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A comparative study of surfactant-treated natural latex foam morphology, thermodynamic relationships and energy absorption: Talalay vs. dunlop processing

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ABSTRACT

This study investigates the relationships between the morphology, energy absorption, and thermodynamic parameters of natural latex foams (NLFs) processed by the Dunlop and in-house Talalay methods, using different surfactant blends. Both methods involved mixing, moulding, and heating; the additional steps for the Talalay method involved cooling and gelation, a gel-freezing technique wherein the frozen foam is exposed to CO2 gas, inducing its transformation into a gel. The morphology of the internal structure of the NLFs was studied using 2D scanning electron micrographs and 3D micro- computerised tomography images. Two different surfactants, potassium laurate and pluronic, were used. Adding the blended surfactants reduced the porosity and increased the foam density of the NLF samples, improving mechanical properties. The cell size distribution of the NLF samples prepared using the Talalay method was broader than that of those prepared using the Dunlop method. In terms of the mechanical properties and energy absorption capabilities, the Talalay process resulted in samples with 20% lower compressive strength and 7% lower energy absorption than the control sample. A power-law relationship between the energy absorption per unit volume and the compression speed of the different foam samples was also observed. The ratio of the internal energy to the total compression force of the NLF samples prepared using the Talalay process was also lower than those prepared using the Dunlop process. The empirical insights derived from this study show how the mechanical properties and process technology associated with the producing of material foams could be improved.

1. Introduction

Natural latex foams (NLFs) are structural foams derived from concentrated latex compounds harvested from rubber plants, such as *Hevea brasiliensis*. They feature a solid matrix with interconnected microvoids. These foams have exceptional qualities that make them useful for manufacturing rubber products, notably rubber foams (Kunam et al., 2023; Ng et al., 2022). The foam structure confers a high level of comfort as well as strong resistance to failure under cyclic loading

(Prasopdee et al., 2021). Thus, NLFs are applied in everyday products, such as cushioned car seats and furniture, footwear, mattresses, and pillows (Lin et al., 2023; Oliveira-Salmazo et al., 2016; Ramli, 2022; Sirikulchaikij et al., 2020). In addition to the micro-voids or pores, NLFs may be fabricated to feature a series of parallel regular-spaced cells or compartments resembling a honeycomb-like structure. Honeycomb-like materials are commonly used to manufacture lightweight structural components (Montgomery-Liljeroth et al., 2023; Sun et al., 2016).

Rubber foams are typically prepared using the Dunlop (Blackley,

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1997a; Hui Mei and Singh, 2010; Suksup et al., 2019) or Talalay methods (Klommueang and Smitthipong, 2023). The Dunlop method creates rubber foam by mixing the latex sap with a vulcanising agent, casting the mixture into a mould, and baking it to produce a structure with varying cell sizes. In contrast, the Talalay method involves two additional steps. After blending the latex sap with the vulcanising agent, the mixture is vacuum-sealed and frozen. This gel-freezing technique transforms the frozen foam into a gel by exposing it to CO₂ gas. After freezing, it is heat-treated. This vacuum-sealing and freezing process produces an expanded cell structure throughout the foam, resulting in softer rubber foams with improved flexibility.

The mechanical stability of natural latex can be improved by adding surfactants with higher numbers of carbon-carbon double bonds, double bonds with *cis* orientations, or hydroxyl groups (Singh and Mei., 2013). The ability of the foam materials to absorb energy is an important characteristic that can be exploited for impact resistance. There has been increasing interest in extending foam applications beyond traditional areas, including exploring their energy absorption properties in structural components for transportation, packaging, lightweight materials, and even cellular-level gradational materials.

In 2017, Singh et al. (Singh and Mei., 2013) purified natural latex using a mixture of sodium dodecyl sulfate (SDS) surfactant and urea. Their results demonstrated that the latex particles and films made from the purified natural latex were more homogeneous and had more distinct particles, allowing these purified natural latex films to exhibit mechanical properties comparable to that of commercial natural latex. Dhaliwal et al. (Dhaliwal et al., 2020) have also studied the mechanical effects of surfactants on soy-based polyurethane foams by focusing on the morphology of the foam samples. They found that increasing the surfactant concentration from 0.5 to 5.0 g resulted in a 17-fold reduction in cell size; the surfactant-rich samples also possessed a larger percentage of closed cells. Moameri et al. (Al-Moameri et al., 2021) have studied the effects of silicone and anionic surfactants on polyurethane foams. They found that the mechanical properties, closed-cell content, and thermal conductivity of the polyurethane foams depended on the type of surfactant used. The surfactant can influence the bubble size within the foam structure.

In addition to the processing method and surfactant treatment, rubber foams exhibit different microstructures depending on the preparation method used to create the bubbles. Katkeaw et al. have investigated using nitrogen gas during the preparation of NLFs (Katkeaw et al., 2019). They observed bubble-like shapes similar to those produced using the Dunlop process but with greater size uniformity. Sirikulchaikij et al. (Sirikulchaikij et al., 2019) have also investigated modifying preparatory methods by introducing air microbubbles and fillings. prepared microbubble The samples using this microbubble-filling method featured bubble-like shapes that were nearly spherical compared with those processed using the Dunlop process. Thus, the various preparation processes result in distinct microstructures, which, in turn, can significantly influence the mechanical properties of the foam samples (Katkeaw et al., 2021).

There is currently a lack of research regarding the effects of different surfactant blends on the relationship between the structure and mechanical properties of NLFs, especially in the context of the differences between the Dunlop and the Talalay processes. The Dunlop approach to NLF production is well-documented, whereas the Talalay method lacks sufficient technical data. Thus, this study presents a novel method of producing NLFs treated with surfactants based on the in-house Talalay process. Furthermore, this work investigates the influence of surfactant additives on the NLFs produced using the Dunlop and Talalay methods. This research studied various surfactants and assessed how they affect the foams produced using them. Moreover, an empirical model for determining the optimal processing conditions for producing NLFs with specific properties was presented, and the surfactant-treated NLFs produced using the Talalay and Dunlop methods were compared. Consequently, these findings will be valuable for rubber scientists looking to improve NLF mechanical properties with surfactants and are of interest to the rubber industry as it develops a more sustainable approach to natural latex rubber foam production. This innovation may have applications beyond traditional cushion seats, including structural components in transportation, packaging materials, and lightweight products.

2. Materials and methods

2.1. Materials

Natural latex with a high ammonia concentration (60% dry rubber content) was provided by Num Rubber and Latex Co., Ltd., Trang, Thailand. The chemicals used in the production of the NLFs included 50% sulfur dispersion (S; vulcanising agent), 50% zinc-2-mercaptobenzothiazole dispersion (ZMBT; primary accelerator), and 50% zinc diethyldithiocarbamate dispersion (ZDEC; secondary accelerator). The compounds 50% Wingstay L dispersion (WingL; antioxidant), 50% zinc oxide dispersion (ZnO; activator), 33% diphenylguanidine dispersion (DPG; foam stabiliser), and 12.5% sodium silicofluoride dispersion (SSF; gelling agent) were only used in the Dunlop process. All chemicals were supplied by Thanodom Technology Co., Ltd., Thailand.

The natural latex and chemicals used in the production of the NLFs were selected following previous studies (Prasopdee and Smitthipong, 2020; Suethao et al., 2021b); these included 0.62 M 10% potassium oleate (KO) solution, which is an anionic surfactant and blowing agent, with a critical micelle concentration (CMC) of 1.2×10^{-3} M (Constantinides and Steim, 1985). Two additional types of surfactants, pluronic (PL) and potassium laurate (KL), were used. PL is a non-ionic surfactant, containing 3.9×10^{-3} M 5% pluronic F-127 solution with a CMC of 0.56×10^{-3} M (Thapa et al., 2020); KL is an anionic surfactant, containing 0.419 M 10% potassium laurate solution with a CMC of 2.51×10^{-2} M (Malik and Jain, 1967). PL and KL were supplied by S.M. Chemical Supplies Co.,Ltd, Bangkok, Thailand. Carbon dioxide gas with a purity of 99.5% was acquired from Bangkok Industrial Gas Company Limited, Bangkok, Thailand.

Table 1 presents the notations used in referencing the samples. Table 2 presents the composition of the different samples of NLFs prepared using the Dunlop and Talalay methods.

The PL and KL solutions were used to prepare the samples. No useful samples could be manufactured for D-PL75/KO25, D-KL75/KO25, and

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ample	reference	notations.

Sample ID	Description
DC-KO100	Dunlop control sample treated with 100% KO^a
D-PL100/	Dunlop test sample, treated with 100% PL ^b and 100% KO
KO100	
D-PL25/KO75	Dunlop test sample, treated with 25% PL and 75% KO
D-PL50/KO50	Dunlop test sample, treated with 50% PL and 50% KO
D-KL25/KO75	Dunlop test sample, treated with 25% KL ^c and 75% KO
D-KL50/KO50	Dunlop test sample, treated with 50% KL and 50% KO
TC100-KO100	Talalay control sample, 100% foam volume in the mould, treated
	with 100% KO
TC80-KO100	Talalay control sample, 80% foam volume in the mould, treated
	with 100% KO
TC60-KO100	Talalay control sample, 60% foam volume in the mould, treated
	with 100% KO
T100-PL100/	Talalay test sample, 100% foam volume in the mould, treated
KO100	with 100% PL and 100% KO
T100-PL50/	Talalay test sample, 100% foam volume in the mould, treated
KO50	with 50% PL and 50% KO
T100-KL50/	Talalay test sample, 100% foam volume in the mould, treated
KO50	with 50% KL and 50% KO
^a KO represented	potassium oleate solution

^b PL represented pluronic solution.

^c KL represented potassium laurate solution.

Table 2

Chemical agents (Fig. S1) used to prepare samples according to the Dunlop and the in-house Talalay methods. Different surfactants were used in each sample. See Table 1 for sample notations.

Sample ID Chemicals	DC- KO100	D-PL100/ KO100	D-PL25/ KO75	D-PL50/ KO50	D-KL25/ KO75	D-KL50/ KO50	TC100- KO100	TC80- KO100	TC60- KO100	T100- PL100/ KO100	T100- PL50/ KO50	T100- KL50/ KO50
	Wet weigh	nt (g)										
NRL ^a	166.67	166.67	166.67	166.67	166.67	166.67	166.67	166.67	166.67	166.67	166.67	166.67
KO	16.50	16.50	12.38	8.25	12.38	8.25	16.50	16.50	16.50	16.50	8.25	8.25
S ^b	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
ZMBT ^c	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
ZDEC ^d	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Wing L ^e	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
ZnO ^f	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
DPG ⁸	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
SSF ^h	8.00	8.00	8.00	8.00	8.00	8.00	-	-	-	-	-	-
PL	-	33.00	8.25	16.50	-	-	-	-	-	33.00	16.50	-
KL	-	-	-	-	4.12	8.25	-	-	-	-	-	8.25

^a NRL represented natural latex.

^b S represented sulfur dispersion.

^c ZMBT represented zinc-2-mercaptobenzothiazole dispersion.

^d ZDEC represented zinc diethyldithiocarbamate dispersion.

 $^{\rm e}~$ Wing L represented wingstay L dispersion.

^f ZnO represented zinc oxide dispersion.

^g DPG represented diphenylguanidine dispersion.

^h SSF represented sodium silicofluoride dispersion.

D-KL100/KO100. The D-PL75/KO25 and D-KL75/KO25 samples collapsed; the limited amount of KO in these combinations resulted in low foam volumes, which, in turn, prevented the samples from achieving the gelling process. The D-KL100/KO100 sample also experienced a collapse, primarily attributed to the bubbles generated by the KL and KO solution.

2.2. Preparation of NLFs using the Dunlop method

Rubber foams were manufactured via the Dunlop method using the steps shown in Fig. 1a; the sample preparation method described follows the procedures outlined by previous studies (Prasopdee et al., 2021; Suethao et al., 2021b). The natural latex and the necessary chemicals were weighed and blended before pouring into the mould (step I). The moulds were left at room temperature for 45 min until they reached their gel point (step II). They were then heated to 90°C in a hot-air oven. Finally, the NLFs were removed from the moulds, washed, and dried for 4 h at 70°C (step III).

2.3. Preparation of NLFs using the in-house Talalay method

The Talalay method developed in this study is illustrated in Fig. 1b. The rubber foam was initially blended at 80 rpm for 1 min to remove ammonia. After adding the surfactant, the solution was mixed for 10 min at 160 rpm. The vulcanising agent, comprised of S, ZMBT, ZDEC, and Wing L, was added to the mixture and blended for 1 min. Similarly, a mixture of ZnO and DPG was obtained and blended for 1 minute (step I). Following this, various volumes of the latex mixture (60%, 80%, or 100%) were poured into the moulds (step II). The moulds were securely sealed and placed within a temperature chamber. The vacuum pressure was gradually reduced to 710 mmHg for 5 min, allowing the foam to expand to its maximum capacity (step III). The foam was cooled to -30°C for 10 min utilising a mechanical single-stage refrigeration system (step IV). In step V, gaseous carbon dioxide was fed to the moulds at a flow rate of 10 L/min for 5 min to initiate gelation. The foam was subsequently vulcanised by heating the samples at 90° C for 1.45 h (step VI). The NLFs were subsequently removed from the moulds, rinsed, and dried for 4 h at 70°C (step VII).

Both Talalay and Dunlop methods involve mixing, moulding, and post-processing. However, the Talalay method has additional processes,



Fig. 1. Preparation of NLFs from concentrated natural latex (a) using the Dunlop method, (b) using the in-house Talalay method.

namely cooling and gelation.

2.4. Characterisation of the rubber foams

The foam density, including of the standard deviation, was calculated using the weight and volume of the NLFs. The foam composition was tested using at least three replicates, following the methodologies outlined in prior research (Prasopdee and Smitthipong, 2020; Suethao et al., 2021b). All functional groups were identified by attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy based on the method described in previous studies (Prasopdee and Smitthipong, 2020; Suethao et al., 2021b). A Ge crystal probe (VERTEX 70, Bruker, Billerica, MA, USA) was used to measure the FTIR spectrum of each sample between 500 and 4000 cm⁻¹.

X-ray diffraction (XRD) was used to obtain structural data from each sample. The XRD patterns of the NLF samples were collected using a diffractometer at 40 kV and 40 mA (Bruker AXS Model D8 Advance, Germany). Diffraction measurements were performed at room temperature using Cu–K α radiation with a wavelength of 0.1546 nm and $2\theta=5^{\circ}-40^{\circ}$.

A scanning electron microscope (SEM; FEI, Quanta 450, Eindhoven, Netherlands) was used to investigate the morphology of the foam samples in two dimensions. At least three samples from each foam composition were inspected after the foam samples were coated with gold. The average cell size and porosity including the standard deviation of the NLFs were obtained by examining the micrographs of all samples using ImageJ (Suethao et al., 2021a, 2021b).

Several physical properties were visualised in three dimensions using X-ray micro-computed tomography (micro-CT; SkyScan1173, Bruker, USA). The examination was conducted using CT Analyzer software version 1.18.9.0+, which analysed the parameters of sub-volume and mid-range diameter. Function by structure thickness to determine the percentage volume of voids present in the mid-range diameter. These visualisations were used to calculate the permeability of the porous structures. The X-ray tube used a voltage of 70 kV and a current of 114 μ A. A voxel size of 7 μ m was used with a total of 800 slices. Submicron calibration was performed based on pixel size, measuring voids or gaps with dimensions of at least 7 μ m.

Compression testing was conducted on each NLF sample in triplicate. Samples 21.5 mm thick and $45 \times 45 \text{ mm}^2$ in area were prepared from each foam mixture. A texture analyser (TA.XT Plus, Stable Micro Systems, Godalming, Surrey, UK) was used to measure the compression of each NLF to 75% of its original size at room temperature. The test probe had a diameter of 100 mm and a speed of 0.1 mm/s. Each NLF was also thermo-mechanically evaluated by dynamic mechanical analysis (DMA; Mettler Toledo, Columbus, OH) over a temperature range of -80 to 80° C using the temperature sweep mode (Suethao et al., 2021a, 2021b).

The thermodynamic characteristics of each sample were investigated using the texture analyser described in the compression test. Each NLF was exposed to temperatures of 298.15, 308.15, 318.15, 328.15, 338.15, and 348.15 K, respectively, for 10 min and then compressed in increments of 30% strain to a strain of 70%. The results were used to generate a force–temperature graph and fit to a linear equation. The yintercept and slope of the linear equation were used to calculate the total compression force (*F*), which parameterised the sum of the internal energy (F_u) and the entropy (F_s) at the compression limit (Suethao et al., 2021a, 2021b).

A One-Way ANOVA, followed by a post hoc Tukey test, was conducted (using SPSS Statistics version 29.0.2.0 (20)) to determine the statistical significance of differences in sample means among the various treatment groups.

3. Results and discussion

3.1. Surfactant-treated NLFs prepared by Dunlop method

Fundamental to the production of latex from colloids is the ability to regulate the stability of the latex. Both anionic and non-ionic surfactants are frequently used to stabilise anionic latexes in colloids. Typically, a single surfactant may be insufficient to produce a latex that satisfies all required criteria. Non-ionic surfactants improve the steric stability of electrolytes through heating and cooling cycles (Wang et al., 2009), while anionic surfactants improve the mechanical stability of latex through electrostatic stabilisation (Castelvetro et al., 2006). Thus, anionic and non-ionic surfactants are preferred over cationic surfactants in acidic conditions because they can attach to negatively charged rubber molecules. The chemical structures of PL, KL, and KO are shown in Fig. S1.

In applications involving the manufacture of rubber foams by latex gelation, the stability of the NLF must be sufficient to achieve latex gelation without significant mould collapse (Blackley, 1997b). In typical gel processes, a carboxylate surfactant is applied alone in combination with other surfactants. Combinations of carboxylate soaps often increase the foam volume more than components used singly. The foaming tendency of long-chain carboxylates in aqueous solutions depends on the pH; in particular, the foaming potential of latex is sensitive to pH in the range of 6-9, even over short durations (Micheau et al., 2013). This sensitivity arises due to the weak nature of the acids used to make these soaps, as well as the tendency of un-ionised carboxylic acids and acid soaps to form as the pH of the solution decreases. The hydrophobic component in the anionic soap also influences its ability to create and stabilise foam (Mulligan, 2007). The length of the hydrocarbon chain contributes to improving the foaming capacity of the soap while decreasing its solubility in water.

3.1.1. Structure and morphology

The FTIR spectra of the NLFs, derived from the respective preparatory methods, are presented in Fig. 2 to examine the differences in the main peaks in the FTIR spectra from NLFs prepared with different surfactants (Johns and Rao, 2008; Karolewicz et al., 2014; Nisha et al., 2012; Prasopdee et al., 2021; Suethao et al., 2021a). The transmittance bands of the NLFs exhibited typical bands at 2851-2959 cm⁻¹, 1663 cm⁻¹, and 1450 cm⁻¹, which correspond to the presence of CH₃ groups and CH₂ stretching, C=C stretching, and the C-H bending of CH₂, respectively. The absorption peak between 926 and 1127 cm⁻¹ was attributed to C-S stretching, suggesting that the sulfur atoms are crosslinked to the rubber molecules. Additionally, NLFs produced using the pluronic exhibited C-O-C stretching at 1016 cm⁻¹, which correlated with the predominant band of the pluronic solution. A band that represented C=C stretching was observed at 1663 cm⁻¹. Asymmetric COO- and symmetric KO and KL stretching bands were observed at $1548\ \text{cm}^{-1}$ and $1526\ \text{cm}^{-1},$ respectively.

The spectra of the NLFs revealed no appreciable differences. The molecular structure of the rubber foam was then analysed using XRD (Fig. 3). The XRD patterns of all the NLF samples exhibited a characteristic NR peak at $2\theta = \sim 19^{\circ}$ (Johns and Rao, 2008), corresponding to solid styrene–butadiene rubber (Eyssa et al., 2021).

Fig. 3 presents the crystalline peaks of the samples prepared with PL and KL, which were consistent with those reported in previous studies (Lomer, 1958; Wenchao et al., 2018). Despite variations in experimental conditions, the XRD patterns of the NLF samples remained relatively similar. This consistency can be attributed to each sample containing the same amount of rubber and added chemicals, with only a 10–20 wt% difference accounted for by the use of different surfactants. The crystalline peaks of the pluronic can be clearly seen at $2\theta = 19.12^{\circ}$ and 23.27°, which correspond to the crystal planes (hkl) at (100) and (200), respectively. In the PL, there was an overlap due to the distinctive rubber peaks. Hence, the peaks in this area of the spectrum were obscured. In



Fig. 2. ATR-FTIR spectra of the NLF samples: (a, b) NLFs produced using PL, (c,d) NLFs produced using KL.



Fig. 3. XRD spectra of the NLF samples: (a) NLFs produced with pluronic loading, (b) NLFs produced with potassium laurate loading.

the KL, distinct peaks at $2\theta = 8.33^{\circ}$ and 28.77° and a small broad peak at 36.23° were observed at (003), (–214), and (218), respectively; these can be attributed to the influence of KL.

Fig. 4 shows that all NLF samples exhibited an open-cell morphology with all cells connected. Although this structure has been observed in polyurethane foams (lizuka et al., 2021), they were prepared by crushing the foam until all cell walls were destroyed, resulting in a highly connected, open-cell structure. In contrast, these NLF samples were prepared by stirring the foam, following the Dunlop method. The foaming process of the Dunlop preparation method resulted in heterogeneous bubbles of varying sizes, which consequently led to a mixture of large and small cells. The interconnectivity between each cell means that the cell walls were also connected, with cells of different sizes containing varying amounts of matrix resembling the microstructures commonly found in natural structures, such as bamboo plants and human bones (Andrew et al., 2021). In closed-cell structures, the foam cells are separated by thin walls, unlike in open-cell structures, in which the foam cells are linked to other cells (Zhang et al., 2012). Foam possesses superior mechanical and physical properties, allowing it to serve as both a structural and functional material. These properties encompass specific flexibility, sound absorption capacity, and energy absorption capacity. In particular, the ability of foam materials to absorb energy can be exploited for impact resistance applications (Alem et al., 2014; Tao et al., 2021; Zhang et al., 2020).

The morphology of the foams prepared using the Dunlop method depended on the chemical formula used. The cell density of each NLF



Fig. 4. SEM images of the NLF samples produced using the Dunlop method: (a1) DC-KO100, (b1) D-PL100/KO100, (c1) D-PL25/KO75, (d1) D-PL50/KO50, (e1) D-KL25/KO75, and (f1) D-KL50/KO50. All images displayed at 50× magnification. Images processed using ImageJ in Fig. S4.

sample was calculated following the methods described in a previous study (Prasopdee and Smitthipong, 2020); the results of these calculations are presented in Table 3. Images produced by ImageJ are also presented in Fig. S2.

In samples produced using PL (DC-KO100), the foam volume decreased as the KO content decreased (Table 3). In addition, PL acted as a filler: as the PL content increased, the matrix content also increased. This increased matrix content increased density, as seen in D-PL50/KO50. However, the D-PL100/KO100 formula had a slightly higher density than the DC-KO100 formula, which could be attributed to the increased amount of PL.

In samples produced using KL, increasing the amount of KL used resulted in increased density due to the more compact molecular structure of KL compared with KO. Carboxylate soaps are typically employed in the Dunlop method, and the nature of the hydrophobic component in an anionic soap also influences its ability to create and stabilise foam. In general, increasing the length of the hydrocarbon chain improves the foaming capacity of the surfactant while diminishing its solubility in water (Denkov et al., 2020).

Table 3 also describes the differences in the morphology of the samples manufactured with PL; however, the average cell size did not differ significantly due to the heterogeneous nature of the cell size distribution across the samples. Of the samples analysed, D-PL50/KO50 had a low percentage of porosity and the highest density; this was due to the increased amount of matrix in this sample from the reduced KO and increased PL content. D-KL50/KO50 had the lowest porosity due to its low KO and high KL content, reducing cell density. Thus, despite all samples exhibiting similar average cell sizes, the cell density increased with increasing porosity, consistent with previous studies (Prasopdee and Smitthipong, 2020; Yang et al., 2017). This study shows that this relationship holds even with blended surfactants (KO + PL or KO + KL) at varying concentrations. Previous studies had only focused on varying the KO concentration (Prasopdee and Smitthipong, 2020).

Three-dimensional images of the morphology of the control NLF and the prepared NLF samples were obtained using an X-ray micro-CT system. Initially, 2D projections (radiographs) of the morphology of each sample were captured from various angles. A 360° rotation was required to visualize the 3D structure of the sample in this study. Subsequently, the cross-section of each sample was reconstructed from the projection data to create a 3D image, as shown in Fig. 6. In this image, the grey area represents the interconnected foam, while the blue area represents the pore area, which can be utilized to calculate the cell size distribution. The control formula (DC-KO100; Fig. 5a) had a cell size distribution that was relatively large compared with samples containing both surfactants. In contrast, samples with added PL and KL exhibited remarkably narrow cell size distributions, particularly in the case of D-KL50/KO50 (Fig. 5c).

Table 3

The foam density, average cell size, porosity, and cell density of all NLFs prepared using different surfactants. All values were calculated from measurements made with ImageJ.

Sample ID	Foam density (kg/m ³)	Average cell size (±100 μm)	Porosity (±1.00%)	Cell density ($\pm 1000 \text{ cm}^{-3}$)	
DC-KO100	96 ± 2^a	379 ^a	46.51^{b}	31,562 ^a	
D-PL100/	$99{\pm}2^a$	379 ^a	42.82 ^{ab}	31,496 ^a	
KO100					
D-PL25/	96±4 ^a	380^a	44.43 ^{ab}	31,266 ^a	
KO75					
D-PL50/	$107{\pm}1^b$	385^{a}	39.89 ^a	$29,553^{b}$	
KO50					
D-KL25/	102 ± 1^{b}	355 ^a	41.30^{b}	37,988 ^c	
KO75					
D-KL50/	105 ± 1^{b}	394 ^a	34.00 ^c	27,671 ^b	
KO50					

 $^{a\cdot c}$: Different letters within the same column represent statistically significant differences (*p < 0.05, Tukey test).

This may be due to the addition of KL, which increased the foam density of the latex, resulting in smaller cell sizes, as observed from the SEM images. In addition, samples containing PL were found to have narrower and smaller cell size distributions (Fig. 5b), similar to the properties of samples containing added KL. However, the cell size distribution of the NLF sample was heterogeneous, which was consistent with the SEM measurements.

The CT analyser software was used to determine the average cell size and percent porosity of the control NLF and the NLFs prepared using PL and KL. These foam samples were chosen because D-PL50/KO50 and D-KL50/KO50 exhibited high foam densities and low porosities, indicating superior mechanical properties. Table S1 shows that all samples measured by micro-CT had average cell sizes and porosities that were twice as large as those measured by SEM. Furthermore, the micro-CT analyses of the foam samples provided more information about the open pore characteristics and the randomness of the cell distributions. Consequently, the 3D images obtained from micro-CT analysis were more precise than the average cell sizes obtained from 2D SEM images. In addition, the control DC-KO100 sample had a slightly higher cell volume than the other samples. In general, the addition of blended surfactants resulted in a decrease in total cell volume.

3.1.2. Physical and mechanical properties

The compressive stress-strain curve of the NLF samples prepared using the PL and KL surfactants is presented in Fig. 7. D-PL25/KO75 had a density similar to that of the control NLF (Fig. 7a). As the amount of KO decreases and the amount of PL increases, the long hydrocarbon chains of the micelles in the pluronic solution micelles can become entangled (Jeong et al., 2016), resulting in increased tensile strength owing to presence of a chained network, consequently leading to higher densities than the control. This effect can be seen in the D-PL50/KO50. In the NLFs prepared using KL (Fig. 7b), the KL formed small bubbles, reducing bubble volumes and significantly increasing densities (Atrafi and Pawlik, 2017). These results showed that the KL has a slightly greater influence on the structure of the NLFs than the PL. There was a noticeable effect on the sample density even when only 25% KL and 75% KO were used.

Table 4 shows that the energy absorption capabilities of the NLF samples are related to their mechanical properties. Among the PL samples, D-PL50/KO50 exhibited the greatest energy absorption capability (134 kJ/m³); this was higher compared with the results obtained from the KL samples, in which the energy absorbed by D-KL50/KO50 was 124 kJ/m³. However, the addition of surfactants (both PL and KL) improved the mechanical properties and energy absorption of the NLF samples.

The effects of compression speed on the energy absorption of the control rubber foam were studied by subjecting the sample to compression rates of 0.1, 0.3, 0.5, 2.0, and 5.0 mm/s at 25°C (Fig. 7c). As the compression speed increased, the absorbed energy also increased, suggesting an improvement in the sample mechanical properties. This improvement could be attributed to the elastic response of the NLF at different compression speeds. The compression speed affected the compressive response of the NLFs, which is consistent with the behaviour of polystyrene and polypropylene foams (Krundaeva et al., 2016; Morton et al., 2020). Furthermore, a power-law relationship between the energy absorption capabilities (*W*) of the NLFs and the speed of compression (*Y*) can be expressed as follows: $W \sim V^{0.02}$. The influence of the compression speed on the mechanical properties of the NLF samples is also consistent with the time–temperature law (Ferry, 1980).

The normalised energy absorption tests for all samples are presented in Fig. S3. The foam samples were compressed at speeds of 0.1 and 5 mm/s. The *x*-axis of the graph describes the normalised peak stress, which was calculated by dividing the stress at 50% strain by the Young's modulus of vulcanised rubber (Gibson and Ashby, 1997). The *y*-axis represents the normalised energy per unit volume, which was determined by dividing the energy absorption (*W*) of each sample by the

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Fig. 5. Histograms of cell volume versus cell size illustrating the cell size distributions of NLFs determined from 3D micro-CT images, using foam samples produced using the Dunlop method: (a) DC-KO100, (b) D-PL50/KO50, and (c) D-KL50/KO50.



Fig. 6. Three-dimensional micro-CT images of the foam samples: (a) DC-KO100, (b) D-PL50/KO50, and (c) D-KL50/KO50.



Fig. 7. Graphs of the stress versus strain curves of the NLFs prepared using the Dunlop method with (a) PL and (b) KL surfactants, compared with NLFs with only KO surfactant treatment. The final densities are presented at the end of each curve. (c) Graph of log *W* versus log *V* describing the influence of compression speed on the energy absorption capabilities of the control samples of NLF (i.e. with only KO surfactant treatment) following a power-law relationship. ^{a-d}: Different letters within the same figure represent statistically significant differences in compressive strength, *p < 0.05, Tukey test.

Young's modulus. Fig. S3 shows that the normalised energy per unit volume increased as the density and normalised peak stress increased, which is consistent with the behaviour of polypropylene foams (Rumianek et al., 2021). In particular, higher compression speeds resulted in higher normalised energy absorption capabilities and peak stresses. D-PL50/KO50 exhibited the greatest peak stress and energy absorption values at both compression speeds. The energy absorption values were primarily calculated from the plateau region in the

cell-buckling phase, which occurred at approximately 50% strain. ^{*a,b*}: Different letters within the same figure represent statistically significant differences at the rubbery plateau, *p < 0.05, Tukey test.

The storage modulus (E) of all samples was measured using DMA. The DC-KO100 sample had a storage modulus at the rubbery plateau higher than those observed in the other foam samples, regardless of the surfactants used (Fig. 8). This result was due to the high porosity of the control sample, suggesting that the rubber matrix was much more

Table 4

Energy absorption of foam samples at 25°C at a compression speed of 0.1 mm/s. All values were calculated from Figs. 5a and 5b using Origin, version 9.0, by determining the area under the curve at 50% strain, a linear plateau zone that is not influenced by the densification zone. Thus, an increase in the area under the stress–strain graph in this section indicates an increase in energy absorption.

Sample ID	Energy absorption ($\pm 3 \text{ kJ/m}^3$ or kPa)
DC-KO100	88 ^a
D-PL100/KO100	117 ^{ab}
D-PL25/KO75	113 ^{ab}
D-PL50/KO50	134 ^c
D-KL25/KO75	117 ^{ab}
D-KL50/KO50	124 ^b

 $^{a\,c}$: Different letters represent statistically significant differences (*p < 0.05, Tukey test).

compressible due to its many air bubbles, resulting in longer relaxation times compared with the other samples (Phuhiangpa et al., 2020). The samples containing the KL and PL had similar trends, with the control sample and D-KL25/KO75 exhibiting higher porosities, implying greater air bubble volumes, increased compressibility, and longer relaxation times.

The value of tan δ (Fig. S4) represents the energy loss exhibited by the sample. The value of tan δ was not appreciably different in the samples prepared using a PL surfactant because the viscoelastic properties of the sample matrices were relatively similar. The value of tan δ in D-KL50/KO50 was high due to its low porosity and high matrix content, resulting in a high degree of energy loss.

3.1.3. Thermodynamic parameters

This section describes the foaming thermodynamics, the process of gas diffusion in foams, its influence on foam instability, and the kinetics and processes associated with film fractures that eventually result in foam collapse. Aqueous foams are sufficiently stable when the fluid phase contains one or more surface-active compounds. Disparate gas pressures between foam bubbles of varying sizes cause gases to move between the smaller bubbles and the larger bubbles that surround them.

As noted in Section 2.4, the total compression force (*F*) is the sum of the forces related to the internal energy (F_u) and the entropy (F_s). The force contributed by F_u is related to the mechanical properties of the foam at the compression level, while the force contributed by F_s relates to the molecular structure at the compression level. In Fig. S5, the ratio of F_u/F decreased slightly when the temperature increased from 298.15 to 338.15 K. At higher temperatures, the ability of natural rubber to flow can also explain the discrepancy in the F_u/F ratios (Prasopdee et al., 2021; Suethao et al., 2021b). The rubber molecules in the control foam exhibit similar degrees of freedom at various compression strains

(compression limits) (Prasopdee et al., 2021; Suethao et al., 2021b). However, the data indicated that the compression limit at high strain falls within the range at which stress-induced crystallisation occurs, which is out of the scope of this study. In addition, previous studies have revealed the presence of a phenomenon known as thermoplastic inversion that occurs during thermal expansion at low deformations (Prasopdee and Smitthipong, 2020; Suethao et al., 2021a). All of the foam samples (from both scenarios) exhibited higher foam density levels than the control DC-KO100 sample, suggesting that they had a similar degree of freedom at various compression limits due to the stability of the degrees of freedom exhibited by the molecules at both temperatures.

3.2. Surfactant-treated NLFs produced using the Talalay method

This section described the results of the Talalay method in fabricating surfactant-treated NLFs. The findings were compared with those derived from the Dunlop method, as presented in <u>Section 3.1</u>.

3.2.1. Structure and morphology

Fig. 7 presents the 2D SEM images of the foam samples produced using the Talalay method. The foams produced by the modified Talalay method exhibited an open-cell structure and heterogeneous cell sizes. The TC100-KO100 sample (Fig. 9a) exhibited larger cell sizes than the corresponding DC-KO100 (Fig. 4a) sample, almost certainly due to the vacuum system utilised in the Talalay method, which causes smaller cells to combine into larger cells. Moulds containing 60%, 80%, and 100% foam by volume were prepared before being transferred. Samples produced with lower foam volumes exhibited larger cell sizes (Fig. 9a–c). The average cell size and porosity were determined from the SEM images using ImageJ, as described in Section 3.1.1 (Table 5).

Table 5 presents the data obtained from the SEM images of the NLFs produced using the Talalay method (Fig. 9). The morphological analysis of the samples was complicated by the combination of stirring techniques and vacuum processes used in this method. In contrast, the foam samples produced using the Dunlop method were only subjected to stirring. Blended surfactants (i.e. KO + PL or KO + KL) also affect the morphology of the foam samples produced using the Talalay method; both the addition of PL (filler effect) and KL (small bubble effect) resulted in foam samples with low porosities and high matrix contents. However, T100-PL100/KO100 exhibited a high foam density and low porosity because of the vacuum used during the Talalay method. Because PL acts as a type of filler, the matrix content of the samples increased, resulting in a higher foam density and, consequently, a morphology significantly different from the control sample.

The 3D morphological information and the cell size distribution of the NLFs were investigated using micro-CT. Fig. 10 presents the 3D morphology of TC100-KO100. The cell size distribution of this sample



Fig. 8. Graphs of the storage modulus (*E*') versus temperature to illustrate the dynamic mechanical properties of the NLFs produced by the Dunlop method using (a) PL surfactants and (b) KL surfactants compared with NLFs with only KO surfactant treatment. ^{a,b}: Different letters within the same figure represent statistically significant differences at the rubbery plateau, *p < 0.05, Tukey test.

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Fig. 9. SEM images of the NLF samples derived from the Talalay method. (a1) TC100-KO100, (b1) TC80-KO100, (c1) TC60-KO100, (d1) T100-PL50/KO50, (e1) T100-PL100/KO100, and (f1) T100-KL50/KO50. All images were displayed at 50× magnification. Images processed using ImageJ can be found in Fig. S6.

Table 5

A comparison between the samples prepared using the Talalay-based method. Properties include foam density, average cell size, porosity, and cell density of the NLFs. All data were calculated using ImageJ.

Sample ID	Foam density (kg/m ³)	Average cell size (±100 μm)	Porosity (±1.00%)	Cell density ($\pm 1000 \text{ cm}^{-3}$)
TC100- KO100	$94{\pm}3^{bc}$	396 ^{bc}	49.12 ^d	27,658 ^c
TC80- KO100	$82{\pm}3^{b}$	425 ^c	56.81 ^e	22,691 ^b
TC60- KO100	$72{\pm}3^a$	468 ^d	62.63 ^f	17,006 ^a
T100- PL100/ KO100	110±4 ^c	276 ^a	29.75 ^b	79,789 ^f
T100- PL50/ KO50	93±3 ^{bc}	324 ^{ab}	25.89 ^a	50,490 ^e
T100- KL50/ KO50	$90{\pm}4^{bc}$	363 ^b	32.69 ^c	35,998 ^d

 $^{af:}$ Different letters within the same column represent statistically significant differences (*p < 0.05, Tukey test).



Fig. 10. Three-dimensional images of the foam samples produced using the custom Talalay-based method acquired by micro-CT using the CT analyser software, version 1.18.9.0+: (a) TC100-KO100, and (b) T100-KL50/KO50. The grey area in the 3D images represents volumes of interconnected foam, while the blue area describes the pore area.

(Fig. 11a) was wider than the DC-KO100 control sample (Fig. 5a). Similarly, TC100-KL50/KO50 (Fig. 11b) exhibited a cell size distribution wider than that of D-KL50/KO50 (Fig. 5c), suggesting that the cell size distributions in the NLFs produced using the Dunlop method were narrower than those produced using the Talalay method. The Talalay method implemented in this study consists of two main stages: (i) the stirring stage that homogenises the foam and the added chemicals and (ii) the vacuum stage that modifies the morphology of the foam sample. These could contribute to the broader cell size distribution results from the foam samples processed by the Talalay method.

Table 6 presents the morphological information acquired from the SEM images and micro-CT scans and compares the effect of different surfactants and processes on the morphology of the foam samples. The porosity of the foam samples produced by both preparation methods tended to decrease when blended surfactants were added, as did the total cell volume of the foam samples. However, both preparation methods resulted in foams with highly heterogeneous cell sizes — it was thus difficult to determine the average cell sizes obtained from each method. The average cell size and porosity of the NLFs obtained from the micro-CT scan technique were double those obtained from the SEM images due to the 3D nature of the morphological data obtained from the micro-CT scan, which allowed more detailed morphological analyses.

3.2.2. Physical and mechanical properties

In general, the morphology of the NLFs influences the mechanical properties of the foams. The NLFs obtained from the Dunlop method had higher compressive strengths than those obtained from the Talalay method, regardless of the chemical formulation used (Figs. 12a, 12b, and 12d). The improved mechanical properties of the NLFs produced using the Dunlop method compared with those produced using the Talalay method can be explained by the narrower cell size distribution exhibited by the former samples. This is consistent with the behaviour of polypropylene and rubber foams, as revealed in previous studies (Gong et al., 2020; Rostami-Tapeh-Esmaeil et al., 2021). DC-KO100 and TC100-KO100 exhibited similar foam densities but different cell size distributions and compressive strengths (Fig. 12a).

Fig. 12a also shows how the volume of foam in the mould affects the mechanical properties of the foams produced using the Talalay method. The compressive strength of NLFs increased as the foam volume in the mould increased, consistent with the morphological data. The T100-PL100/KO100 sample exhibited the highest compressive strength (Fig. 12c), consistent with its morphology.

The compressive energy absorbed by the NLFs bends and buckles the cell walls. Table S2 presents the energy absorption capabilities of the different NLF samples obtained from the two preparation methods used in this study. The compressive strengths and energy absorption capabilities of NLFs produced by the Talalay method were lower than those produced by the Dunlop method, likely due to the stirring and vacuum techniques used in the former method.

Fig. 13a presents the linear relationship between the normalised energy per unit volume and the normalised peak stress of foam samples produced by the two preparation methods. The samples produced using the Dunlop method had higher normalised peak stresses and higher



Fig. 11. Histograms of the cell volume versus cell size illustrating the cell size distributions of NLFs determined from 3D micro-CT images, using foam samples derived from the Talalay method: (a) TC100-KO100 and (b) T100-KL50/KO50.

Table 6

Foam density, average cell size, porosity, and cell density of NLFs produced using different preparation methods and different surfactants.

Sample	Average cel	verage cell size			Total cell	
ID	SEM (±150μm)	Micro-CT (±300µm)	SEM (±1.00%)	Micro-CT (±1.00%)	from micro- CT (±5 mm ³)	
DC- KO100	379 ^a	725 ^b	46.51 ^c	89.38 ^{ab}	311 ^b	
D-KL50/ KO50	394 ^a	535 ^a	34.00 ^b	88.58 ^{ab}	302 ^a	
TC100- KO100	396 ^a	880 ^c	49.12 ^d	90.13 ^b	309 ^b	
T100- KL50/ KO50	363 ^a	753 ^{bc}	32.69 ^a	87.88 ^a	300 ^a	

 $^{a\cdot d}$: Different letters within the same column represent statistically significant differences (*p < 0.05, Tukey test).

energy absorption capabilities than those produced by the Talalay method. The energy absorbed by the foam samples depended on the formulation and the preparation techniques used. Fig. 13b shows that the energy absorption is related to the compression speed via a power law, according to the behaviour of the control samples produced using both preparation methods. Regardless of the preparation method, the energy absorbed by the NLFs increased with compression speed. DC-KO100 exhibited a higher energy absorption than TC100-KO100 for a given compression speed.

The power-law relationship between the energy absorption per unit volume (*W*) and the compression speed (*V*) of the different rubber foams was investigated in greater detail. The specific trends were found to differ depending on the preparation method used. According to the rheological model of rubber, the energy dissipation characteristics of rubber foams are related to their viscoelastic properties (Smitthipong et al., 2004). The power-law relationship between the energy absorbed and the compression speed could be described using the dissipation function of a rubber foam with a fractional exponent (β); the value of β was similar for all rubber foams tested. In most cases, the logarithmic energy absorption per unit volume (*W*) increased linearly with



Fig. 12. Graphs of the compressive stress versus strain curves of the NLFs: (a) samples produced using the Talalay method with only KO surfactant treatment (compared with control sample produced using the Dunlop method), (b) comparing surfactant-treated samples produced using the Talalay (T100-PL50/KO50) and the Dunlop (D-PL50/KO50) methods, (c) surfactant-treated samples (compared with control sample) produced using the Talalay (T100-RL50/KO50) and the Dunlop (D-RL50/KO50) methods, (c) surfactant-treated samples (compared with control sample) produced using the Talalay (T100-RL50/KO50) and the Dunlop (D-KL50/KO50) methods. ^{*a-d*}: Different letters within the same figure represent statistically significant differences in compressive strength, *p < 0.05, Tukey test and One-way ANOVA.



Fig. 13. Graphical representations the energy absorption capacities of NLFs. (a) Scatter plot of normalised energy per unit volume versus normalised peak stress describing the energy absorption capacities of NLFs produced by the Dunlop and Talalay methods with different surfactants, and (b) graph of log W versus log V showing the influence of compression speed on the energy absorption capabilities of control samples of NLF derived from the Dunlop and Talalay methods (i.e. with only KO surfactant treatment) following a power-law relationship.

logarithmic compression speed (*V*), which can be described in the form $W \sim V^{\beta}$. Here, the fractional exponent (β) is dependent on the test method, as well as the properties of the rubber foam matrix. For example, in the case of a rubber foam sample prepared using both methods, the value of β was approximately 0.01–0.02.

Considering the dynamic mechanical properties, DC-KO100 had the highest storage modulus at the rubbery plateau (Fig. 14a), consistent with its observed foam morphology. Typically, the static and dynamic mechanical properties of NLFs depend on their morphology and foam density. Fig. S7a shows that DC-KO100 exhibited a smaller degree of hysteresis than TC100-KO100 due to narrower cell size distribution, consistent with the results of previous studies (Rostami-Tapeh-Esmaeil et al., 2021). Fig. S7a also shows that TC60-KO100 exhibited the lowest degree of hysteresis, consistent with this sample exhibiting the lowest foam density and, consequently, the lowest viscoelastic properties (Suethao et al., 2021a). Fig. 14b shows that T100-PL50/KO50 exhibited a higher storage modulus at the rubbery plateau than D-PL50/KO50, reflecting the difference in cell density between the two samples. However, the overall effects of the fillers and their morphology gave both samples similar hysteresis behaviours (Fig. S7b).

Fig. S7c shows that all the samples produced with the Talalay method had similar storage moduli. Rubber foams exhibiting lower percentage porosities (T100-PL50/KO50) and higher matrix contents also exhibited higher degrees of hysteresis (Fig. S7d). This result is similar to those observed in aluminium alloy–polyurethane porous composites (Bao and Li, 2019). Fig. S7e indicates that T100-KL50/KO50 displayed a greater storage modulus on the rubbery plateau than D-KL50/KO50 while demonstrating comparable hysteresis behaviours (Fig. S7f). This was consistent with the behaviours observed in the T100-PL50/KO50 and D-PL50/KO50 samples.

3.2.3. Thermodynamic parameters

This section elaborates on the influence of process design technology on the thermodynamics of rubber foams. Figs. 14c and 14d show that the F_{u}/F of the control sample prepared using the Talalay method (TC100-KO100) was lower than the F_{u}/F of the control sample prepared by the Dunlop method (DC-KO100); this was consistent with the results of the compression test. Generally, the internal energy of a polymer is related to the added heat, the work required to change its volume, and the work required to deform the polymer (Suethao et al., 2021b). Hence, polymers with higher compressive strengths (i.e. a higher force per area



Fig. 14. Graphs of storage moduli (*E*') versus temperature for NLF (a) samples produced using the Talalay and Dunlop methods with only KO surfactant treatment, and (b) surfactant-blended samples, i.e. T100-PL50/KO50 and D-PL50/KO50, produced using the Talalay and Dunlop methods. Graphs of compression force (F_u/F) versus compression limit of the NLFs, from samples produced using the Talalay and Dunlop methods with only KO surfactant treatment, at (c) 298.15 K and (d) 338.15 K., ^{*a.b.*} Different letters within the same figure represent statistically significant differences at the rubbery plateau, *p < 0.05, Tukey test and Oneway ANOVA.

required to deform the rubber) tend to exhibit higher internal energies. However, due to their high foam densities, both samples exhibited similar entropic stabilities at both temperatures, consistent with previous studies (Prasopdee et al., 2021; Suethao et al., 2021b). Due to the wide distribution of cell sizes in TC100-KO100, its thermal expansion tended to vary under low deformations or high compression limits, overshadowing potential entropic effects. Generally, rubber foams with higher compressive strength exhibit superior mechanical properties. while those with high tan δ values exhibit high hysteresis or high energy losses. The foam density of the samples produced using the Talalay method could be controlled by varying the volume of foam added to the moulds, especially when the same formulation was used (TC100-KO100, TC80-KO100, or TC60-KO100). When two rubber foams with similarly low foam densities obtained through the use of different formulas and preparation methods were compared, TC100-KO100 was observed to have a higher compressive strength and lower degree of hysteresis than a rubber foam with 4 phr of charcoal produced using the Dunlop method (Prasopdee and Smitthipong, 2020). In other words, the Talalay method presented in this study can be used to prepare rubber foams with low foam densities, good mechanical properties, and low levels of energy loss.

4. Conclusions

While the Dunlop and custom Talalay methods for foaming natural rubber are well-established, there is a notable lack of information about the effects of surfactant treatments on this process. This study presents the effects of different surfactants on NLFs for the first time through a comprehensive assessment of the relationships between the foam structure, energy absorption, and thermodynamic properties. To provide a basis for comparison, the findings from the surfactant-treated NLFs produced through the custom Talalay method were compared with those from the Dunlop method. This study is summarised as follows.

The morphological structure of the NLFs produced using the Dunlop method had a narrow distribution of small cell sizes determined from 2D SEM images and 3D micro-CT images. However, the overall cell size was found to be heterogeneous. Adding PL and KL surfactants resulted in lower porosities, yielding higher foam densities and enhanced mechanical properties. Increased amounts of PL increased the matrix content of the NLFs, while increasing the KL content resulted in the formation of small bubbles, decreasing the bubble volume of the foam. Another observation was that the energy absorbed by the foam increased as its compression speed increased, consistent with the effect of the time-temperature relationship on the energy absorption capabilities of the NLFs.

The distribution of cell sizes in the NLFs produced using the Talalay method was broader than those produced using the Dunlop method due to the addition of stirring and vacuuming techniques. The NLFs produced using the Talalay method also exhibited 20% lower compressive strengths and absorbed 7% less energy compared to those produced using the Dunlop process, regardless of the formulation. This difference can be attributed to the aeration during the foaming process. Different energy absorption values and morphologies were observed with distinct preparation methods. The NLFs produced via the Talalay method exhibited lower $F_{\rm u}/F$ ratios than those produced using the Dunlop process, leading to variations in the mechanical properties of the samples despite their comparable entropic stabilities.

This study showed that Talalay-produced, surfactant-treated NLFs have lower densities, enhanced mechanical properties, and reduced energy loss compared with Dunlop-produced NLFs. However, the Dunlop method remains the more cost-effective choice. Additionally, this study is important because it presents a novel and comprehensive understanding of the thermodynamics and structure properties of NLF between the Dunlop and in-house Talalay methods, which has not been done previously. A potential limitation of this research is challenge of controlling conditions during sample preparation. Furthermore, the influence of temperature and humidity is also significant. Consequently, it is essential to consistently maintain optimal conditions during sample preparation. Nevertheless, the main finding underscores the crucial need to choose the NLF production method most suited to the specific application requirements.

Ethical approval

Not Applicable

CRediT authorship contribution statement

Noppawan Tundiew: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. Peerayut Kunklang: Writing – original draft, Investigation, Formal analysis, Data curation. Supitta Suethao: Methodology, Investigation. Jirasak Wong-Ekkabut: Supervision. Jukkrit Mahujchariyawong: Supervision. Kheng Lim Goh: Writing – review & editing, Supervision. Wirasak Smitthipong: Writing – review & editing, Validation, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Supplementary information

The article contains supplementary material, which is available to authorized users.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2024.118631.

References

- Alem, A., Drew, R.A.L., Pugh, M.D., 2014. The influence of the nitriding parameters on the microstructure and strength of the open-cell reaction bonded silicon nitride foams fabricated via wet processing. J. Mater. Sci. 49, 4780–4789. https://doi.org/ 10.1007/s10853-014-8177-4.
- Al-Moameri, H., Zhao, Y., Ghoreishi, R., Suppes, G., 2021. Simulation silicon surfactant rule on polyurethane foaming reactions. Iran. J. Chem. Chem. Eng. 40, 1256–1268. https://doi.org/10.30492/ijcce.2020.43332.
- Andrew, J.J., Alhashmi, H., Schiffer, A., Kumar, S., Deshpande, V.S., 2021. Energy absorption and self-sensing performance of 3D printed CF/PEEK cellular composites. Mater Des 208 109863 https://doi.org/10.1016/j.mates.2021.109863
- Mater. Des. 208, 109863 https://doi.org/10.1016/j.matdes.2021.109863.
 Atrafi, A., Pawlik, M., 2017. Foamability of fatty acid solutions and surfactant transfer between foam and solution phases. Miner. Eng. 100, 99–108. https://doi.org/10.1016/j.mineng.2016.10.012.
- Bao, H., Li, A., 2019. Characterization of spherical cell porous aluminum alloypolyurethane interpenetrating phase composites at different temperatures. Mater. Res. Express 6, 125506. https://doi.org/10.1088/2053/1591/ab534a
- Res. Express 6, 125506. https://doi.org/10.1088/2053-1591/ab534a.
 Blackley, D.C., 1997a. Latex foam rubber. Polymer Latices: Science and Technology Volume 3: Applications of latices, 229-326. https://doi.org/10.1007/978-94-011-5848-0.
- Blackley, D.C., 1997b. Polymer Latices. XVII, 592 second edition 1997, XVII, 592. http:// 10.1007/978-94-011-5866-4.

Industrial Crops & Products 216 (2024) 118631

- Castelvetro, V., Vita, C., Giannini, G., Giaiacopi, S., 2006. Role of anionic and nonionic surfactants on the control of particle size and latex colloidal stability in the seeded emulsion polymerization of butyl methacrylate. J. Appl. Polym. Sci. 102, 3083–3094. https://doi.org/10.1002/apn.23717.
- 3083–3094. https://doi.org/10.1002/app.23717.
 Constantinides, P.P., Steim, J.M., 1985. Physical properties of fatty acyl-CoA. Critical micelle concentrations and micellar size and shape. J. Biol. Chem. 260, 7573–7580. https://doi.org/10.1016/S0021-9258(17)39646-1.
- Denkov, N., Tcholakova, S., Politova-Brinkova, N., 2020. Physicochemical control of foam properties. Curr. Opin. Colloid Interface Sci. 50, 101376 https://doi.org/ 10.1016/j.cocis.2020.08.001.
- Dhaliwal, G., Anandan, S., Bose, M., Chandrashekhara, K., Nam, P., 2020. Effects of surfactants on mechanical and thermal properties of soy-based polyurethane foams, 0021955×2091220 J. Cell. Plast. 56. https://doi.org/10.1177/0021955×20912200.
- Eyssa, H.M., Mogy, El, Youssef, H.A, S.A., 2021. Impact of foaming agent and nanoparticle fillers on the properties of irradiated rubber. Radiochim. Acta 109, 127–142. https://doi.org/10.1515/ract-2020-0015
- 127–142. https://doi.org/10.1515/ract-2020-0015. Ferry, J.D., 1980. Viscoelastic Properties of Polymers. Springer, Boston, MA. Gibson, L.J., Ashby, M.F., 1997. Cellular Solids: Structure and Properties, 2 ed.
- Cambridge University Press, Cambridge.
 Gong, W., Jiang, T.-H., Zeng, X.-B., He, L., Zhang, C., 2020. Experimental-numerical studies of the effect of cell structure on the mechanical properties of polypropylene foams. E-Polym. 20, 713–723. https://doi.org/10.1515/epoly-2020-0060.
- Hui Mei, E.L., Singh, M., 2010. The Dunlop process in natural rubber latex foam Malaysian rubber development. Technology 10, 23–26.
- Iizuka, M., Goto, R., Siegkas, P., Simpson, B., Mansfield, N., 2021. Large deformation finite element analyses for 3D X-ray CT scanned microscopic structures of polyurethane foams. Materials 14. https://doi.org/10.3390/ma14040949.
- Jeong, S.H., Kim, J.M., Yoon, J., Tzoumanekas, C., Kröger, M., Baig, C., 2016. Influence of molecular architecture on the entanglement network: topological analysis of linear, long- and short-chain branched polyethylene melts via Monte Carlo simulations. Soft Mater. 12, 3770–3786. https://doi.org/10.1039/CSSM03016A.
- Johns, J., Rao, V., 2008. Characterization of natural rubber latex/chitosan blends. Int. J. Polym. Anal. 13, 280–291. https://doi.org/10.1080/10236660802190104.
- Karolewicz, B., Górniak, A., Owczarek, A., Żurawska-Płaksej, E., Piwowar, A., Pluta, J., 2014. Thermal, spectroscopic, and dissolution studies of ketoconazole-Pluronic. F127 Syst. J. Therm. Anal. 115, 2487–2493. https://doi.org/10.1007/s10973-014-3661-2.
- Katkeaw, K., Nooklay, B., Kokoo, R., Kooptarnond, K., Khangkhamano, M., 2019. The effect of nitrogen bubbles on microstructure of natural rubber foams produced by bubbling process. Mater. Sci. Forum 962, 91–95. https://doi.org/10.4028/www. scientific.net/MSF.962.91.
- Katkeaw, K., Khangkhamano, M., Kokoo, R., 2021. Microbubble technology for natural rubber latex foam production: The use of various gas-filled microbubbles. Cell. Polym. 41, 21–29. https://doi.org/10.1177/02624893211053672.
- Klommueang, H., Smitthipong, W., 2023. Development of natural rubber foam by inhouse Talalay method. IOP Conf. Ser.: Mater. Sci. Eng. 1280, 012021 https://doi. org/10.1088/1757-899X/1280/1/012021.
- Krundaeva, A., De Bruyne, G., Gagliardi, F., Van Paepegem, W., 2016. Dynamic compressive strength and crushing properties of expanded polystyrene foam for different strain rates and different temperatures. Polym. Test. 55, 61–68. https://doi. org/10.1016/j.polymertesting.2016.08.005.
- Kunam, P.K., Anushikha, Gaikwad, K.K., 2023. Water resistant paper based on natural rubber latex from Hevea brasiliensis and butyl stearate hydrophobic coating for packaging applications. Ind. Crops Prod. 205, 117480 https://doi.org/10.1016/j. indcrop.2023.117480.
- Lin, L., Zheng, Z., Li, X., Park, S., Zhang, W., Diao, G., Piao, Y., 2023. Design strategy for porous carbon nanomaterials from rational utilization of natural rubber latex foam scraps. Ind. Crops Prod. 192, 116036 https://doi.org/10.1016/j. indcrop.2022.116036
- Lomer, T., 1958. The identification of sorbitol by X-ray diffraction. Acta Crystallogr 11, 665. https://doi.org/10.1107/S0365110×58001730.
- Malik, W.U., Jain, A.K., 1967. Electrometric determination of critical micelle concentration of soap solutions. J. Electroanal. Chem. Interfacial Electrochem. 14, 37–41. https://doi.org/10.1016/0022-0728(67)80131-1.
- Micheau, C., Bauduin, P., Diat, O., Faure, S., 2013. Specific Salt and pH effects on foam film of a pH sensitive surfactant. Langmuir 29. https://doi.org/10.1021/la400879t.
- Montgomery-Liljeroth, E., Schievano, S., Burriesci, G., 2023. Elastic properties of 2D auxetic honeycomb structures- a review. Appl. Mater. Today 30, 101722. https:// doi.org/10.1016/j.apmt.2022.101722.
- Morton, D.T., Reyes, A., Clausen, A.H., Hopperstad, O.S., 2020. Mechanical response of low density expanded polypropylene foams in compression and tension at different loading rates and temperatures. Mater. Today Commun. 23, 100917 https://doi.org/ 10.1016/j.mtcomm.2020.100917.
- Mulligan, C.N., 2007. Chapter 15 Rhamnolipid biosurfactants: solubility and environmental issues. Thermodyn., Solubility Environ. Issues 279–298. https://doi. org/10.1016/B978-044452707-3/50017-3.

- Ng, J.W., Othman, N., Yusof, N.H., 2022. Various coagulation techniques and their impacts towards the properties of natural rubber latex from Hevea brasiliensis — a comprehensive review related to tyre application. Ind. Crops Prod. 181, 114835 https://doi.org/10.1016/j.indcrop.2022.114835.Nisha, S., Sanyogita, D., Verghese, S., 2012. Physico-chemical characterization and
- Nisha, S., Sanyogita, D., Verghese, S., 2012. Physico-chemical characterization and synthesis of potassium laurate as herbicides against Moss. Int. J. Res. Chem. Environ 2, 306–309306.
- Oliveira-Salmazo, L., Lopez-Gil, A., Silva-Bellucci, F., Job, A.E., Rodriguez-Perez, M.A., 2016. Natural rubber foams with anisotropic cellular structures: Mechanical properties and modeling. Ind. Crops Prod. 80, 26–35. https://doi.org/10.1016/j. indcrop.2015.10.050.
- Phuhiangpa, N., Ponloa, W., Phongphanphanee, S., Smitthipong, W., 2020. Performance of nano- and microcalcium carbonate in uncrosslinked natural rubber composites: new results of structure-properties relationship. Polymers 12. https://doi.org/ 10.3390/polym12092002.
- Prasopdee, T., Smitthipong, W., 2020. Effect of fillers on the recovery of rubber foam: from theory to applications. Polymers 12. https://doi.org/10.3390/ polym12112745.
- Prasopdee, T., Shah, D.U., Smitthipong, W., 2021. Approaches toward high resilience rubber foams: morphology–mechanics–thermodynamics relationships. Macromol. Mater. Eng. 306, 2100337 https://doi.org/10.1002/mame.202100337.
- Ramli, R., 2022. Natural rubber latex foam technology for bedding industry. Sci. Eng. Health Stud. https://doi.org/10.14456/sehs.2022.18.
- Rostami-Tapeh-Esmaeil, E., Vahidifar, A., Esmizadeh, E., Rodrigue, D., 2021. Chemistry, processing, properties, and applications of rubber foams. Polymers 13. https://doi. org/10.3390/polym13101565.
- Rumianek, P., Dobosz, T., Nowak, R., Dziewit, P., Aromiński, A., 2021. Static mechanical properties of expanded polypropylene crushable foam. Materials 14, 249. https:// doi.org/10.3390/ma14020249.

Singh, M., Hui Mei, E.L., 2013. Surfactants and their use in latex technology. MRB Rubber Technol. Dev. 13, 33–36.

- Sirikulchaikij, S., Nooklay, B., Kokoo, R., Khangkhamano, M., 2019. Rubber foam processing via bubbling technique. Mater. Sci. Forum 962, 96–100. (http:// 10.4028/www.scientific.net/MSF.962.96).
- Sirikulchaikij, S., Kokoo, R., Khangkhamano, M., 2020. Natural rubber latex foam production using air microbubbles: microstructure and physical properties. Mater. Lett. 260, 126916 https://doi.org/10.1016/j.matlet.2019.126916.
 Smitthipong, W., Nardin, M., Schultz, J., Nipithakul, T., Suchiva, K., 2004. Study of tack
- Smitthipong, W., Nardin, M., Schultz, J., Nipithakul, T., Suchiva, K., 2004. Study of tack properties of uncrosslinked natural rubber. J. Adhes. Sci. Technol. 18, 1449–1463. https://doi.org/10.1163/1568561042323248.
- Suethao, S., Ponloa, W., Phongphanphanee, S., Wong-Ekkabut, J., Smitthipong, W., 2021b. Current challenges in thermodynamic aspects of rubber foam. Sci. Rep. 11, 6097. https://doi.org/10.1038/s41598-021-85638-z.
- Suethao, S., Phongphanphanee, S., Wong-Ekkabut, J., Smitthipong, W., 2021a. The relationship between the morphology and elasticity of natural rubber foam based on the concentration of the chemical blowing agent. Polymers 13. https://doi.org/ 10.3390/polym13071091.
- Suksup, R., Sun, Y., Sukatta, U., Smitthipong, W., 2019. Foam rubber from centrifuged and creamed latex. J. Polym. Eng. 39, 336–342. https://doi.org/10.1515/polyeng-2018-0219.
- Sun, G., Jiang, H., Fang, J., Li, G., Li, Q., 2016. Crashworthiness of vertex based hierarchical honeycombs in out-of-plane impact. Mater. Des. 110, 705–719. https:// doi.org/10.1016/j.matdes.2016.08.032.
- Tao, Y., Ren, M., Zhang, H., Peijs, T., 2021. Recent progress in acoustic materials and noise control strategies – a review. Appl. Mater. Today 24, 101141. https://doi.org/ 10.1016/j.apmt.2021.101141.
- Thapa, R.K., Cazzador, F., Grønlien, K.G., Tønnesen, H.H., 2020. Effect of curcumin and cosolvents on the micellization of Pluronic F127 in aqueous solution. Colloids Surf. B 195, 111250. https://doi.org/10.1016/j.colsurfb.2020.111250.
- Wang, L., Tabor, R., Eastoe, J., Li, X., Heenan, R., Dong, J., 2009. Formation and stability of nanoemulsions with ionic-nonionic surfactants. Phys. Chem. Chem. Phys. 11, 9772–9778. https://doi.org/10.1039/b912460h.
- Wenchao, L., Hu, Y., Shi, L., Zhang, X., Xiong, L., Zhang, W., Ullah, I., 2018. Electrospinning of Polycaprolactone/Pluronic F127 dissolved in glacial acetic acid: fibrous scaffolds fabrication, characterization and in vitro evaluation. In: J Biomater Sci Polym Ed, 29, pp. 1–24. https://doi.org/10.1080/09205063.2018.1439431.
- Yang, W., Wang, T., Fan, Z., Miao, Q., Deng, Z., Zhu, Y., 2017. Foams stabilized by in situ-modified nanoparticles and anionic surfactants for enhanced oil recovery. Energy Fuels 31, 4721–4730. https://doi.org/10.1021/acs.energyfuels.6b03217.
- Zhang, H., Suszynski, W.J., Agrawal, K.V., Tsapatsis, M., Al Hashimi, S., Francis, L.F., 2012. Coating of open cell foams. Ind. amp; Eng. Chem. Res 51, 9250–9259. https:// doi.org/10.1021/ie300266p.
- Zhang, Q., Lu, W., Scarpa, F., Barton, D., Lakes, R.S., Zhu, Y., Lang, Z., Peng, H.-X., 2020. Large stiffness thermoformed open cell foams with auxeticity. Appl. Mater. Today 20, 100775. https://doi.org/10.1016/j.apmt.2020.100775.