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The Effects Of Matrix Mixing On The Properties Of Castor Oil-Based Polyurethane Foams.

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Abstract: - Mixing of materials above the required speed in foam production leads to energy loss and affects foam properties such as: foam rise height, density, compressibility, resilience and openness of foam thus; this study was done to analyze the effect of matrix mixing on the properties of castor oil based polyurethane foams. By using the one sheet technique, castor oil based polyurethane foams were prepared from two formulations at different stirrer speed ranging from 120 – 1180 rev/min. The formulation consisted of castor oil as polyol, Toluene diisocyanate, Water, Dimethyl ethanol amine (DMEA), Silicone oil and stannous octoate. Foam properties like Foam height, Density, Tensile strength, Elongation at break and Compression set were tested, it was observed that these properties of the polyurethane foams were very sensitive to mixing; with increase in stirrer speed, strong turbulence at the gas-liquid interface created bubbles which were broken by the stirrer which led to formation of finely dispersed bubbles enhancing the mass transfer rate, a physical examination of the foams revealed that for both foam formulations A and B at low stirrer speeds, big sized cells were formed because the polymerization reaction was not encouraged. But at higher stirrer speeds, smaller cells were formed.

Keywords: *Castor oil, Toluene diisocyanate, Dimethyl ethanol amine, Polymerization, Stannous octoate, Polyurethane, Mixing.*

I. INTRODUCTION

The interest in using composites from biological sources in the production of polyurethane (PU) foams has increased over the years, due to the depletion of fossil resources and the environmental effects caused by their use [1], [2]. Some researchers investigated the possibilities of converting various renewable resources such as abundant and cheap vegetable oils into polyols for polyurethane foams. The most promising natural oils for the industrial development of bio-based polyols are soybean oil, castor oil, palm oil, and canola oil [3], [4]. PUs can be flexible or rigid, solid, and partially or fully foamed, depending on the chemicals employed, initial reactant ratios, and reaction conditions [5], [6]. PU products are used everywhere in people's daily lives and in engineering applications such as automotive parts, structural materials, insulations packaging and footwear, as a result there is an increase in consumption worldwide [7], [8]. Castor oil is viscous, pale yellow, non-volatile and non-drying oil with a bland taste and is sometimes used as a purgative. Castor oil is a strong polyol due to its low cost, low toxicity and availability, relative to other vegetable oils, it has a good shelf life and it does not turn rancid unless subjected to excessive heat, it contains mainly esters of 1,2-hydroxyl-9-octadecanoic acid [9], [10]. In order to increase the substitution level of natural oil polyols, it is oftentimes required that natural oil polyols have good compatibility with the conventional petrochemical-based polyurethane systems [11].Several works have been done to improve the quality and yield of PU foams: [12], [13], [14] . In foam manufacture, it has been noticed that improper mixing during production affects the foam properties where foams of low resilience or elasticity and foams of too big cell size that could lead to closed foams are gotten. Mixing operation is important as it tends to reduce gradients in composition, properties or temperature of materials in bulk, the rigidity of PU foam is closely associated with the formation of cross-linked structures and urea linkages. The objective of this study is to investigate the effect of mixing on the properties of castor oil based polyurethane foams by varying the stirrer speeds and knowing the required speed for mixing in order to save energy.

II. METHODS AND MATERIALS

2.1 Foam Preparation

The foams were prepared using the one shot technique. The mixing equipment was calibrated using a tachometer in order to determine the stirrer speed in rev/min, the formulations in parts by weight were translated to actual weight of the required chemicals after which castor oil, water, silicone oil, dimethyl ethanol amine, stannous octoate and toluene diisocyanate were weighed accordingly then they were added sequentially into the cardboard mould stirrer and mixed for 10 seconds by using the stirrer at a set stirrer speed, the stirrer speed was varied. The foam formed was allowed to rise steadily undisturbed in a fume cupboard where it was kept to cure for three days, the impeller was then cleaned using methylene chloride.

2.2 Test Procedure

The density, compression set, tensile strength and Elongation at break were tested. In testing the density, test pieces were cut from the various formations and measured, the weight of the test pieces was taken using a weighing balance after which the sample weight was divided by its volume to get the desired density. The compression set was carried out by placing the sample in a compression device consisting of two flat surfaces and the samples were compressed to 50% of its thickness and maintained for 10 mins after which they were removed and placed on a surface of low thermal conductivity (wood). It was left for another 10 mins then its thickness was measured. The compression set was calculated using the formula:

$$\text{Compression set} = \frac{T_o - T_r}{T_o} \times 100 \qquad (1)$$

Where, T_o = original thickness of the test piece.
T_r = thickness of the test piece after recovery.

The tensile strength was carried out by die-cutting two samples each of the various formulations into dumbbell shapes and their thickness measured for five evenly distributed points then the average was found. The samples were symmetrically positioned in the grips of the testing machine in order that tension is uniformly distributed over the cross-section, the machine was started; the maximum force and the distance between the wide edges of the two reference lines were taken prior to break of the sample. The value for the tensile strength test was obtained by the formula:

$$\text{Average tensile strength} = (F/A) \div 10 \qquad (2)$$

Where, F is the breaking force in Newton
A is the critical cross-sectional area in square centimeters.

From the tensile strength test, the initial length prior to break of the test piece and the final length were obtained; the values of the elongation at break were obtained by using the formula:

$$\text{Elongation at break} = \frac{L_1 - L_o}{L_o} \times 100 \qquad (3)$$

Where, L_o is the initial gauge length.
L_1 is the final gauge length.

III. RESULTS AND DISCUSSION

Two different formulations were used in this investigation as presented in Tables 1 and 2:

Tables 1. Castor Oil-based Polyurethane Foam Formulation A

Component	p.b.w	Actual weight (g)
Castor oil	100.0	20.0
Water	25.0	5.0
Toluene diisocyanate (TDI)	63.7	12.74
Silicone oil	3.8	0.76
Dimethyl Ethanol Amine(DMEA)	0.2	0.04
Stannous octoate	0.35	0.07

Tables 2. Castor Oil-based Polyurethane Foam Formulation B

Component	p.b.w	Actual weight (g)
Castor oil	100.0	20.0
Water	20.0	4.0
Toluene diisocyanate (TDI)	54.03	10.81
Silicone oil	3.8	0.76
Dimethyl Ethanol Amine(DMEA)	0.2	0.04
Stannous octoate	0.35	0.07

The addition of TDI to the other chemical reactants results in the chemical reaction proceeding at a very fast rate to form the polyurethane almost immediately. It can be recalled that the degree of homogeneity is given as the ratio of mixing time to reaction time:

$$\text{Degree of homogeneity} = \frac{\text{mixing time}}{\text{reaction time}} \qquad (4)$$

For the polyurethane reaction, the time required for the chemical reactants to become homogeneous is not short with respect to the time for reaction to take place, hence reaction occurs during the mixing process, and the problem of mixing becomes important. Moreover when reactants are viscous fluids, their mixing in a stirred tank or batch reactor often places layers or "streaks" of one fluid next to the other. As a result, reaction occurs at different rates from point to point in the reactor giving a non-uniform product which may be commercially unacceptable. Such is the case in polymerization reactions of PU foam in which monomer must be intimately mixed with a catalyst. For reactions such as this, proper mixing is of primary importance and often the rate of reaction and product uniformity correlate well with the mixing energy input into the fluid. For a reaction to take place between two separate places there needs to be contact, this contact is enhanced by mass transfer phenomena. Hence the overall rate of reaction is influenced by both mass transfer and chemical reaction. Mixing enhances mass transfer of reactant molecules which in turn enhances contact between them.

3.1 Variation in foam height

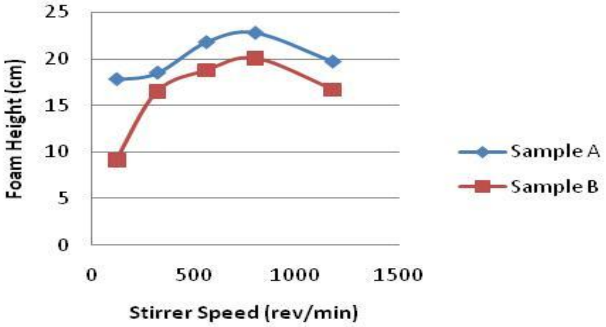

Figure 1. Variation of foam height with variation in stirrer speed for formulation A and B.

It can be observed from Fig. 1 that foam height increases to a point then decreases. Samples A_1 and B_1 gave the lowest foam heights as compared to the other samples because at low stirrer speed of 120 rev/min, mixing time was too long as compared to reaction time hence, it took a longer time to reach homogeneity. This resulted in reactant molecules not contacting properly thus the gas blowing reaction was not enhanced; as a result enough CO_2 responsible for the rise of foam was not released and thus low foam height resulted as can be observed in samples A_1 and B_1. As stirrer speed was increased, foam height also increased from samples A_2 and B_2 at stirrer speed of 320 rev/min to A_3 and B_3 at stirrer speed of 560 rev/min until it reached a threshold around A_4 and B_4 at stirrer speed of 800 rev/min. This can be explained by the fact that as A_4 and B_4 were being approached, mixing time was getting shorter compared to reaction time and the time required to reach homogeneity decreased so that molecules of the reactants were beginning to contact properly and the reaction responsible for the gas blowing reaction (reaction between TDI and water) was enhanced so that foam height in the samples rose as a result of enough CO_2 being produced and retained in polymer structure. A4 and B4 gave the highest heights, this is because in A_4 and B_4 at stirrer speed of 800 rev/min, proper contact of reactants had occurred and as such enough CO_2 was released and retained in the polymer structure that had been formed. It was observed that as stirrer speed was increased, all reactions including gas blowing and polymerization reactions were encouraged. In A_5 and B_5 at 1180 rev/min, there was a drop in foam height, this can be explained by the fact that at increased stirrer speed, polymerization was encouraged so that more cells were renewed resulting in increased surface areas of cells required for CO_2 to diffuse through so that as the gas blowing reaction was enhanced, CO_2 was lost into the surroundings than was retained in the polymer structure.

3.2 Variation in foam density

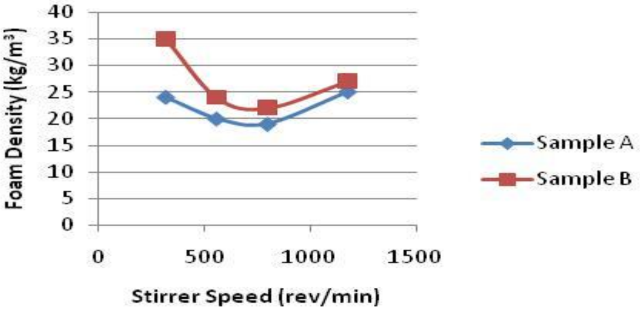

Figure 2. Variations in foam density with variation in stirrer speed for formulation A and B.

It can be observed from Fig. 2 that foam density falls from A_2 and B_2 to A_3 and B_3 to a threshold at A_4 and B_4, and then rises again at A_5 and B_5. A_1 and B_1 have no values because at 120 rev/min there was poor mixing resulting in poor foams. A_2 and B_2 have the highest densities probably because at low stirrer speeds homogeneity was not reached in time, as a result, the gas blowing reaction was not enhanced thus resulting in denser foams.

It can be recalled that:

Expected weight of foam = Total chemical weight (p.b.w) – Gas loss (p.b.w) (5)

Where, Gas loss (p.b.w) or Blow index = 2.44 x parts by weight (p.b.w) (6)

The volumes of all samples tested gave approximately the same values so that variation in density can mainly be attributed to mass of the foams. When the mass of a foam changes, its density will also change for a given volume of foam. Change in the mass of a foam can be explained by the fact that when the gas blowing reaction is enhanced, the total volume of the foam increases, the concentration of molecules in a given cross-sectional area of a foam decreases hence, its mass also decreases and subsequently, its density also decreases which can be seen in moving from A_2 and B_2 at stirrer speed of 320 rev/min to A_3 and B_3 at stirrer speed of 560 rev/min to A_4 and B_4 at stirrer speed of 800 rev/min. At A_5 and B_5 density begins to rise again, because at increased stirrer speeds, polymerization reaction was enhanced which resulted in more cells being renewed so that more CO_2 was lost into the surrounding than was retained in the polymer structure. This resulted in decrease in total volume of the foam, increase of molecular concentration in a given cross-sectional area of foam; increase in the mass of the foam hence, density of the foam also increases.

3.3. Variation in Foam Tensile Strength

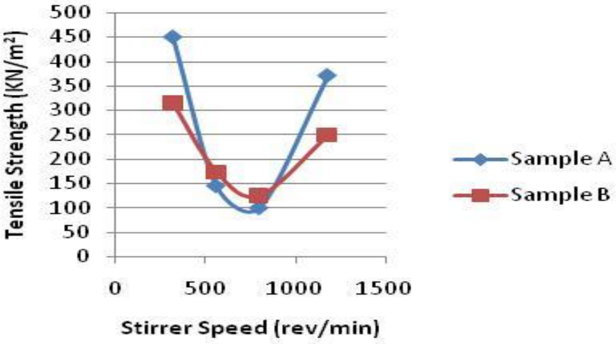

Figure 3. Variation in foam tensile strength with variation in stirrer speed for formulation A and B.

Most properties of polymer change as the molecular weight increases and vice versa. Properties that increase in value as the molecular weight increases include tensile strength, melting point, elongation, elasticity and glass transition temperature. Therefore since tensile strength is affected by change in molecular weight also, it can be observed from Fig.3 that tensile strength values followed the same trend as density, by decreasing from A_2 and B_2 at stirrer speed of 320 rev/min to A_3 and B_3 at stirrer speed of 560 rev/min until it reaches a threshold value at A_4 and B_4 at stirrer speed of 800 rev/min. At A_5 and B_5, tensile strength begins to increase again due to the over enhancement of gas blowing and cross linking reactions so that more of CO_2 is being lost to the surroundings than should have filled the nucleated cells.

3.4. Variation in foam elongation at break

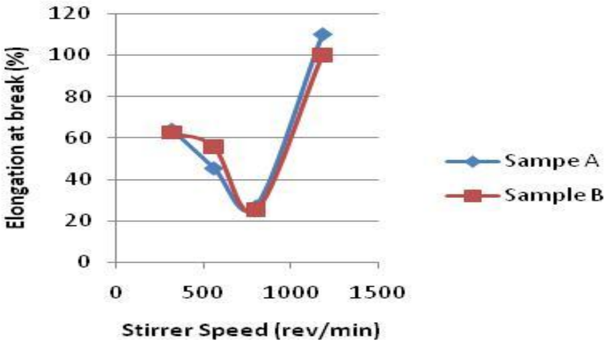

Figure 4. Variation in foam elongation at break with variation in stirrer speed for formulation A and B.

Increasing the degree of cross linking of polyol increases the rigidity, elastic modulus and usually a reduction in the ultimate elongation or the elongation at break of resulting foam. As the degree of cross-linking is enhanced by increasing mixer stirrer speed, elongation at break decreases as can be seen in Fig. 4. Elongation at break decreases in value from A_2 and B_2 at stirrer speed of 320 rev/min to A_3 and B_3 at stirrer speed of 560 rev/min until it reach a threshold value at A_4 and B_4. At A_5 and B_5, values for elongation at break began to rise again. Therefore, mixer speed exceeding 560rev/min will affect the stability of the foam under harsh conditions.

3.5. Variation in foam compression set

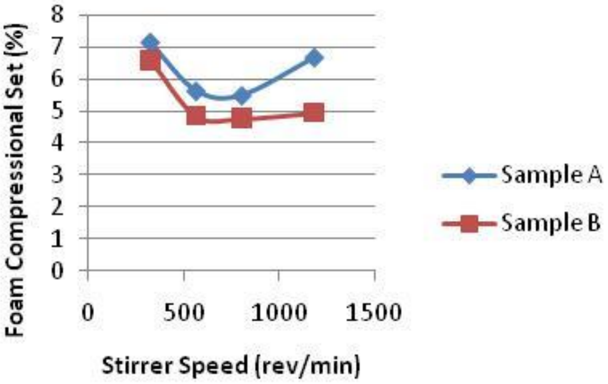

Figure 5. Variation in foam compression set with variation in stirrer speed for formulation A and B

The compression set of foam is determined by its rigidity because the more rigid a material is, the harder it is to compress hence, its compression set or ability to recover its form after being compressed is high, increasing the degree of cross-linking increases the rigidity of foams. Ogunleye et al., [1] carried out a work where castor oil based polyurethane foam gave lower percentage of compression set compared to silicone oil based polyurethane foam which was due to reduced voidage fraction which improved recovery ability. It can be observed in Fig.5 that compression set falls from A_2 and B_2 at stirrer speed of 120 rev/min to A_3 and B_3 at stirrer speed of 320 rev/min to A_4 and B_4 at stirrer speed of 800 rev/min. This is because at increased stirrer speeds the degree of cross-linking and gas blowing reaction are both enhanced. The gas blowing reaction enhances the release of CO_2 which decreases the overall rigidity of the foam. Thus, overall rigidity of the foam decreases resulting in decrease in compression set. Compression set increased again in A_5 and B_5 at stirrer speed of 1180 rev/min because at these samples, the enhancement of polymerization reaction results in more cells being renewed so that the surface area needed for CO_2 loss to the surrounding is increased and the overall rigidity now increases, hence, the compression set also increases.

IV. CONCLUSION

This investigation has evaluated two castor oil based foam formulations by varying mixer stirrer speed and the resulting properties were investigated. It was observed that the properties of castor oil based polyurethane foams were very sensitive to mixing, the polyurethane formation reaction is mass transfer limiting because increasing mixing by increasing mixer stirrer speeds increased contact between reacting molecules, decreased the time to reach homogeneity hence, all the polyurethane formation reactions were enhanced i.e. the polymerization reactions; the gas blowing reactions; urea formation reactions (degree of cross-linking), etc., which eventually influenced the properties of the foams produced. The amount of CO_2 produced determined the total volume and height of foams; the molecular weight determined foam density and tensile strength; the degree of cross-linking determined foam elongation at break and compression set. For good foam product quality, the choice of mixer speed should be geared towards formation of foams with high resilience, open foam of moderate cell size with no pinholes. Furthermore, properties like densities, compression set, tensile strength, etc should fall within expected range. Mixer speed of 320 rev/min gave a favourable result in all the foam properties analyzed.

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