

Research Article

Synthesis and Morphology of Flexible Polyurethane Foams Containing Neem Oil and Clove Powder

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Received 7 October 2023; Revised 14 November 2023; Accepted 28 November 2023; Published 5 January 2024

Academic Editor: Cristiano Fragassa

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Polyurethane foams are a versatile class of polymeric materials whose physico-chemical structure and properties can be modified by incorporating additives. This study examined the effect of naturally occurring insect-repelling additives such as neem oil (NO) and clove powder (CP) on the formulation and morphology of flexible polyurethane foam (FPUF) composites. The foams were prepared by the prepolymer method using a box test as applied in the foam industry. The composite material was formulated by varying the isocyanate index (103 and 108) as an excess amount of isocyanate was required to react with the additives. The formulation at 103 was unsuccessful as the foams collapsed immediately after rising. However, at 108, two main categories of foams were successfully prepared: foams containing either NO or CP and the other containing both additives. The effect of these additives on the formulation was examined by monitoring the foam reaction using the cream, tack-free, and rising times. It was observed that the cream, tack-free, and rising times increased with increasing NO/CP content. Conversely, the morphology was studied using scanning electron microscopy (SEM) and optical microscope (OP). The SEM images revealed disruption of the foam network with 1 wt% NO, likewise those containing 1 wt% CP. The cellular network of the foams with simultaneous addition of NO and CP was similar to that of the neat foams and had no broken cell joints and struts due to better dispersion of the additives in the polyurethane matrix. The study indicates that the combined addition of NO and CP modifies the morphology of FPUF, which can influence their physico-mechanical properties.

1. Introduction

Flexible polyurethane foams (FPUF) are cellular foam materials blown by water during synthesis to achieve their cellular structures [1]. Currently, its usefulness has moved from furniture and bedding products to several other innovative products with tailored applications in diverse industries due to its better mechanical and thermal properties, resilience, and the fact that it can be produced in a wide range of densities (from 20 kg/m³ to 900 kg/m³) [2]. Generally, polyurethane foams are made through polycondensation reaction when an isocyanate group (-NCO-) reacts with the hydroxyl group (-OH) of a polyol in the presence of water as a blowing agent and a surfactant to create urethane linkages (-NH-COO) without generating any byproducts [3]. The surfactant stabilizes the foam cells during formation and lowers the surface tension of the polyol making it easily miscible with the isocyanate compound. Due to the slow nature of the reaction, catalysts are added to speed up the rate of reaction. Catalysts normally used are blowing catalyst which speeds up the rate of the blowing reaction (between water and isocyanate which generates CO_2 responsible for the foam's expansion) and gelling catalyst which speeds up the polymerization/gelling reaction (occurs between the isocyanate and polyol) [1]. Apart from this, other side reactions occur which result in the formation of biurets and allophanate that contribute towards cross-linking in the foam structure [4]. Though the production of FPUF is generally safe, the exposure to hazardous levels of isocyanate can pose health effects such as occupational asthma, irritations to the nose, eye, skin, and throat when precautions are not taken. Therefore, the use of appropriate protective equipment and adherence to safety protocols are advised when using isocyanate [5].

Structurally, FPUF consists of a network of open cells and pores connected by smooth cell walls [6]. For this to be possible, the two reactions, which are polymerization/gelling and blowing, occur simultaneously due to the high reactivity of the -NCO- group. The gelling reaction formed between polyol and isocyanate is to build the urethane bond. Also, the blowing reaction is due to a reaction between isocyanate and water to produce CO₂, which causes the foam to rise, expand, and form the polymer network [7]. If the polyurethane networks (consisting of cells) build too rapidly, the polymer's cell growth will be disrupted leading to the formation of large holes and cavities thereby destroying the open cellular network of the foam [8]. In situations where the gelling reaction occurs faster than the blowing reaction, the foam will shrink leading to more closed than open cells which is a result of unstable and poor foam expansion [9, 10]. Therefore, a delicate balance of these reactions is essential in the production of FPUF with an open porous cellular network [8].

Generally, the structure, properties, and applications of polyurethane foams (PUF) are primarily influenced by the chemistry of the main starting materials (isocyanate and polyol), additives, and isocyanate index [11]. For instance, incorporating additives in the formulation of PUF, especially fillers, influences the kinetics of foam formation and the chemical equilibrium of the foaming reaction in addition to enhancing/reinforcing the properties of the resulting PUF composite [12, 13]. To corroborate this finding, Zieleniewska et al. explored using a halogen-free additive (fryol) and keratin fibres to improve the flammability of viscoelastic polyurethane foams. They also observed that adding the keratin and fryol increased the rising and gelling times of the PUF [14]. In a similar study, Wrzesniewska-Tosik et al. developed viscoelastic foams by incorporating keratin, fryol, expandable graphite, and inorganic flame-retarding fillers. They prepared various composite foams by varying the concentration of the additives in the formulation. However, they recorded little difference in the rising and gelling times among the composite foams [15].

Another factor that affects the foam reaction is the relative amounts of fillers/additives used in the formulation [2]. For instance, Ribeiro da Silva et al. observed that adding various concentrations of rice husk ash (from 2 wt% to 5 wt%) increased the creaming time of the foaming reaction from 15 s to 22 s [16]. Similarly, Zukowska et al. discovered that increasing the content of waste ground tire rubber particles from 5 wt% to 20 wt% in a PUF formulation led to an increase in the tack-free time [17]. Yet again, Chris-Okafor et al. prepared PUF composite using various concentrations of eggshell and groundnut husk powder as fillers and examined the effects of the filler load on the rise and cream times. They observed that the cream and rise time of the polyurethane foam mixture increased as the filler load was increased from 0 wt% to 50 wt% [18]. Their findings corroborated that of Ribeiro da Silva et al. [16] and Żukowska et al. [17]. For

an additive to be successfully incorporated into FPUF composite foam, it must contain reactive functional groups that can bond with the isocyanate group, where the extent of bonding can affect the foam's morphology [19, 20]. Secondly, they must not break the balance of the gelling and blowing reactions as this can produce foams with defects and undesirable properties [21]. In the absence of additives, the foam's cells have a symmetrical polyhedral regular shape [21, 22]. However, the presence of an additive affects this structure by the formation of a network of hydrogen bonding between the urethane group, urea groups, or the carbonyl groups in the polyurethane network [22]. Wrzesniewska-Tosik et al. observed that though adding flame retardant additives improved the fire resistance of the foam, the foam's morphology also changed by a decrease in pore size and an increase in cell wall thickness. They further reported that increasing the additive load resulted in irregular pore shapes, decreased cell wall thickness, and increased disruption of pore walls as compared to the neat foams [15]. On the contrary, Imran et al. made a different observation when they improved the stability of nanoclayfilled PUF where the nanoclay did not affect the morphology of the resulting composite foams. They attributed this observation to the uniform dispersion of the nanoclay in the PUF matrix [23].

In the last decade, FPUFs and their composites have become one of the sought-after engineering materials due to the ease with which their properties can be tailored to suit diverse application requirements [18]. To develop a foam with the desired properties, formulations conducted are accompanied by multiple small-scale tests to ensure that the necessary properties have been achieved before scaling up is done. Conventionally, formulating FPUF involves calculating and using the correct quantities of the basic components (isocyanate, polyol, surfactant, catalyst, additives, and water) and mixing them within an appropriate time [1]. For example, to achieve a specific density, the amount of blowing agents (water and methylene chloride) must be controlled, and for an increased hardness, a polyol with a higher solid content must be used. Also, increasing the isocyanate index, polyol solid content and inorganic filler content while decreasing the methylene chloride can result in a decrease in hardness [24, 25]. A delicate balance of these materials is therefore needed to produce a foam with specified properties.

The formulation of FPUF and their composites are largely affected by the isocyanate index and water content. These two parameters influence the foam' properties such as density [25]. The water content influences the foam's density which is because a higher water content produces more gas (since water reacts with diisocyanate to produce CO_2), and this results in a lower foam density [24]. Also, an important parameter, the isocyanate index which is the percentage of isocyanate groups relative to the total active hydrogen from water and the hydroxyl groups in the foam's formulation [26], provides the balance between the isocyanate and hydroxyl from the polyol as well as other functional groups that may be present in the PU matrix [11]. This is important because the reactivity of the isocyanate moiety drives the polyurethane foam formation [27]. By convention, the

isocyanate index normally used in PUF formulations ranges from 90% to 110% where an index of 100 suggests that there is enough isocyanate to completely react with all the water and polyol in the formulation. An index of 110 indicates that there is 10% extra isocyanate in the system which is normally consumed by the side reactions increasing the crosslinking in the PU structure [26]. It is well established that the isocyanate index influences the processing parameters and properties of the FPUF. For instance, increasing the index is likely to affect the gelling and curing time, and the growth rate of the foam due to an increase in the production of CO_2 for the blowing reaction [28]. Furthermore, it increases the rigid/hard segments of the foam which also affects the mechanical properties such as hardness but reduces the elasticity [28, 29].

The objective of this research is to explore the versatility of PUF by synthesizing flexible polyurethane foams with insect-repelling properties using a combination of neem oil (NO) and clove powder (CP) as repellents. The insecticidal properties of neem oil are due to the presence of bioactive compounds such as azadirachtin, nimbin, and salannin [30]. Eugenol is known to be the main component responsible for insect-repelling activity in cloves [31].

Even though the insect-repelling properties of NO and CP are well documented in the literature [32, 33], there is little information on their combined effect in PUFs as insectrepelling additives. A review of literature reveals that clove powder has been used as fillers in PUF. Notable among such studies is by Czlonka et al. who developed a PUF using clove powder as filler and discovered the inclusion of these material-imparted antibacterial properties on the foam [34]. Neem oil, on the other hand, has been used as a precursor to synthesize biobased polyol due to the presence of unsaturated bonds in its chemical structure. In this regard, Liao et al. prepared a neem-based polyol by the transesterified of neem oil and glycerol, and blended this material with castor oil in various ratios to produce a biobased PUF with improved density and thermal properties [35].

Therefore, harnessing the properties of clove powder and neem oil with the overall objective of making PUF that can repel insects makes this study both innovative and worth pursuing. Due to the reactive nature of these additives, this study discusses their effect on foaming reaction (using the creaming, rising, and tack-free times). Popularly known as the characteristic times, the cream, rising, and tack-free times are influenced by the chemical nature of the polyol, the ratio of primary to secondary hydroxyl groups in the reaction mixture, the combination of hydroxyl groups from additive and polyol (polyol mixture), and the amount of water used in the foam's formulation [1, 9]. Generally, the creaming time of FPUF marks the time that the foam mixture begins to cream until it begins rising. Thus, it indicates the commencement of the gelling/polymerization reaction where the viscosity of the reaction mixture increases [36]. The rising time also measures the time that the reaction mixture ceases to cream and begins to rise thus indicating how the blowing reaction progresses. When well formulated, the foam rises slowly and progressively to a few inches above the end of the mould where rising stops. The foam is then allowed to cure for a short period where a sticky "skin" forms at its surface [37]. The tack-free time, therefore, measures the time that the foam ceases to rise, and its surface stops have been sticky. At this point, the foam is demoulded and allowed to cure further for the polymer network to be well formed [1].

Apart from assessing the additives impart on the characteristic times, this study finally examines how these additives affect the foam's formulation (effect of isocyanate index) and morphology.

2. Experimental: Materials and Methods

2.1. Preparation of Clove Powder. A 500 g of clove buds obtained from a local community in Madina Market in Accra, Ghana, was dried for 24 hr at 50°C in an oven. The dried buds were continuously milled using a Brook Crompton ball mill for 5 min. This was repeated for two other cycles of 5 min each to reduce the size of the particles. The milled clove powder was collected and sieved using a sieve shaker (Retsch, AS 200) to obtain the sample of a particle size of 90 μ m.

2.2. Synthesis of Flexible Polyurethane Foam. The FPUFs were prepared using the prepolymer method and a modification of the formulation by Czlonka et al. [34] by varying the isocyanate index (using 103 and 108) since an excess of isocyanate is required in the foam system to react with the additives. Three categories of composite foams were produced: the neat foam, foams containing either one of the additives (clove powder:CO or neem oil:NO), and those with both additives (clove powder and neem oil). For the neat foam, specific quantities of the polyether polyol, water, surfactant, and catalyst were weighed into a container and mixed. These quantities were calculated using the total weight of foam to be produced and the parts per polyol of each component as indicated in the formulation in Table 1. The toluene diisocyanate (TDI with an index of 103 and 108 was obtained from Dow Europe GmBH, Switzerland) and methylene chloride (obtained from Latex Foam Rubber Product Ltd, Accra, Ghana) were also weighed into a different container and added to the container with the polyol (HL 808, obtained from Dow Europe GmBH, Switzerland). The resulting mixture was thoroughly mixed at room temperature for 10 seconds at 2500 rpm until it creamed where the creaming time was recorded. The creamed mixture was immediately poured into a wooden moulding box lined with kraft paper. The resulting mixture began to rise steadily until a point where it ceased, and the corresponding time was recorded. The risen mixture was demoulded, and the foam was allowed to cure for 24 hrs at a temperature of $25 \pm 3^{\circ}$ C and a relative humidity of $60 \pm 10\%$. Similarly, the other two (2) categories of the foams were prepared by varying the contents of the additives (neem oil and clove powder) as described in Table 1. The quantities of the silicone surfactant (Tegostab B, obtained from Evonik Operations, Germany), stannous octoate catalyst (T-9, obtained from Evonik Operations, Germany) and amine-glycol catalyst (Tegoamine, obtained from Evonik Operations, Germany), deionized water, and

Foam ID	Description		Total weight of sample (15 Weight of raw materials	(g)	
	Description	HL 108 polyol	TDI index (108)	NO	СР
PU-0	FPUF without any additives	941.3	836.0	0	0
PUC-1	FPUF with 0.5% CP	601.0	836.0	0.0	7.7
PUC-2	FPUF with 1.0% CP	593.2	836.0	0.0	15.5
PUN-1	FPUF with 0.5% NO	601.0	836.0	7.7	0.0
PUN-2	FPUF with 1.0% NO	593.2	836.0	15.5	0.0
PUCN-1	FPUF with 0.5% NO and 1.0% CP	585.5	836.0	7.7	15.5
PUCN-2	FPUF with 1.0% NO and 1.0% CP	577.7	836.0	15.5	15.5
PUCN-3	FPUF with 1.5% NO and 1.5% CP	562.2	836.0	23.3	23.3

TABLE 1: Foam formulation parts by weight (g) using an isocyanate index of 108.

methylene chloride used at the isocyanate index of 108 remained unchanged (as stated in Table 2). All the chemicals used were without further purification. The effect of the additives on the foaming reaction for each synthesized FPUF was measured in terms of creaming, tack-free, and rising times using a digital stopped clock.

2.3. Characterization of Additives and the Synthesized FPUF. The interactive behaviour of the additives with the FPUF was studied for the functional groups present in the CP and NO using the Fourier transform infrared (FTIR) spectroscopy. The FTIR equipment used (PerkinElmer Spectrum Two) was equipped with a universal attenuated total reflectance (ATR) accessory and a DGTS/KBr detector. The instrument was equipped with a spectrum 10.5.2.636 software with measurements performed at a wavelength range of 4400–350 cm⁻¹ with a maximum resolution of 4 cm⁻¹. The appearance of the foams was visually examined for holes, tears, and other visible defects. The synthesized FPUF was imaged with an optical microscope (Meji, fitted with a 9.0MP digital camera) to examine their open cellular structure which includes cavities, and interconnecting pores. Additionally, the effect of the additives on the foam's cellular network, struts, and their distribution in the PU matrix were analyzed using a scanning electron microscope (MIRA3 TES-CAN SEM). The samples were coated with gold using a sputter coater, and images were observed at a voltage of 15 kV using a magnification of 200x with a resolution of $200 \,\mu m$.

3. Results and Discussion

3.1. FTIR Result of Clove Additive. The FTIR spectra of CP in Figure 1 show characteristic bands at 3335 cm^{-1} (-OH vibrations) and 2924 cm^{-1} (-CH₂ vibration), which correlate to the cellulose and hemicellulose content in the CP. The peak localized at 1604 cm⁻¹ indicated the presence of a symmetric aromatic ring (C=C). Furthermore, there were peaks at 1512 cm⁻¹ and 1450–1430 cm⁻¹, which are both bands related to the C=C aromatic stretching modes connected to the structure of eugenol. Other distinctive bands within the range of 1370–1310 cm⁻¹ (C–OH deformation vibrations) and 1170–1110 cm⁻¹ (C–OH stretching vibrations) are also associated with the phenol group. The FTIR spectra were comparable to that of Czlonka et al. [34], who also used clove powder as a cellulosic

D	% weight of components (parts per hundred polyol)			
Foam components	At an isocyanate index of 103	At an isocyanate index of 108		
Polyol	100	100		
TDI	51.44	53.42		
Surfactant	0.20	0.45		
Water	3.75	4.57		
Methylene chloride	1.50	1.50		
Tin catalyst	0.246	0.246		
Amine catalyst	0.028	0.028		
Naam ail	0.5	0.5		
Neem on	1.0	1.0		
Clava navidar	0.5	0.5		
Clove powder	1.0	1.0		

TABLE 2: Foam formulations with different isocyanate index.

filler to create biobased polyurethane foams. Additionally, the distinctive bands found in this study matched those in the FTIR spectra of clove oil used by Nagaraju et al., who investigated the therapeutic effects of a nanoemulsion of clove oil. Their spectra also contained characteristic bands such as 3515 cm⁻¹ -OH stretching, 2837 cm⁻¹ (-CH₂ vibrations), and 1511 cm⁻¹ and 1431 cm⁻¹ due to C=C aromatic stretching mode [38]. The spectrum of clove powder shows that it has functional groups (OH group) that can react with the NCO group of the isocyanate during the synthesis of the foams.

3.2. FTIR Result of NO Additive. The aliphatic C-H stretching was visible at $2852-2921 \text{ cm}^{-1}$ in the FTIR spectra of the cold-pressed NO (Figure 2). The presence of esters that are associated with the structure of azadirachtin was indicated by a peak in 1744 cm^{-1} that was attributed to the C=O stretching of a triglyceride ester. This was supported by two peaks, one at 721 cm^{-1} due to methylene (-CH₃) rocking vibrations and the other at 1159 cm^{-1} due to C-O-C stretching vibrations of esters. These results were similar to the spectra obtained by Bhargava and Madhav who determined the spectroscopic rheological characterization of NO and its isolated fractions and a corresponding C=O stretching at 1750 cm^{-1} [39]. Additionally, the spectra of neem oil



FIGURE 2: FTIR spectrum of NO.

also corroborated with the findings of Das et al. who observed a peak at 1749 cm⁻¹ due to C=O stretching of the triglyceride ester [40]. However, their other peaks for CH₃ rocking vibrations and C-O-C stretching vibrations appeared at slightly different frequencies than those mentioned in this study. The FTIR spectra of neem oil indicate the presence of functional groups such as esters, which can react with the NCO group of the isocyanate and hence are a suitable additive to produce FPUF. 3.3. Effect of Additives on Foam Formation. For the formulation of the synthesized FPUF, an excess of isocyanate was required due to the presence of reactive functional groups in the additives as shown by FTIR spectra (Figures 1 and 2). As a result, an isocyanate index above 100 was required together with an appropriate amount of surfactant in the formulation to control and maintain the foam's stability during its formation [41]. At an isocyanate index of 103 and additive content of 0.5 parts per polyol (php), the

		Foams mad	de with isocyanate in	dex (103)			Foam	s made with isocyan	ate index (108)	
Foam ID	Nature of cells	Splits	Collapse of foam after rising	Presence of cavities	Blow holes	Nature of cells	Splits	Collapse of foam after rising	Presence of cavities	Blow holes
PU-0	Open cells	No splits	No collapse	No cavities	No holes	Open cells	No splits	No collapse	No cavities	No holes
PUC-1	Closed	N/A	Collapse	N/A	N/A	Open cells	No splits	No collapse	No cavities	No holes
PUC-2	Closed cells	N/A	Collapse	N/A	N/A	Open cells	No split	Partial collapse	Cavities	Holes seen
PUN-1	Closed cells	N/A	Collapse	N/A	N/A	Open cells	No split	No collapse	No cavities	No holes
PUN-2	Closed cells	N/A	Collapse	N/A	N/A	Open cells	Partial split	Partial collapse	Cavities observed	Holes seen
PUNC-1	N/A	N/A	N/A	N/A	N/A	Open cells	No splits	No collapse	No cavities	No holes observed
PUNC-2	N/A	N/A	N/A	N/A	N/A	Open cells	No splits	No collapse	No cavities	No holes observed
PUNC-3	N/A	N/A	N/A	N/A	N/A	Open cells	No splits	No collapse	No cavities	No holes observed

TABLE 3: Physical defects of foams under different isocyanate indices.



FIGURE 3: SEM images of foams at 200x magnification.

foam collapsed after rising as the polymer cellular network was not well formed. The foam's cells were broken and disintegrated into crumbs. This could be attributed to factors such as low levels of surfactant in the formulation, and insufficient reaction between the TDI and the additives [25, 42]. When the isocyanate index was increased to 108, and the surfactant increased from 0.2 to 0.45 php with the same additive amount of 0.5 php, no collapse was observed after rising. The physical appearance of the foams containing either the NO or the CP was comparable to that of the neat foam except with a slight difference in colour. However, when the additive amount was increased to 1.0 php, the foam partially collapsed after rising, and there were large cavities and splits as compared to the neat foam which did not have these deformities.

Interestingly, at the same isocyanate index and surfactant content, the foam containing both additives (0.5php NO and 1.0php CP) was well formed comparable to the neat foams.

There was no collapse of foam, splits, or large cavities (Table 3). A similar observation was made for the foams each containing 1.0 php and 1.5 php of the NO and CP, respectively. Thus, when the additives were used together, a better cellular network was obtained as revealed by their SEM images (Figures 3 and 4). It is therefore worth noting that the successful inclusion of neem oil and clove powder in the formulation of FPUF depends on the isocyanate index, surfactant, and the amount of additives added. Depending on the amount of additive added, the rising of the foam can be impeded which can lead to a collapsed or poorly formed foam structure.

3.4. Additive Effect on FPUF Appearance and Morphology

3.4.1. Visual Appearance of the FPUF. The foams were visually examined for foam defects during production and after curing (Figure 5). First, the foams are made with 1 wt% CP



FIGURE 4: SEM images of foams at 1000x magnification.

and NO collapsed after the foam expansion where the rising ceased. Therefore, they had coarser closed-cell contents than the other foams with more open uniform cells. Secondly, there were splits, holes, and internal cracks compared to the blank foam with no splits, holes, or cracks. The splits and cracks in the PUN-1 (1 wt% NO FPUF) were more significant than those observed in the 1 wt% CP FPUF (PUC-1). These observations were due to the high reactivity of these additives at 1 wt% concentration and low surfactant levels, which could not stabilize the reaction mixture and resulted in instability and collapse of the foam after the foam expansion process.

The FPUF with combined addition of 0.5 wt% NO and 0.5 wt% CP (PUC-1) also had open cell structures without any signs of cavities, cracks, or holes. This was because the foaming reaction was stable, and there was no collapse after the foam attained a full rise. Likewise, the appearance of the FPUFs containing both NO and CP was stable during pro-

duction. This resulted in FPUFs without cracks, splits, and/ or holes. The FPUF with NO and CP had uniform open cells comparable to the reference foam. This can be attributed to the use of sufficient amounts of surfactant, water, and catalysts in the reaction system, which provided a suitable environment for the additives to react with excess isocyanate.

3.5. Optical Microscopy of FPUF. Typically, the cell structure of a PUF consists of a porous structure made up of cell walls, struts, and strut joints [43], and the incorporation of additives affects their uniformity, homogeneity, and cell wall diameter [44]. The optical microscope image of the neat foam (PUN-0) reveals a network of open cells linked with struts (Figure 6(a)). However, the morphology of the foams containing either NO or CP (PUN/PUC as in Figures 6(b)–6(e)) had a distorted cellular network rupturing the foam's struts at certain points in the network. This observation corroborates that

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FIGURE 5: The appearance of polyurethane foams containing various percentages of CP and NO.

<u>30 mm</u>



(a) Blank

(b) PUC-1 (0.5% CP-FPUF)



(c) PUC-2 (1% CP-FPUF)

(d) PUN-1 (0.5% NO-FPUF)



(e) PUN-2(1% NO-FPUF)

(f) PUNC-1 (0.5% NO and 1% CP)



(g) PUNC-2 (1% NO and 1% CP)

(h) PUNC-3 (1.5% NO and 1.5% CP)

FIGURE 6: Optical images of FPUF at 5x magnification.

of Mukherjee et al. whose work optimized the morphological, physiochemical, and mechanical properties of biodegradable PUF [45].

On the other hand, the FPUF composites containing both additives (PUNC foams) had a structure made up of porous cavities and open cells linked together by struts forming a continuous cellular network of open cells possibly attributable to better dispersion of additives in PU matrix as compared to the foams containing either of the additives. This observation was further confirmed with images of the scanning electron microscope (Figures 3 and 4). 3.6. Scanning Electron Microscopy of FPUF. The effect of neem oil and clove powder on the surface morphology of FPUF was studied with a scanning electron microscope at 200 (Figure 3) and 1000 (Figure 4) magnifications. The SEM images of the neat foam reveal a porous interconnected structure with cell walls, pores, and cavity characteristic of FPUF cellular structure. The interconnected porous structure is responsible for the resilience and breathability required during application [46]. As revealed in the SEM images, the additives disrupted the cell wall network and caused numerous broken cells in the PU network in the PUN and PUC foams.



FIGURE 7: Effect of additives on creaming, rising, and tack-free time of FPUF.

Specifically, the PUC-2 and PUN-2, which contained 1 wt% CP and NO, had broken cell walls, cavities, and the destruction of the foam's struts. This was expected as, during synthesis, the foams collapsed after rising. The SEM images of these foams show particles of these additives agglomerating on the struts of the foams. This result agrees with the work of Protzek et al., who also located cellulose fibres in the struts of the foam's cells [47]. This was observed because the size of the additive was larger than the diameter of the foam's cell wall and could not be embedded in the cell walls, which caused the walls to rupture [48]. The cells of PUN-1 and PUC-1 were uniform, with fewer cell walls ruptured as compared to PUN-2 or PUC-2. As expected, smaller quantities of clove powder were seen on the struts of the cells of PUC-1 compared to PUC-2, which had more powder on the struts (Figure 3).

The SEM images of the PUNC foams also showed a porous structure with interconnected cells. However, the pore sizes of the cells increased compared to the neat foams. Additionally, the additives were located both in the cell walls and the struts, especially for PUNC-3, which had a higher content of both NO and CP than the other foams. Finally, the SEM images indicate that the additives were well dispersed in the foams at lower additive concentrations. Generally, the additives modified the cellular structure of the FPUF by changing the cell shape and homogeneity and creating more breakages in the cell network at higher concentrations.

3.7. Additive Effect on Foaming Reaction: Creaming, Rising, and Tack-Free Time. The rate of foam formation was determined by creaming, rising, and tack-free time as given in Figure 7. The creaming time was recorded from when the TDI was added to the mixture until it creamed and began to rise [49]. In this study, adding the clove powder and neem oil influenced the creaming, rising, and tack-free time. For example, the creaming time was reduced from 16 seconds (blank foam-PU-0) to 13 seconds for PUC-1, which further decreased to 12 seconds for PUC-2 (1.0 wt% CP foam). The same trend was observed for PUN-1 (0.5 wt% NO) and PUN-2 (1.0 wt% NO). The reduction in the creaming time was due to the high reactivity of the additives in the system, which caused the foam reaction to commence earlier than the blank foam. The rising times are also reduced as the amount of either CP or NO is increased.

In contrast, the foams with combined amounts of neem oil and neem oil showed a different trend where their creaming times increased with increasing additive content as seen in Figure 7. For PUNC-1 (0.5 wt% NO and 1.0 wt% CP), the creaming time (15s) was slightly lower than the blank foam (16 s). However, this increased from 17 s to 18 s when the concentration of both additives was increased to 1.0 wt% (PUNC-2) and 1.5 wt% (PUNC-3), respectively. The increase in their creaming time compared to the blank was due to competition of the functional groups in these additives to react with the NCO group of the isocyanate, which slightly slowed down the initiation of the blowing reaction due to resistance in bubble expansion [50]. A similar pattern was observed in the rising time, as the concentration of the additives increased, and the rising time also increased. These findings corroborated with that of Zhang et al., who observed an increase in creaming and rising times when the content of their straw filler content increased [50]. Strakowska et al. also made a similar observation with increasing content of their additive/filler (POSS) [51]. Another reason is the less homogenous dispersion of the additives in the polyurethane matrix due to the increase in viscosity of the reaction mixture, which delayed the initiation of the blowing and gelling reactions [16].

The tack-free time was also similar to the creaming and rising times; however, as the content of the additive increases, the tack-free time decreases. For example, as the CP amount increased from 0.5 wt% to 1.0 wt%, the tack-free time decreased from 245 to 260 s compared to the blank foam, which was 230 s. This observation was similar to that of Munawar et al., who observed a decrease in the tack-free time with increasing content of the palm oil trunk filler [52]. Similarly, Ni et al. recorded a decrease in tack-free time (46 s to 28 s) as the content of lead oxide (PbO) filler increased from 10 wt% to 70 wt% in PUFbased materials with gamma-ray shielding effect [37].

However, in the combined PUNC foams, the tack-free time increased as the amount of additives increased. For example, from PUNC-1 to PUNC-3, the tack-free time increased from 290 to 310 s. A similar pattern was also observed for the creaming and rising times. This can be attributed to reactions between the NO and CP in the foaming system, which might have served as additional nucleating sites for bubble formation, slowing down the blowing and polymerization reactions. This led to a longer creaming, rising, and tack-free time than the blank foam [52]. However, Rattanapan [53] made a different observation in the creaming, rising, and tack-free time of biobased polyurethane foams prepared using telechelic hydroxyl oligomers from natural rubber (HTNR), waste tire crumbs (HTWT), and polycaprolactone diol (PCL). In the foams containing HTNR and PCL, the weight percent of PCL increased from 0 and 0.5 to 1, while HTNR was maintained at 1 wt%. As a result, they observed an increase in creaming, rising, and tack-free time but noticed a decrease in these times when the wt% of HTNR reduced to 0.5, and that of PCL was kept at 1 wt%. They attributed this to the high reactivity of the hydroxy groups in HTNR compared to the PCL, which allowed the foam reaction to proceed faster [53]. This shows that the presence of highly reactive functional groups of additives will shorten the creaming, rising, and tack-free time of FPUF while less reactive ones will increase them.

4. Conclusions

This study examined the effect of incorporating insectrepelling additives neem oil and clove powder (NO and CP) on the formulation and morphology of flexible polyurethane foams. Using FTIR, the feasibility of using these additives was examined by determining the presence of a functional group that can react with the isocyanate group in the foam formulation. The appropriate formulation for the FPUF was determined by varying the isocyanate index (103 and 108) due to the reactivity of the additives. At an isocyanate index of 103 and additive content of 0.5 wt%, the foams collapsed after rising. However, at an isocyanate index of 108 and 0.5 wt% additive concentration, the foam was well formed. In this regard, three (3) different foams were produced: NO foam, CP foam, and the third type containing a combination of the two additives. Unfortunately, foams containing 1.0 wt% NO ruptured and partially collapsed. The same observation was made for foams containing 1.0 wt% CP. This showed that 0.5 wt% of the additive was adequate for the foams to be well formed. Interestingly, the foams containing both additives were well-formed without any rupture, collapse, or shrinking after their full rise times. As the concentration of the additives increased from 0.5 wt% to 1.0 wt%, both the NO and CP foams had coarse closed cells with cracks and relatively bigger holes than the neat foam. The cells of the foams, which had both additives, were without cracks or splits. However, at 1.5 wt% concentration of both additives, there were slight splits on the edges.

The effect of these additives on the foam reaction (creaming, rising, and tack-free time) of the foam mixture and the physical appearance of the foam were also studied. The creaming and rising time were reduced compared to the blanks as the additive concentration increased for foams containing only one type of additive. However, foams containing both additives recorded increased creaming, rising, and tack-free times as the concentration increased.

The optical microscope and SEM images showed that the addition of neem oil and clove powder modified the cellular morphology of the foams, as there were large pores and cavities compared to the neat foam in the foams containing 1 wt% of the additives. Moreover, the foam's cells collapsed, disrupting their cellular network for the PUN and PUC foams. The SEM images at 1000 magnification of PUN-2 and PUC-2 foams reveal that the additives occupied the struts of the foams. The results of this study indicate that CP and NO can be added to produce FPUF composite materials. However, the formulations must be optimized to prevent foam collapse, which was observed at 1 wt% in both NO and CP foams.

Data Availability

The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

Charles Kuranchie is grateful to the management of the Ghana Standards Authority and Carnegie Foundation through the BANGA-Africa project of the University of Ghana for funding the research component of this study. A special appreciation goes to Saibabu Manchalla and Ernest Darfah of Latex Foam Rubber Products Ltd, Accra, Ghana, for their technical support during this study.

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