD) latex foam, but for DPNR (HD) latex foam, 0.8 phr of SSF was required. This could be due to the presence of non-ionic surfactants in the DPNR latex system reacting with the chemical gelling agents thus preventing and delaying the gelling process.[53] In addition, gelling pH of DPNR (HD) latex was observed lower than LATZ (HD) latex foam. A similar trend was observed on each density level of DPNR latex foam. Figure 8
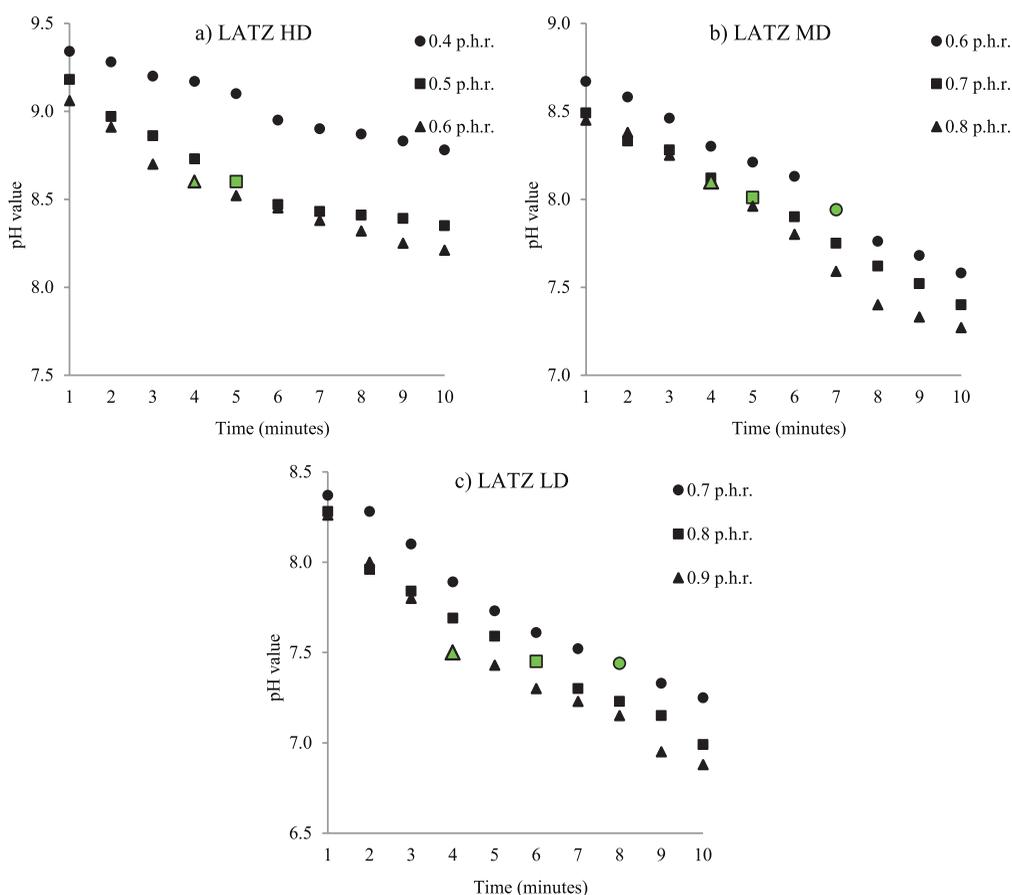
FIG. 7. — Effect of SSF levels on gelling time of LATZ latex foam. Green color indicates gelling time.

shows that HD, MD, and LD of DPNR latex foam were gel at pH 8.15, 7.50, and 7.40, at gelling times of 6, 6 and 7 min using SSF levels of 0.8, 1.0, and 1.2 phr, respectively.

On the other hand, ENR latex shows a longer gelling time than LATZ and DPNR latex foam. HD, MD, and LD of ENR latex foam were observed to gel at the gelling time of 7 min, at pH 8.29, 7.70, and 7.50, using SSF levels of 0.9, 1.10, and 1.20 phr, respectively. This could be due to different chemical compositions in the ENR latex system as a result of the epoxidation process. Further to that, NR latex is stabilized by protein molecules, fatty acid soaps, and surfactants (carboxylic anions) adsorbed on the surface of rubber particles.[16] This negative charge produces repulsive forces and ensures the absence of aggregation. Reduction in pH by the addition of acid gelling agent reduces ionization of adsorbed anions and decreases the repulsive forces due to which gelation takes place.[41,52] Therefore, the slower rate of gelation of ENR latex foam in comparison to LATZ foam might be due to the presence of additional stabilizers or surfactants (i.e., ammonium laurate, potassium oleate).

APPEARANCE

Figure 10 shows the appearance of LATZ, DPNR, and ENR latex foam produced in this study. The color of the dried latex foam appeared slightly different, where LATZ and DPNR latex foam
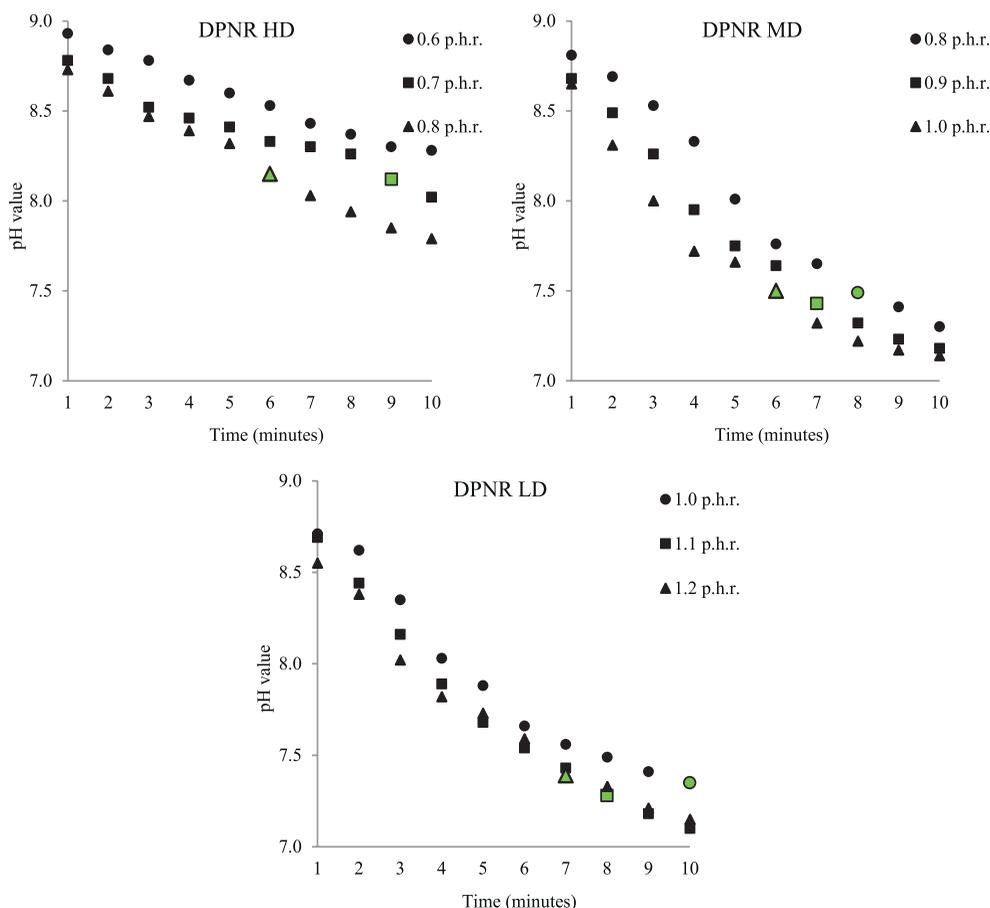
FIG. 8. — Effect of SSF levels on gelling time of DPNR latex foam. Green color indicates gelling time.

appeared to be an off-white color, but ENR latex foam appeared as a creamy-yellow color. The creamy-yellow color of ENR latex foam could be due to epoxidation reactions as well as a heating process that was conducted at elevated temperatures for 24 h. All latexes were able to foam at three different density levels and labeled as HD, MD, and LD foams. However, after the vulcanization process, only LATZ and DPNR latex foam were successfully fabricated at three density levels. For ENR latex, ENR (LD) latex foam was observed to flop down to the center of the latex foam sample like a crater after the vulcanization process. The reason behind this is not clear, but it may be due to the poor wet gel strength of the material, as a result of the high level of stabilizer presence in the latex system. During the vulcanization process, the mold is closed with a lid. The lid has been manufactured with a small hole to allow vapor materials including water and ammonia to evaporate from mold leaving a solid latex foam material. However, during the evaporation process, the wet latex foam suffered from pressure differences in between the lid and top surface of the latex foam. At this stage, the foam-cell structure of the latex foam has not solidified, therefore, the pressure tended to push the latex foam to flop down. LD latex foam is a low-density latex foam, thus it is expected to have low wet strength compared to HD and MD latex foam. Therefore, this study assumes that the weak wet gel strength of ENR (LD) latex foam is unable to oppose the pressure, thus leading the latex foam to flop down, creating a crater during the vulcanization process.
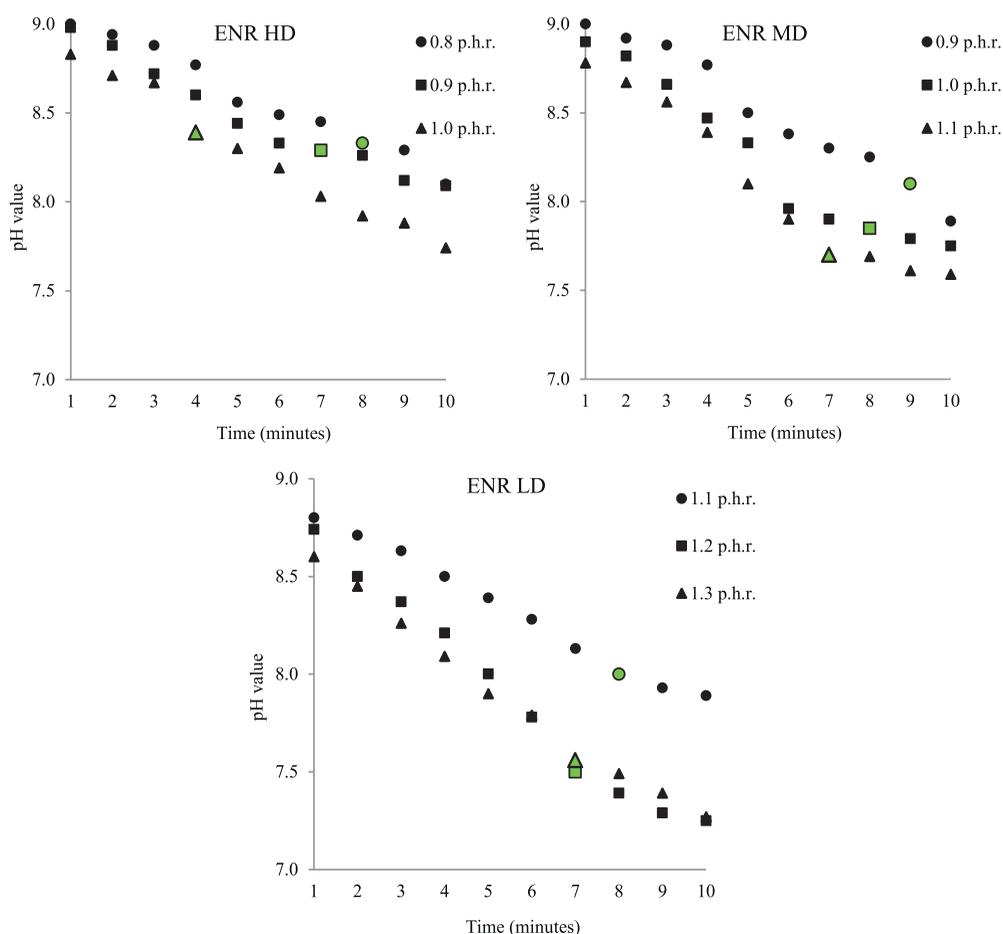
FIG. 9. — Effect of SSF levels on gelling time of ENR latex foam. Green color indicates gelling time.

MORPHOLOGICAL STUDY

Figure 11 shows morphological structures of LATZ, DPNR, and ENR latex foam prepared in this study. All latex foams exhibit interconnected microporous structure. The Dunlop method is a mechanical foaming process that regulates pore formation poorly, leading to a non-homogeneous foam distribution.[54] Observation on the pore size of HD latex foam showed that it is smaller compared to MD and LD latex foam. This is expected because the lower the density the higher the volume expansion. Consequently, the higher the volume expansion the bigger the growth of foam-cell size. Figure 11 also visualized the morphological structure of LD ENR latex foam. Apparently, the foam-cells collapsed and coalesced to each other.

To further investigate the effect of density on pores size and porosity of the latex foams, ImageJ software was used. Figure 12 indicated that decreasing the density of the latex foam would increase the mean pore size of the latex foam. The smallest mean pore size was observed on ENR (HD) latex foam, while the largest mean pore size was visible by DPNR (LD) latex foam. Porosity value corelates with the mean pore size, where porosity values increase when the mean pore size increases. DPNR (LD) latex foam exhibits the most porous material, where the porosity of the material is more than 50%. On the other hand, DPNR (HD) latex foam exhibits the most resistant
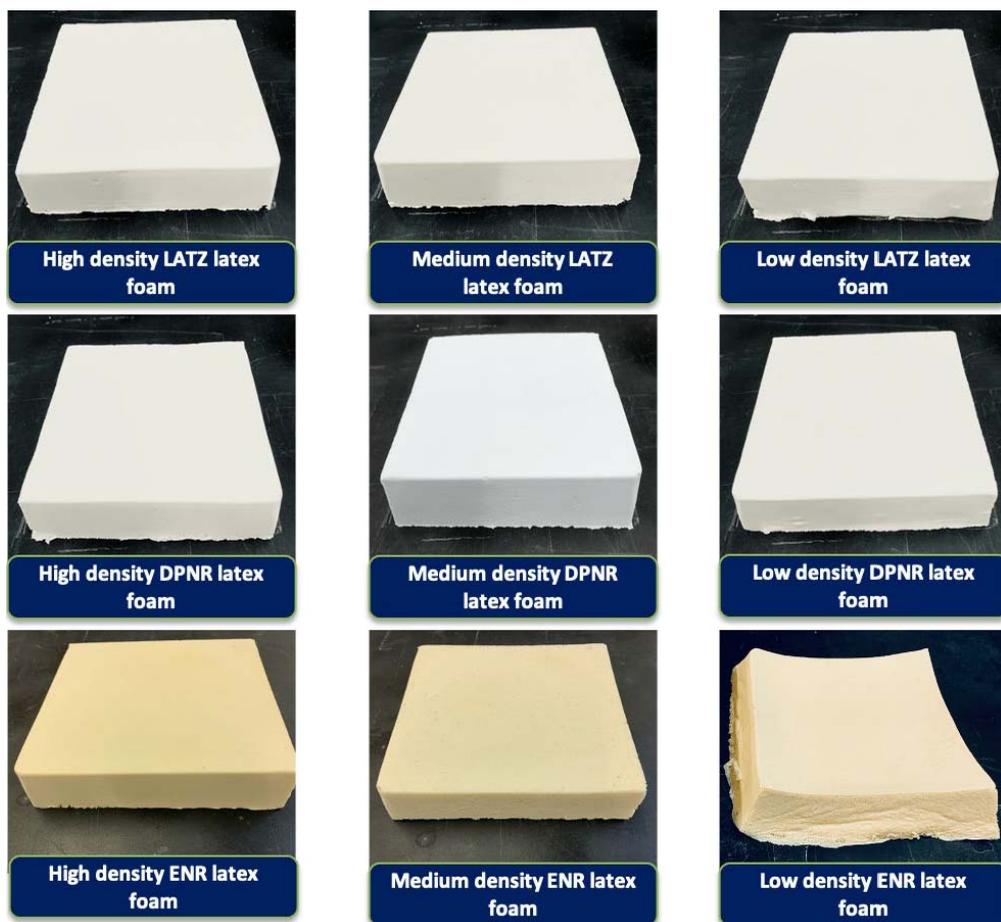
FIG. 10. — Appearance of LATZ, DPNR, and ENR latex foam.

material. For medium-density foam material, ENR (MD) latex foam exhibits the lowest porosity, followed by LATZ (MD) and DPNR (MD) latex foam.

EFFECT OF DENSITY ON VOLUME SHRINKAGE

Table VI shows the dry density and volume shrinkage of latex foam fabricated in this study. The dry density of all latex foams fabricated in this study was decreased to almost half of the wet density value.

This study also found that higher density latex foam exhibits higher volume shrinkage. No significant difference of volume shrinkage between LATZ and DPNR latex foam was observed. However, the volume shrinkage of ENR latex foam is higher than LATZ and DPNR latex foam. The reason behind this is not clear, but it could be due to chemical epoxidation reactions on the molecular structure of rubber which lead to changes in physical properties of the rubber material including volume shrinkage. Additionally, the higher volume shrinkage of ENR latex foam also might be due to higher SSF added during the gelling process.[41,52]
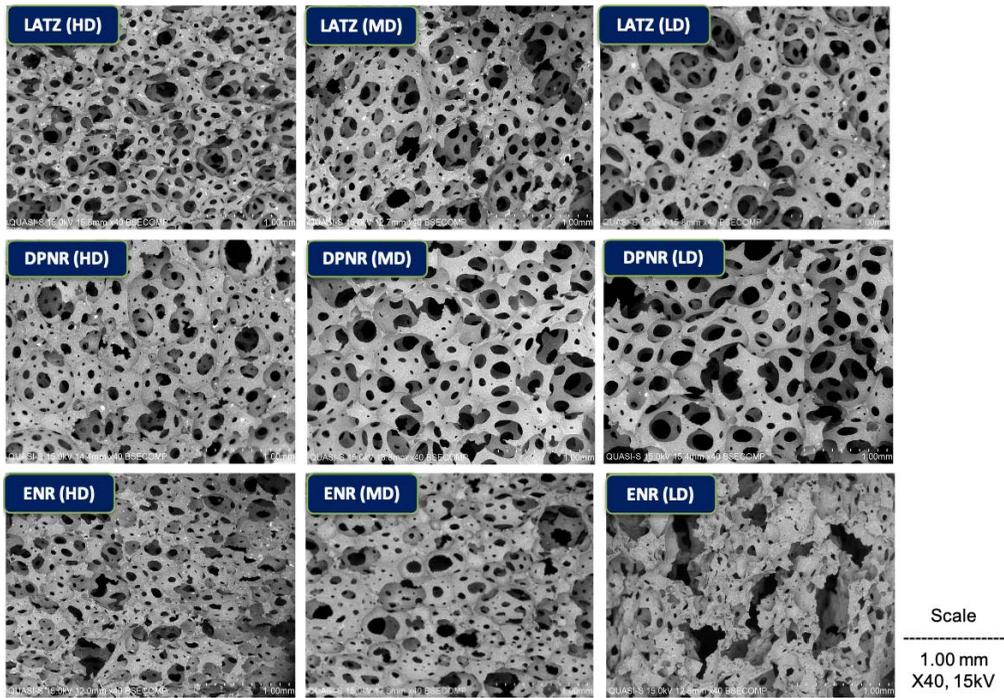
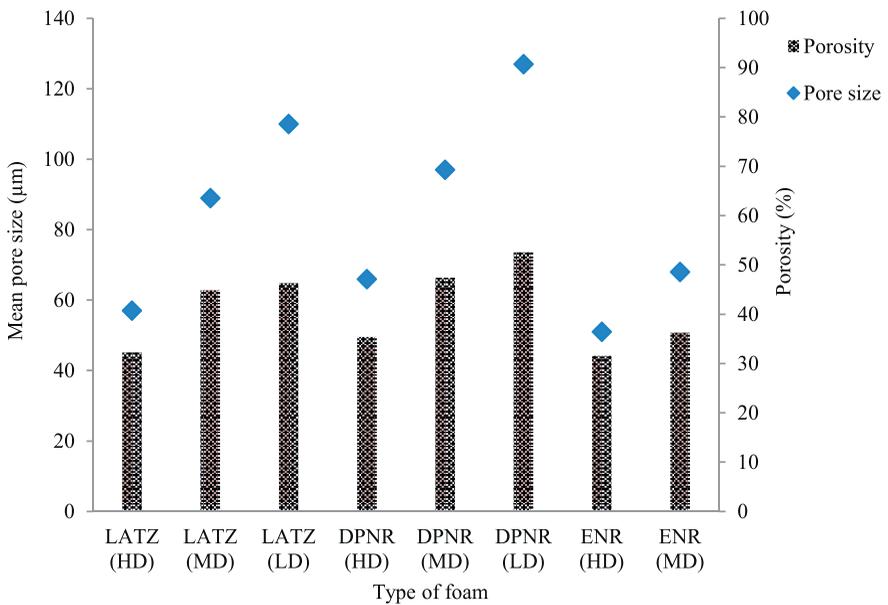FIG. 11. — Micrographs of LATZ, DPNR, and ENR latex foam.

FIG. 12. — Mean pore size and porosity of latex foams.

TABLE VI
EFFECT OF DENSITY LEVELS ON VOLUME SHRINKAGE

Parameters	LATZ		ENR		DPNR	
	Dry density (g/cm³)	Volume shrinkage (%)	Dry density (g/cm³)	Volume shrinkage (%)	Dry density (g/cm³)	Volume shrinkage (%)
HD	0.10	12	0.11	13	0.10	12
MD	0.08	11	0.09	12.5	0.08	11
LD	0.06	10	N/A	N/A	0.06	11

HYSTERESIS STUDY

Figure 13 shows the stress–strain curve of DPNR and ENR latex foam obtained from the compression test. In this work, the third cycle of compression force-displacement curve was chosen because it has been suggested as the stable curve for the hysteresis study by the previous study.[44] To the authors' knowledge, this is the first time the stress–strain curve of DPNR and ENR latex foam has been presented, since no literature can be found. The results indicated that at the first 0.2 strain, DPNR latex foam exhibits higher uploading stress value compared to ENR latex foam. However, beyond that strain value, ENR latex foam exhibits higher uploading stress value. This could be the formation of epoxy group in the rubber chains that increased the stiffness of ENR latex foam, especially at high percentage of deformation.

Figure 13 also demonstrates the hysteresis loop (between loading and unloading curve) of the DPNR and ENR latex foams. The hysteresis is defined as the energy loss (dissipation energy) per cycle of deformation.[55] It is well understood that the area under the loading curve is the total mechanical energy input, while the area under the unloading curve is the return of stored energy, and the area between the two curves is the dissipated energy that converted to heat.[51] The
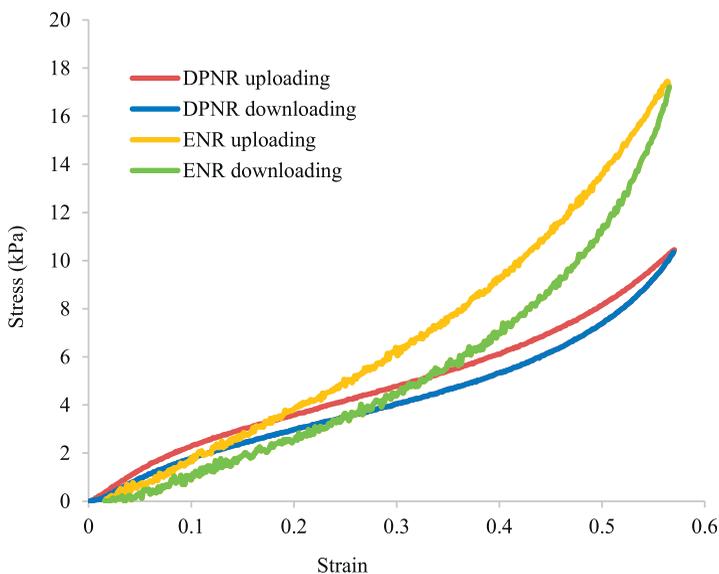

FIG. 13. — Hysteresis loop of medium-density DPNR and ENR latex foams.
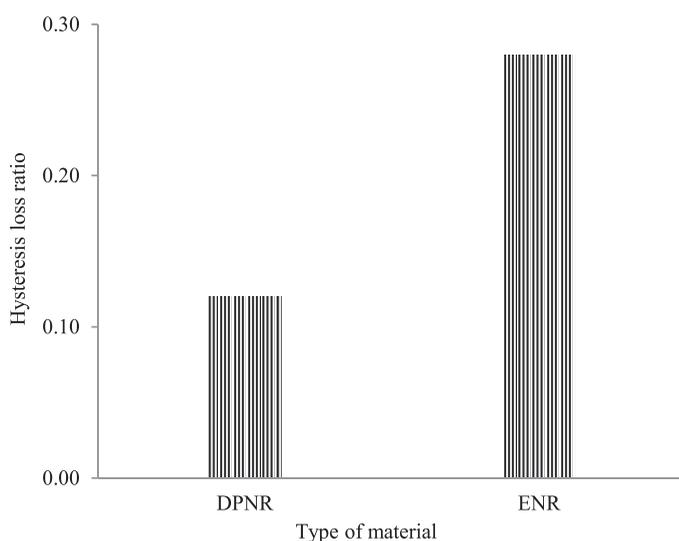
FIG. 14. — Hysteresis loss ratio of DPNR and ENR latex foams.

importance of the hysteresis measurement is that it gives a strong indicator about the material capacity to absorb energy and/or relieve pressure.[56,57] Apparently, ENR latex foam exhibits a larger hysteresis loop compared to DPNR latex foam. Previous studies[44] stated that hysteresis loss ratio can be calculated from a stable hysteresis loop, and the hysteresis loss ratio equation is given as follows,

$$\text{Hysteresis loss ratio} = \frac{H}{E} \qquad (4)$$

where H is the amount of hysteresis (dissipated energy, given by the difference of the area under the uploading and the unloading curve) and E is the equivalent energy during uploading (given by the area under the unloading curve).

Figure 14 indicates that hysteresis loss ratio of ENR latex foam is higher than DPNR latex foam. The higher the hysteresis loss ratio is, the higher the damping property of the material will be. Since the compounding formulation and density level (medium-density) of both DPNR and ENR latex foam are the same, the higher hysteresis loss ratio of ENR latex foam might be due to its high-damping property originated from the epoxy group in the rubber chains.

CONCLUSION

This study proved that SpNR latex concentrate can be used to produce latex foam. Foamability of SpNR latex is lower compared to normal latex (LATZ) but shows a longer stability time after foaming. Foam collapse and foam coagulate are two main challenges in the fabrication of SpNR latex foam, which can be solved by altering the foaming levels and gelling ingredients. Each type of latex requires different quantities of gelling ingredients. Gelling time and gelling pH are influenced by latex foam density and gelling agent added. This work provides ideal compounding, foaming, and gelling formulations for the fabrication of SpNR latex foam via Dunlop batch foaming process. DPNR latex can be used to produce low-density latex foam similar to LATZ latex foam. On the other hand, ENR latex can only be used to produce medium- and high-density latex foam. The morphological study indicated all latex foams are open-cell structures, where lower density foam

exhibits higher porosity and mean pore size. Comparison of hysteresis behavior between DPNR and ENR latex foam indicated that ENR latex foam exhibits a higher hysteresis loss ratio compared to DPNR latex foam.

ACKNOWLEDGEMENT

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