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Research Article

Use of Chicken Eggshells as Fillers in Flexible Polyurethane Foam Production

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Abstract

Every year, chicken eggshell waste is on the increase due to the high demand of poultry produce across the globe. However, only a few percentage of this eggshell waste is used up in various industrial processes, with a larger percentage disposed inappropriately thereby increasing environmental pollution. With the ever increasing demand for flexible polyurethane foam, chicken eggshells were considered as an inexpensive alternative to commercial $CaCO_3$ as fillers in polyurethane foam production in this research. Four samples of fillers containing 5%, 10%, 15%, and 20% of chicken eggshells were blended with 95%, 90%, 85% and 80% of commercial $CaCO_3$ and this was used to produce flexible polyurethane foams of 24kg/m^3 density labelled S_1, S_2, S_3 and S_4 respectively. Results from the physicomechanical tests carried out on these samples revealed that S_4 had promising properties than other samples as compared with a control sample (S_0) made with 100% commercial $CaCO_3$. S_4 had a cream time and rise time value of 8 and 40 sec respectively which was found to be the same as S_0. S_4 had the lowest gel time of 54 sec, hence the lowest demoulding time, which is another positive development. Elongation at break point and % compression set values of S_4 were found to be 26.02 and 6.25 respectively. This was a huge improvement when compared with S_0 and the other samples. Hence, chicken eggshells can be confidently explored as fillers or as filler-blends in the production of flexible polyurethane foam.

Keywords: Polyurethane; Fillers; Chicken eggshells; Elongation at break point; Compression set.

Introduction

Polyurethanes (PUs) are unique polymers formed by the reaction between the hydroxyl group of a polyol and the isocyanate functional group of an isocyanate [1-4]. PUs are used as everyday life products [5], as they are one of the most important classes of polymers that has helped to change the quality of human life. Generally, PUs are produced at the processing stage by the metering and mixing of two or more streams of liquid components containing PU precursors [6], which are majorly polyol and isocyanate. However, the cost of petrochemical based polyol which is the largest percentage of raw material used in foam production and which also possess the ability to induce outstanding mechanical characteristics in foam is very high and this can be attributed to the rising cost of petrochemical feedstocks [7].

Industries that are involved with flexible PU foam production use fillers to reduce the cost of production as they are used to replace some weights of the petrochemical based polyol. In addition, even though the mechanical properties of PU foams are suitable for almost every application, they can be tailored to meet the new requirements of advanced applications by adding fillers which can help to improve the structural and mechanical properties of the foam [8]. Fillers help to not just modify foam properties such as dimensional stability, ease of retraction from the mould, service density [9-10], but also help to promote resistance to compression, a characteristic highly needed in foam mattresses.

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However, they reduce resilience and increase the possibility of permanent deformation in flexible foams (FFs) [11]. Their addition may also lead to a decrease or an increase of the urethane/urea linkages ratio, altering the cross-linking density and affecting the morphology of the foams, and also the mechanical and thermal properties of the ensuing composites [12-17]. Most importantly, attention must be paid to the tendency of the addition of fillers to the PU matrix affecting the reaction between the polyol and the isocyanate [18]. [19] have widely studied the use of several fillers to achieve improved properties in polyurethane foam (PUF). Among these fillers are calcium carbonate, dolomite, titanium dioxide [19-20], natural fibers, glass fibers, carbon black, etc [21-25]. Studies on the suitability of calcium carbonate as fillers in flexible PUF composite have also be carried out by [26-28]. While [26,27] showed that foam properties are optimized at specific filler composition and particle size distribution, [28] gave cost implication a prime consideration in their work.

The use of calcium carbonate as fillers in FF production increases the rate of the blowing/gas production reaction between toluene diisocyanate (TDI) and water [28] which is a positive development. On the other hand, eggshells are generally composed mainly of a network of protein fibers, associated with crystals of calcium carbonate, magnesium carbonate and calcium phosphate, as well as organic substances [29]. Chicken eggshells have an important constituent of calcium carbonate. Its composition is said to have chemically (by weight); 94% of calcium carbonate, 1% of magnesium carbonate, 1% of calcium phosphate and 4% of organic matter [30]. Eggshells are known to be one of the widely used food processing and manufacturing plants by-products. Due to its high use in bakery and food processing industries, eggshell wastes are produced in several tons daily and this incurs a considerable disposal cost in the world [31]. It is reported that over 250,000 tons of eggshell waste is produced annually in the world [32], most of which are cumulated on-site without any pretreatment [30,33]. Although there have been various biodegradation of eggshell waste, the odour from this process makes this waste management an unpleasant one [34]. This can be attributed to the fact that the processing of eggshell is cumbersome and costly, hence this makes chicken eggshells to easily be classified as waste [35].

However, there have been remarkable uses of eggshells in various aspects of our lives as they can be converted to new materials useful for several applications [36]. Major uses are associated with agriculture where they are used as fertilizer and for pH correction of acidic soils [37]. They are also used as starting materials to prepare calcium phosphate bioceramics such as hydroxyapatite (HAp) [38], low cost adsorbent for removing ionic pollutants from their aqueous solutions [33], and catalyst for producing biodiesel [31]. Furthermore, unprocessed eggshell wastes have showed promising results in providing protection against photo-oxidative degradation of polymers [39].

Commercial and synthetic calcium carbonate particles have been widely used as inorganic fillers for many industrial applications, including construction, healthcare, and coating and majorly in the production of FFs [40], but the use of chicken eggshells might provide significant differences [39]. This is because although chicken eggshells comprises predominantly calcium carbonate, they also contain organic components, and these organic components contain biominerals which have in many cases showed superior properties to their synthetic equivalents [41]. Chicken eggshells were used in this work as a replacement for commercial calcium carbonate, and the physiomechanical properties of the FF produced outlined.

Materials and methods

Materials used

Polyol (PPG 3601), toluene diisocyanate (TDI) (UN 2078), stannous octoate, dimethyl ethy amine, DMEA (LV-33), commercial calcium carbonate ($CaCO_3$), power silicone surfactant (L-620/PDR) and water, were gotten from the production department of Exotic Foam and Chemical Limited, Nkpor, Anambra State. Chicken eggshells were gathered from various food restaurants in Idemili North LGA, Anambra State, Nigeria.

Equipment used

Volume box mould lined with cold water starch, MH 887 electronic digital scale, manual stirrer, safety gloves, safety eye glass, stop watch, reaction container for mixing, beakers, manual grinder.

Methods used

A 24 kg/m^3 density as formulated by [42] was used for this work. However, according to [28], in order to increase the mechanical characteristics of the foam and consequently reduce cost of production, 20% of the polyol was replaced with fillers. Chicken eggshell were washed, dried properly and ground with the help of a manual grinder to fine powder. All the raw materials were weighed in grams (g) using the electronic scale and kept separately in various beakers. DMEA and silicone oil were added to the water, mixed properly and kept. This was done in order to ensure a thorough miscibility of water, DMEA and silicone oil. Polyol was poured into the reaction container. This was followed by $CaCO_3$ and ground eggshell powder. The mixture was properly stirred with the aid of a manual stirrer.

Stannous octoate was added as the stirring continued. Water-DMEA-silicone mixture was added as the stirring continued. TDI was added last and the mixture was immediately stirred before being discharged into the volume box mould. The mixing was necessary for the following reasons; to prepare coagulation of some chemicals and to input atmospheric air into the mixture, which helps to open the cells [42]. The rise time, cream time and gel time were noted. The foam sample was removed and aerated for 20 h to ensure complete curing before characterization. The box mould and reaction container were cleaned and set for another batch of production.

Experimental formulation

The experimental procedure was designed in such a way that as there was a gradual decrease in percentage of $CaCO_3$, there was a corresponding increase in the percentage of chicken eggshells respectively from S_0 to S_4 with an interval of 5% from one formulation to the other. The formulation for the substitution of $CaCO_3$ with chicken eggshell waste is shown in table 1.

Results and discussion

The various characterization of the foam samples produced is presented on table 2. From table 2, the density of S_0 is 24.9kg/m^3. This shows a 2.85% increase when compared with foam sample produced from 100% polyol as reported in [42] which had a density of 24.21kg/m^3. This percentage rise in density is in agreement with [28]. More so, S_3 had a density closer to S_0 than other samples. However, there is a high deviation in density as noticed in S_1. This is due to the closeness and tightness of the interpenetrating polymer network in S_1 [42,43].

Table 1. Experimental formulation for the susbstitution of $CaCO_3$ with chicken eggshell wastes

RM (g)	S_0	S_1	S_2	S_3	S_4
CES %	0	5	10	15	20
Polyol	400	400	400	400	400
$CaCO_3$	100	95	90	85	80
CES	Nil	5	10	15	20
Water	21	21	21	21	21
DME	2	2	2	2	2
SS	5	5	5	5	5
StOt	0.8	0.8	0.8	0.8	0.8
TDI	250	250	250	250	250

*RM= Raw materials; ES= Chicken Eggshell; StOt= Stannous Octoate; SS=Silicone surfactant.

Table 2. Physicomechanical properties of the foam samples produced

	S_0	S_1	S_2	S_3	S_4
DN	24.9	32.2	21.4	23.4	22.0
CT (s)	8	5	9	6	8
RT (s)	40	50	45	53	40
GT (s)	162	151	102	57	54
EP (%)	5.8	4.3	12.5	14.4	26.0
% CS	10.9	33.3	21.9	12.5	6.3

*DN=density (Kg/m^3); CT=cream time; RT=rise time; GT=gell time; EP=elongation at break point; CS=compression set

In fig. 1, the cream time of samples S_1, S_2, S_3 and S_4 are close to S_0. There is a 37.5% and 25% drop in S_1 and S_3 respectively while S_2 increased by 12.5%. However, S_4 maintained the same value of cream time as recorded in S_0. This suggests that the addition of eggshells as a replacement for commercial $CaCO_3$ in S_4 have no effect on the cream time.

In fig. 2, S_3 had the highest rise time while S_4 had the lowest of 40 sec which is the same as that of the control sample S_0. The decrease in rise time in S_4 implies that the blowing or gas production reaction between TDI and water was faster when compared with other samples and this is a positive development.

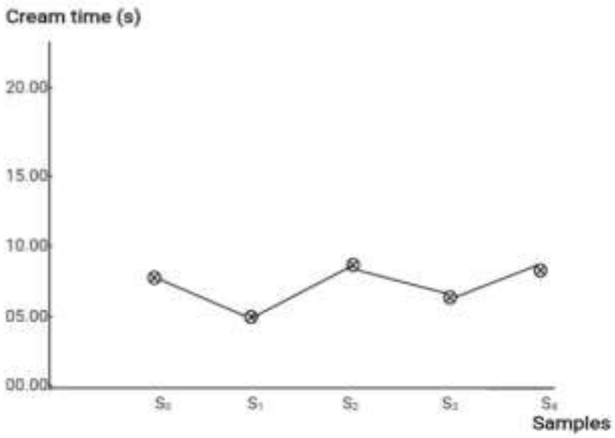

Fig. 1. Graph of cream time of the samples

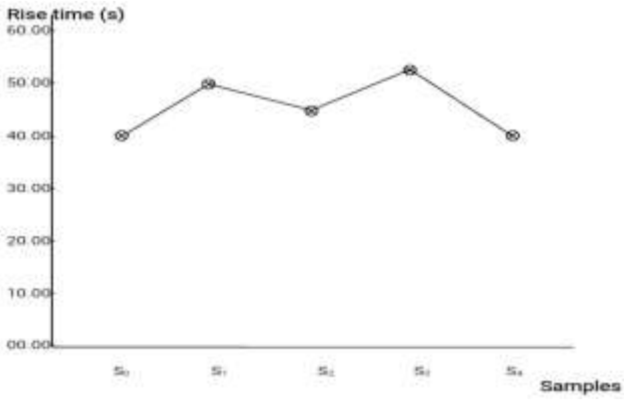

Fig 2. Graph of rise time of the samples

Also, in fig. 3, there was a gradual decrease in gell time from S_0 to S_4. This decrease leads to an increase in the demoulding time which is another positive development.

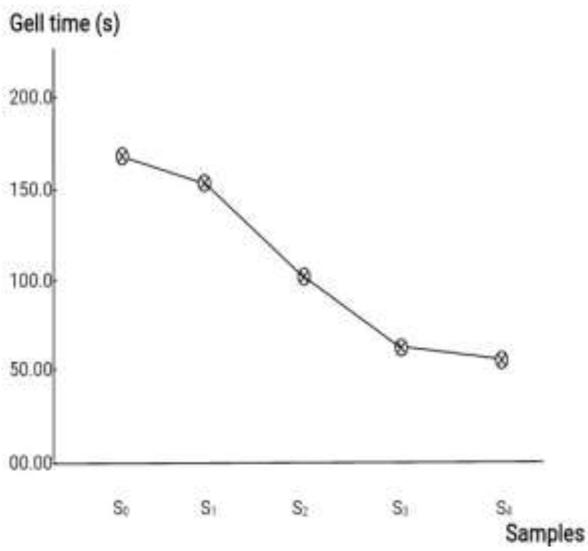

Fig. 3. Graph of gell time of the samples

From table 2 and in fig. 4, the elongation at break point increases steadily from S_1 to S_4. S_4 have the highest value of elongation at break point. This infers that S_4 have a higher elasticity than other samples, and is another appreciable quality for foam mattresses.

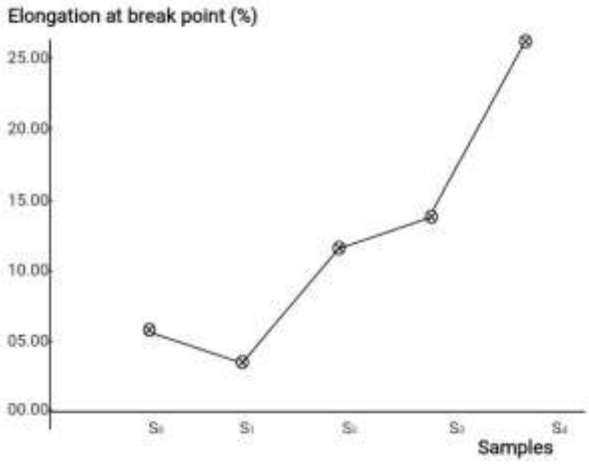

Fig. 4. Graph of elongation at break point of the various samples

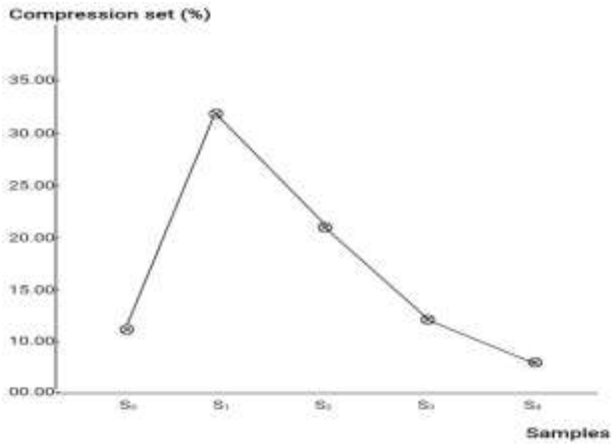

Fig. 5. Graph of % compression set of the various samples

From fig. 5, S_4 is found to have the lowest % compression set value of 6.25%. This value is closest to S_0 which have a value of 10.94%. This implies that S_4 did not recover 6.25% of its original thickness, which is a positive development as compared with the control sample S_0. This further goes to imply that S_4 recorded a lesser permanent deformation than other samples, hence had a higher percentage that remained 'set' after the deformation.

Conclusions

Physicomechanical tests carried out on the various samples have proven that chicken eggshells have unique potentials which can be explored as fillers in flexible PU foam production. Despite the decrease in density of S_4 (which contained 20% of chicken eggshells), the low value of its % compression set is a positive indication of its ability to remain set and resist deformation; a property highly needed in foam mattresses. Hence, there is an urgent need for more research on the use of chicken eggshells as fillers in not just flexible PU foam production but all kinds of PU foam production.

Conflicts of interest

The authors declare no conflict of interest.

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