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Production of Flexible Polyurethane Foam Using Olive Oil as Surfactant

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***Abstract*—Flexible polyurethane foam production has been made more cost effective by incorporating olive oil as a surfactant (stabilizer). The olive oil was substituted for the commonly used expensive silicone oil. Foam formulation was conducted based on 500g polyether polyol in varying proportions: 0, 50, 75, 100% olive oil substitution. The results have shown that olive oil cannot singly act as surfactant in polyurethane foam production, but as a blend with the traditional silicone oil. The olive oil could be substituted up to 75% to yield polyurethane foam with the desired physical and mechanical properties; a threshold limit beyond which the foam formulation collapses. Addition of the olive oil at various proportions was found to slightly influence the physical and mechanical properties of the foam compared with formulation made with 100% silicone oil. For instance, using 75% olive oil as substitute surfactant in the foam formulation increased density of the foam from $22 kgm^{-3}$ to $24.29 kgm^{-3}$, reduced compression set from 6.25 to 4.62% whereas the foam elongation decreased from 124% to 116%. On the other hand, the rising time of the foam increased from 1.24 minutes to 1.37 minutes.**

Keywords — Silicone oil, Polyurethane, Olive oil, Surfactant, Polyol

I. INTRODUCTION

Polyurethane foams have in recent times replaced foams produced from natural and synthetic latex technology. This is primarily because polyurethane gives a tough molecular structure able to withstand high loadings, and it can be prepared to a much lower density than latex foams of same load bearing capability [1]. The production of polyurethane foam requires the presence of additives such as foaming or blowing agent, surfactants and stabilizers [2].

Traditionally silicone oil is used as surfactant in flexible foam synthesis. Silicone oil which is technically known as silicone-polyalkylene oxide block copolymer emulsifies by bringing together incompatible ingredients, homogenizes the chemical mix and lowers the bulk surface tension. It also promotes bubble nucleation during mixing as well as reduces the deforming effect of any solid added, and ensures stabilization of the cell walls during foam expansion [3]. Of these functions, perhaps the most important is the stabilization of the cell walls, without which the foam would behave like a viscous boiling liquid [4]. However, silicon oil is inherently costly, and several efforts have been made to find alternatives to silicon oil so as to reduce production costs.

The natural existence of oil in seeds in varying proportions together with efficient oil extraction techniques, have prompted the use of vegetable oils as substitute for silicon oil in foam manufacture [1]. In this work, silicon oil is blended in various proportion from 0-100% with olive oil; a readily available vegetable oil to synthesize various grades of polyurethane foam.

Vegetable oils contain mainly esters of the type 12-hydroxyl-9-octadecanoic acid [4]. Olive oil is obtained from the olive seed (the fruit of *Olea europaea*; family *Oleaceae*), a traditional tree crop of the Mediterranean basin. The oil is produced either by solvent extraction or mechanical pressing of whole olive seeds. The oil consists of 1.25% stearic acid, 76.33% oleic acid, 10.34% linoleic acid and 0.08% linolenic acid [5]; the last three being unsaturated acids. Other seed oils such as soya oil and castor oil have been used in isocyanate reactions to make polyurethanes elastomers, millables, castables, adhesives and coatings [4, 6].

II. THEORY

A. *Polyurethane*

The pioneering work on polyurethane polymer manufacture was conducted by Otto Bayer and his co-workers in 1937 at the laboratories of I. G. Farben in Leverkusen, Germany. They recognized that using the poly addition principle to produce polyurethanes from liquid di-isocyanates and liquid polyether or polyester diols seems to point to special opportunities especially when compared to already existing plastics that are made by polymerizing olefins or by polycondensation [7].

B. *Polymerization Reaction*

The polyurethane linkage is produced by the reaction of alcohol functional group with an isocyanate group as illustrated in equation (1) [8].

$$R-N=C=O+R^1-CH_2-OH \Rightarrow R-\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{||}{C}}-O-CH_2-R^1$$

$$Isocyanate \quad + \quad Alcohol \quad \Rightarrow \quad urethane \qquad (1)$$

A side reaction that occurs is the production of allophanate which occurs when another isocyanate group reacts with the urethane linkage through the hydrogen on the nitrogen atom, the reactions occurs at high temperature and is reversible as illustrated in equation (2) [8].

$$R-\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{||}{C}}-O-CH_2-R^1+R-N=C=O \Rightarrow R-\underset{\displaystyle R}{\underset{|}{\underset{C=O}{\underset{|}{N}}}}-O-CH_2-R^1$$

$$Isocyante + Urethane \Rightarrow Allophanate \qquad (2)$$

C. Blow Reaction

The reaction between water and isocyanate is termed as blow reaction and occurs in two stages, in addition to the polyurea formed, carbon dioxide is evolved which plays a significant role in blowing the liquid into foam. The initial step of the blow reaction which occurs with an intermediate is illustrated in equation (3) where a thermally unstable carbamic acid is generated. The carbamic acid then undergoes exothermic spontaneous decomposition yielding carbon dioxide and amine [8].

$$R-N=C=O+H_2O \Rightarrow R=N-\overset{\displaystyle O}{\overset{||}{C}}-OH \Rightarrow CO_2+R=NH_2+\Delta$$
$$-\Delta$$

$$Isocyanate + water \Rightarrow carbamic\ acid \Rightarrow carbon\ dioxide + amine + Heat \qquad (3)$$

III. METHODOLOGY

A. Materials and Reagents

Polyol, toluene-di-isocyanate (TDI), industrial grade olive oil, stannous, amine, water, methylene chloride (as ABA) and calcium carbonate powder. All chemicals are of analytical grade obtained from a local store in Maiduguri metropolis.

B. Equipment

The following equipment/instruments were used during box foaming process:

- Electronic laboratory weighing balance (0-2kg)
- Thermometer
- Stop watch
- 2 liters bowl, 5 liters and plastic cups of various sizes ranging from 100 ml to 2 liters
- Wooden stirrer
- Syringes: 2, 5 and 10ml use for dispensing catalysts, surfactants and other additives
- Cardboard box that is lined with removal thin plastic sheet or brown papers, 28cm by 22cm by 7cm measures
- Cleaning solvent (e.g., acetone, methylene chloride, liquid carbon dioxide etc.)

C. Box Foam Preparation

1) Step 1

A batch of 500g of polyol was poured in a container and mixed with 15% calcium carbonate of the polyol and stirred vigorously with wooden stirrer forming a slurry of polyol and $CaCO_3$.

2) Step 2

A 2.5ml of silicone oil was mixed with 18.5ml of water, 1.5ml amine and 2.5ml olive oil in separate bowl and stirred vigorously.

3) Step 3

The slurry of polyol and $CaCO_3$ in step 1 was added to the mixture of amine, silicone, olive oil and water in step 2 and stirred vigorously. Methylene chloride was then added and mixed again thoroughly.

3) Step 4

A 230g of TDI was rapidly added to the mixture in step 3, while stirring. The mixture was continuously stirred until bubbles begin to foam. The mixture was transferred to mold immediately and allowed to cure for 24 hours before it wase tested to ensure complete curing.

IV. RESULTS AND DISCUSSION

A. Mixing Ratio

The mixing ratios for the silicone oil and olive oil for the various foam formulations are presented in Table I. The amount of the silicone oil was substituted at regular intervals of 25% from the control up to 100%.

TABLE I. SILICONE OIL AND OLIVE OIL MIXING RATIOS

Formulation	Silicone Oil (mg)	Olive Oil (mg)
Control	5.00	--
Formulation A	2. 50	2.50
Formulation B	1.25	3.75
Formulation C	0.00	5.00

B. Characterization of the Foam Formulations

The basic physical properties tested according to Foam Manufacturers Association of Nigeria and ISO 9000 requirement to ascertain flexible polyurethane foam equality are: cell openness, elongation, density, and compression set test. The foam development indices are as listed in Table II, while Table III shows the characteristic properties of the foam formulations.

TABLE II. FOAM FORMULATIONS DEVELOPMENT INDICES

Property	Control	Formulation A	Formulation B	Formulation C
Rising Time (s)	77	78	82	82
Foam Height (cm)	24.2	25.1	25.4	∅7
Curing Time (h)	24	24	24	24

∅ - Total collapse

TABLE III. FOAM FORMULATIONS CHARACTERIZATION

Property	Control	Formulation A	Formulation B	Formulation C
Cell Openness	∝	∝	∝	ω
Elongation (%)	124	117	116	∅
Density (kg/m^3)	22.74	23.57	24.29	∅
Compression (%)	6.25	6.25	4.62	∅

∝ - Fine cell; ω - Close cell; ∅ - Total collapse

1) Effects of Olive Oil on Foam Rising Time

It could be seen that the rising time increases as the amount of olive oil increases. However, the rising time did not change appreciably as the amount of silicone oil substituted exceeds 75%.

2) Effects of Olive Oil on Foam Height

The form height also increases with increasing amount of olive oil. More so, the foam formulation totally collapsed after attaining height of 7cm for Sample C. This indicates that replacing the silicone oil could not exceed 75%. This may be as a result of perceived hindered blowing reaction caused by less availability of water that was to react with isocyanate to form amines and carbon (IV) oxide that are responsible for the blowing effect. Presence of the olive oil may be responsible for the shortage of water needed for the reaction.

3) Effects of Olive Oil on Foam Cell Openness

By physical inspection of the four formulation samples, the cell for the control sample was finest and highly open, enough for adequate air to penetrate but the foam was a slightly hard. Samples A and B have good cell structure, fine and smooth to feel which is due to the presence of the olive oil. Sample C collapsed due to the inability of olive oil to act as surfactant.

4) Effects of Olive Oil on Foam Density

It could be seen from Table III that the density increases as the amount of olive oil increases. Substituting 75% of the silicon oil by the olive oil brings about 7% increase in the density of the foam. Increase in the density of formulations with increase in amount of olive oil could be attributed to the increase of high viscosity olive oil that improved the homogeneity of the mixture because of its oleo chemical binding nature. This improves emulsification binding action and enhanced the foam's fine structure and cross linkage of the foam cells, which translates to the increased density.

5) Effects of Olive Oil on Foam Compression

The measurement of the foam's ability to recover after compression was also observed. Whatever value of the percentage obtained shows the loss in thickness after the test. The compression for the control sample was 6.25%. Up to 50% olive oil substitution, there was no appreciable effects on the form compression. At 75% olive oil substitution, the foam compression reduces by more than 20%. This is an indication of increased ability of the foam to recover after compression with increased olive oil, likely due to the fine structure of the foam cells formed as a result of the oleo chemical activities of the olive oil in the mixture. The void fraction was reduced and hence the improved recovery ability.

6) Effects of Olive Oil on Foam Elongation

The strength and elasticity of the foam under tension compared favourably with the control sample. Generally, as olive oil increases the strength and elasticity of the foam formulation under tension decreases but still within the acceptable limit of the standard. For 75% olive oil substitution, the form elongation reduces by nearly 7%. This trend can be attributed to the hardness of the foam which ordinarily has an inverse relationship with the foam elongation.

V. CONCLUSION

Olive oil was successfully used to substitute for the inherently expensive silicone oil in the formulation of polyurethane foam. The produced foam formulations have acceptable properties for olive oil substitution below 75%; beyond which the form formulation generally collapsed. The characterization of the samples shows that all parameters tested compares favourably well relative to the control formulation (using 100% silicone oil). It is therefore asserted that olive oil can be used as a partial substitute for silicone oil up to 75% in polyurethane foam manufacture. The influence of the silicone oil substitution with olive oil slightly increases the density of the foam formulation; and reduces the compression and elongation ability of the form by about 20% and 7% respectively.

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