Investigation and Characterization of Flexible Polyurethane Foams from the use of Chicken Eggshells as Fillers

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ABSTRACT

Chicken egg shells (ES) with 5% wt, 10% wt and 15% wt were incorporated and characterized as fillers in the production of flexible polyurethane foams. The results obtained were compared with conventional application of calcium carbonate (CaCO₃). Physico-mechanical properties of the foam without fillers (unfilled), gave density of 20.87 kg/m³, compression set at room temperature (2.88°C) and at higher temperature (70) had 3.96°C, elongation at break (651.60%), tensile strength (112.10 KPa) and Indentation Force Deflection (hardness at 40°C) was 187.20N. Subsequently, foams with 5% ES and 5% CaCO₃ fillers depicted densities (21.72 and 21.50 kg/m³), compression set at room temperatures (3.66 and 3.45°C), temperature at 70°C (4.33 and 5.46°C), elongation at break (312.70 and 328.50%), tensile strength (78.40 and 81.40 KPa) and Indentation Forces Deflections (Hardness at 40°C) were 241.80 and 198N respectively. Foams with 10% CaCO₃ and 10% ES also revealed densities of 21.68 and 21.80 kg/m³ respectively, Compression set at room temperature (6.96 and 4.12°C), temperature at 70°C (5.79 and 6.16°C), elongation at break (359.50 and 362.40%), tensile strength (85.00 and 94.00 KPa) and Indentation Forces Deflections (Hardness at 40°C) were 203.00 and 186.40N respectively. Consequently, 15% CaCO₃ and 15% ES fillers depicted densities (22.14 and 22.39 kg/m³), compression set at room temperatures (5.24 and 3.03°C), temperature at 70°C (5.50 and 6.25°C), elongation at break (383.10 and 397.50%), tensile strength (90.40 and 97.60 KPa) and Indentation Forces Deflections (Hardness at 40°C) were 197.00 and 169.90N respectively. In all cases, the physcio-mechanical properties increased with increase in fillers weights. However, Eggshell-filled foams showed better quality in terms of density, compression set at room temperature, elongation at break and tensile strength than CaCO₃-filled foams. Unfilled foams (foam without fillers) had the best compression set both at room temperature and intermediate temperature. All foam samples produced fell within the ASTM D-3574 set standard range of 1-10% for compression tests of polyurethane foams.

Keywords: Chicken-eggshells-filler; CaCO₃-filler; Flexible polyurethane foams; Foam without fillers (unfilled); Physico-mechanical properties
1. INTRODUCTION

Polyurethane foams are formed when gas particles are blown through a continuous medium, as in liquid or gas. Based on its ability to retain original shape after compression, it can be classified as either flexible or rigid according to [7].

Flexible or Open-celled polyurethane foams are produced from a combination of two different phases; solid and gaseous phase. The solid phase; a rigid polymer product of the reaction between a poly-functional polyol and a poly-functional isocyanate compound, with a urethane skeleton on which the structure is built, which is blown by the gaseous phase which can be induced internally in the presence of a catalyst or by activation with ultraviolet light [12]. Flexible polyurethane foams have excellent elastic deformation and recovery characteristics that make them suitable for packaging materials, comfort, cushions, bed mattresses, carpet backing and resilient floor covering. However, the flexible polyurethane foams are divided into two groups; polyester- based foams and polyether-based foams. Polyester foam is widely manufactured in Nigerian Polyurethane industries [10]. The basic ingredients for polyurethane production are mostly liquid reagents produced from petrochemical and agro-products. The ingredients used for polyurethane foam production are numerous but the key ones are polyol, polyisocyanate, water, blowing agents, catalyst and surfactants. The polyol forms the backbone of the polymer chain since it serves as the source of the hydroxyl for the isocyanate which determines the hardness of the foam [2].

The others are added so as to improve some end use properties of the foam and are called additives such as fillers, antistatic agent, colorants [9].

Fillers are substances added to other materials (plastic, composite and among others) to lower the consumption of more expensive binder materials or to better some properties of the base
material. In the production of flexible polyurethane foams, fillers are used to modify the morphology and mechanical properties of the foam to be produced. Fillers are introduced into foam formulations to increase foam density, load bearing ability and sound attenuation. When expertly introduced and processed, overall cost of production can also be significantly reduced. However, fillers must be used free of moisture and impurities [10,15].

Largely, fillers are used to reduce the overall cost of end products. Amongst a large variety of fillers, calcium carbonate (CaCO$_3$) retains the largest market volume as compared to other fillers such as dolomite (CaMg(CO$_3$)$_2$), kaolin, talc [9]. At higher concentrations, fillers have the tendency of increasing the viscosity of the reaction mixture which affects the cell growth process thus changing the cell geometry and consequently some physical properties of the foam [5]. Typical types of these fillers include the many grades of barium sulphate and calcium carbonate whose average filler concentration is between 20 and 150 parts per hundred (pph) polyol but may vary with application and from one country to another. In Nigeria, the control is strong and the range is kept between 1 and 50 pph [11]. It is also well known that fillers increase cell density and decreases cell size. By affecting the macroscopic cell in this way they act as reinforcement materials in polyurethane foam composite [5][11]. In flexible polyurethane foams, the fillers promote an increase in foam density, reduces formulation cost and the foam resistance to compression [15]. The ability of the foam to resist compression load which enhance the durability and prevent collapsibility during service. In addition, the use of optimum amounts of filler in the polymer matrix is the main key for achieving a final product with reliable quality [13]. One of the most common fillers is the calcium carbonate, which has been used as a cheap substitute to the polyol for the production of flexible polyurethane foam to enhance mechanical properties of the end product and for reduced production cost [16].
Mechanical properties of polyurethane foams affected by filler loading include; density, creep recovery, elongation, tensile strength, %compression set and thickness [15]. Birds such as chickens use the CaCO$_3$ and other calcium minerals that form part of their food to form the hard outer layer of their eggs- eggshells. Chicken eggshells primarily contain calcium carbonate (95-97) % in the form of calcite, the chemical compound which also makes up the majority of sea shells as well as chalk and limestone [8]. Eggs are one of the most complete foods as they contain protein, lipid, and carbohydrates that are essential for a good diet; they also contain vitamin and mineral elements that are necessary for the development of young and elderly people. The shell membrane together with the external layer of calcite crystals provides the eggs with its outer case. The shell as by-product provides approximately 11wt% of the total weight (65 to75g per egg); it is composed of ceramic materials such as 94wt% calcium carbonate, 1wt% magnesium carbonate, 1wt% calcium phosphate, and 4wt% organic matter [3,8 ].

Hence, this study is aimed to investigate and characterize some physico-mechanical properties of Chicken eggshells (ES) filler in contrast with the conventional calcium carbonate in the production of flexible polyurethane foams.

2. MATERIALS AND METHODS

2.1 Sample Collection

The chicken eggshells (filler material) were collected from the waste bins of fast food outlets at various locations within the Jos Metropolis, Plateau State.

The raw materials used; Polymeric polyol, stannous octanoate, dimethylethanolamine (DMEA), toluene-di-isocyanate, calcium carbonate, polysilicone were obtained from Vita foam Nigeria Plc. Jos.
2.2 Sample Treatment (Eggshells)

The eggshells (ES) were sorted and cleaned up to remove dirt and foreign substances; washed thoroughly with distilled water and air dried for six hours. The cleaned ES were comminuted and turned into powder using an electric blender, then sieved using the same sieve size so as to achieve uniformity in particles size of the filler. Sample was further subjected to bulk drying in an oven maintained at 105 for 18 hours and stored in well-sealed air tight plastic containers.

2.3 Flexible Foam Production

The laboratory mix (discontinuous/box foaming) was used for the flexible foam production with suitable mould of dimension (0.205m X 0.205m X 0.177m) was lined-up with polyethene (the polyethene acts as an external lubricant to prevent the adherence of the polyurethane (PU) foam to the walls of the mould). The polyol, toluene diisocyanate and fillers were accurately weighed into separate beakers using a digital balance. The other raw materials required in small quantities were measured with syringes. The measurement of raw materials were based on part per hundred of polyol. The already measured Polyol, pigment and the filler were placed in a plastic receptacle; the mixture was stirred until complete homogenization. Then Silicone oil and water were measured using a syringe and the mixture was stirred for 2 minutes. Using a micro syringe, amine was added and the mixture stirred further. Shortly after the Tin (stannous octoate) catalyst was added and the mixture was stirred again thoroughly for 30 seconds. After introducing the isocyanate, the mixture was submitted to 10 seconds of vigorous stirring and the whole mixture was carefully poured into the prepared mould as soon as the mixture starts creaming. This normally happens after 1 minute of pouring TDI. The foam rises and was allowed to cure for 24 hours in the mould. The cured foam blocks were cut to standard sample sizes for analysis. Subsequently, the foam
samples produced were subjected to mechanical properties test such as hardness, elongation, density tests, compression using the compression set, hardness index (indentation force deflection), elongation at break, tensile strength. However, the protocol of flexible PU production was followed according to the Table 1. Also, this PU production, 0.8 kg of polyol was consumed per run, and then weight requirement of other parameters were obtained by multiplying their respective P.B.W by a factor of 8.

**TABLE 1. Recipes for Laboratory Foam Formulations with Variation in Filler Content**

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Actual weight (P.B.W/g)</th>
<th>1st weight (P.B.W/g)</th>
<th>2nd weight (P.B.W/g)</th>
<th>3rd weight (P.B.W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>100% (800g)</td>
<td>100% (800g)</td>
<td>100% (800g)</td>
<td>100% (800g)</td>
</tr>
<tr>
<td>ES (FILLERS)</td>
<td>0% (0g)</td>
<td>5% (40g)</td>
<td>10% (80g)</td>
<td>15% (120g)</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0% (0g)</td>
<td>5% (40g)</td>
<td>10% (80g)</td>
<td>15% (120g)</td>
</tr>
<tr>
<td>TDI</td>
<td>54% (432g)</td>
<td>54% (432g)</td>
<td>54% (432g)</td>
<td>54% (432g)</td>
</tr>
<tr>
<td>H₂O</td>
<td>4.1% (32.8g)</td>
<td>4.1% (32.8g)</td>
<td>4.1% (32.8g)</td>
<td>4.1% (32.8g)</td>
</tr>
<tr>
<td>DMEA</td>
<td>0.25% (2g)</td>
<td>0.25% (2g)</td>
<td>0.25% (2g)</td>
<td>0.25% (2g)</td>
</tr>
<tr>
<td>STANNOUS OCTANOATE</td>
<td>0.12% (0.9g)</td>
<td>0.12% (0.9g)</td>
<td>0.12% (0.9g)</td>
<td>0.12% (0.9g)</td>
</tr>
<tr>
<td>SILICONE OIL</td>
<td>1% (8g)</td>
<td>1% (8g)</td>
<td>1% (8g)</td>
<td>1% (8g)</td>
</tr>
<tr>
<td>PIGMENT</td>
<td>RED</td>
<td>GREEN</td>
<td>NEUTRAL</td>
<td>BLUE</td>
</tr>
</tbody>
</table>

TDI INDEX= 116

ES= Egg Shells, PPO= Polymeric Polyol, DMEA= Dimethylethanolamine, P.B.W= Parts by Weight of Polyol, TDI= Toluenedi-isocyanate.

**2.4 Physico-Mechanical Determination of the Produced Foams using Different Fillers**
Standard sample dimensions for density test, compression set test, tensile strength and elongation and indentation tests were produced from the samples. The various tests were carried out on the samples using the ASTM-D3574 standards.

2.4.1 Density Determination

Densities of the PU foams were measured as the mass per unit volume. Density = weight of foam in kilograms/Volume of foam in m\(^3\). Where: volume of foam = l x b x h (length x breadth x height) of foam in m. However, for each foam sample, results were replicated and mean values were obtained according to Table 2.

2.4.2 Compressibility (Compression Set) Test

The compressibility (compression set) test of all the sample foams produced were carried out using standard compression device. This measured the ability of foam samples recovery after subjection to constant deflection compression. The compressibility was calculated using the expression [11].

\[
\text{Compression set} = \left( \frac{T_o - T_r}{T_o} \right) \times 100
\]

Where:

\( T_o \) = original thickness of the foam

\( T_r \) = final thickness of foam after recovery

2.4.3 Determinations of Tensile Strength and Elongation at Break

The produced foams with different fillers were subjected to tensile strength measurements. Since, it is the maximum force required to break a test-piece, divided by its original cross-sectional. The elongation at break was also determined by the change in gauge length of the test-piece (foam) at the time of break and expressed as percentage of its original length [11].
The tensile strength was calculated using the following formula, results were replicated and mean values were obtained.

\[ \text{Tensile Strength} = \frac{\text{Stress}}{\text{Strain}} \]

Stress, \( \sigma = \frac{F}{A} \) (Nm\(^2\)/Pa)

Strain, \( \varepsilon = \frac{L - L_o}{L_o} \)

Where:

\( F \) = breaking force in Newton

\( A \) = cross sectional area in cm

\( L_o \) = original gauge length

\( L \) = final gauge length

Elongation at break = \( \frac{E = L_1 - L_o}{L_1} \times 100 \)

Where:

\( L_o \) = original length

\( L_1 \) = final length

**2.4.4 Indentation Force Deflection (hardness) Test**

The indentation hardness indexes of foams produced were measured by their load bearing properties. According to the force required to depress (by 40%) a small circular plate into the foams.

**3. RESULTS AND DISCUSSION**
The qualities of flexible polyurethane foams are rated based on their physico-mechanical properties. The results of the analyses of the foams produced with eggshells’ fillers and calcium carbonate fillers and unfilled were presented in Table 2.

The density relationship indicated increase in density with variation in quantity of eggshell fillers from 0-15% wt of eggshells as compared to foams produced with CaCO₃, this is mainly because eggshells are denser than CaCO₃ due to other ionic/atomic content of eggshells. Usually, foams with higher densities are preferred, the higher the density, the better the foam. Indeed foams with high density usually retain their original properties and provide the support and comfort it was originally designed to produce [1]. The result showed that foams filled with both CaCO₃ and eggshells fell within the estimated range of density (21-22) kg/m³.

Compression testing is used to measure the retained elastic properties of foam after being subjected to the compressive stresses. Usually foams with lower compression set value offers the best resistance to compression than foams with higher values. However, Table 2 revealed that all foam samples produced fell within the ASTM D-3574 set standard range of 1-10% for compression tests of polyurethane foams. Unfilled foams (foam without fillers) had the best compression set both at room temperature and intermediate temperature, which implies that fillers reduces the tendency of the foam to return to its original size after compression. The compression set for eggshell filled foams were lower than those of mineral calcium carbonate as shown in Table 2 this shows that eggshell filled foams are better in terms of this property. At intermediate temperature (, eggshell-filled foams had poor compression, the increase in compression set was highest at 17.5% wt eggshell with 6.46% compression, while CaCO₃-filled foams exhibited a better compression. The above trend indicates that CaCO₃ are good heat-sink due to its anhydrous nature and will display better compression properties at
extreme weather conditions than at room temperature. Eggshells on the other hand, will give better compression at room temperature.

Elongation at break is a measure of the ductility of the foams, the ability of foams to be stretched or flexed without tearing. Table 2 gave a good percentage (%) of elongation for all foams produced, exceeding the minimum value of (150%). Usually, the % elongation of foam varies directly with tensile strength but varies inversely with the hardness of the foam [17]. There was a steady increase in the % elongation for both fillers. However, eggshell filled foams displayed better % elongation than mineral CaCO$_3$ filled foams.

The tensile strength of the foams, gave information on the elasticity and the strength of the foam under tension. From the results, the tensile was highest at 0%wt filler, while the tensile strength for both eggshell filled foams and CaCO$_3$ filled foams increased with increase in filler weight.

Hardness is a measure of the load bearing properties of foams. This measurement is called Indentation Force Deflection (IFD) and it is an indicator of the firmness of foam. All the foams exceeded the minimum hardness of 150N [17]. There was a steady decrease in the hardness of the foams for both fillers; this conforms to the inverse relationship between hardness and elongation of foam. However the hardness as illustrated in Table 2 showed that CaCO$_3$ filled foams displayed better hardness compared to the counter eggshell-filled foams with the same filler weight content. This may be caused by interference of the atomic and ionic constituents of eggshells with the activity and potency of stannous octanoate and TDI, which are majorly responsible for the hardness of foams.
Table 2

Physico-Mechanical Properties of the Produced Flexible Polyurethane Foams with Different Fillers

<table>
<thead>
<tr>
<th>Filler type and content (% wt)</th>
<th>Density (22kg/m³ Max.)</th>
<th>Compression set (10%Max.) At Room Temperature (27°C) (x)</th>
<th>Compression set (10%Max.) At intermediate temperature (70°C) (x)</th>
<th>Elongation @ break (150%Min.) (x)</th>
<th>Tensile Strength (70kPa Min.) (x)</th>
<th>IFD (Hardness @ 40%) (150N Min.) (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled</td>
<td>20.87</td>
<td>2.88</td>
<td>3.96</td>
<td>651.60</td>
<td>112.10</td>
<td>187.20</td>
</tr>
<tr>
<td>5% CaCO₃</td>
<td>21.50</td>
<td>3.66</td>
<td>4.33</td>
<td>312.70</td>
<td>78.40</td>
<td>241.80</td>
</tr>
<tr>
<td>5% ES</td>
<td>21.72</td>
<td>3.45</td>
<td>5.46</td>
<td>328.50</td>
<td>81.40</td>
<td>198.60</td>
</tr>
<tr>
<td>10% CaCO₃</td>
<td>21.68</td>
<td>6.96</td>
<td>5.79</td>
<td>359.50</td>
<td>85.00</td>
<td>203.00</td>
</tr>
<tr>
<td>10% ES</td>
<td>21.80</td>
<td>4.12</td>
<td>6.16</td>
<td>362.40</td>
<td>94.00</td>
<td>186.40</td>
</tr>
<tr>
<td>15% CaCO₃</td>
<td>22.14</td>
<td>5.24</td>
<td>5.50</td>
<td>383.10</td>
<td>90.40</td>
<td>197.00</td>
</tr>
<tr>
<td>15% ES</td>
<td>22.39</td>
<td>3.03</td>
<td>6.25</td>
<td>397.50</td>
<td>97.60</td>
<td>169.90</td>
</tr>
<tr>
<td>17.5% ES</td>
<td>22.70</td>
<td>4.01</td>
<td>6.46</td>
<td>418.20</td>
<td>85.00</td>
<td>153.00</td>
</tr>
</tbody>
</table>

n = 3, x = mean values, Max. = maximum value, Min. = minimum value, Unfilled= foam without fillers, ES= eggshells

IFD= Indentation Force Deflection.
Conclusion

This study had shown that chicken eggshells can be used as alternative to the conventional calcium carbonate fillers. Eggshell-filled foams showed better properties in terms of density, compression set at room temperature, elongation at break and tensile strength than CaCO$_3$-filled foams. Unfilled foam had the best compression set both at room temperature and intermediate temperature, elongation and tensile strength.

CaCO$_3$-filled foams showed better properties in terms of compression set at intermediate temperature and hardness than eggshell-filled foams. Eggshell-filled foams will survive better in colder climes than in warmer climes like the Tropics.

Therefore, incorporation of eggshells in flexible polyurethane foams will enhance the comfort qualities of foams such as density, durability and support.

It is thus recommended the use of agro-based raw materials like eggshells can be embraced by the foaming industries to help reduce or eliminate the cost of importation of mineral calcium carbonate.

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