



DEVELOPMENT OF POLYURETHANE FOAM USING BIOBASEDPOLYOL: EFFECT OF *Ximenia americana* SEED OIL POLYOL ON SOME PROPERTIES OF POLYURETHANE FOAM



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Abstract: Polyurethane foam (PUF) is used outstandingly for various applications, which is manufactured by propelling liquid isocyanate-polyol mixture to form foams with small proportions of silicon oil, stannuoesoctate, dimethylethylamine, methylene chloride and distilled water. In this study, PU foams were prepared using different levels biopolyol concentration, and the effects of biobasedpolyol level on the physico-chemical properties of the foams were investigated. Results from this research showed that biobasedpolyol level had important effects on physico-chemical properties of the biobased PU foams due to the gas for foaming formed an the chain extension of PU matrix. Physicochemical properties such as, density, support factor, elongation at break, tensile strength and compression set values were investigated. The physical properties of the biobasedpolyol were characterized and studied by Fourier transform infrared spectroscopy (FTIR) and compared to that of the polyester polyol. The results show that the foam density decreased with increasing biobasedpolyol (*Ximenia americana* seed oil polyol) contents up to 12ml and then increased before declining. This tendency was similar to tensile strength, support factor, elongation at break and compressive strength results. Most of these parameters rely on balance between urethane linkages and urea micro domain and/or polyurea ball contents (urea aggregate), which were rapidly generated by isocyanate group and water. The increased biobasedpolyol contents required more isocyanate, this led to the emergence of more urea micro domain been produced. The production of more urea micro domain led to a decrease in the tensile strength and elongation at break. However, the compression set of the foams was dependent upon amount of urea linkages which was formed during the reaction between isocyanate group and water.

Keywords: *Ximenia americana*, seed oil polyol, biobased foam, polyester polyol

Introduction

Majorly components for synthesise of PUFs were produced from petroleum oil as the feedstock. Therefore, the fluctuation in prices of petroleum feedstock dangerously affected the price of raw materials for the industries. Many factors limiting the effectiveness of natural polyols in the production of PUFs include inadequate molecular weight, high viscosity in some cases, large functionality distribution in natural oils and its heterogeneous structure (Groud *et al.*, 2006).

Recently there is a new awareness on the utilization of vegetable oils for industrial use and in the production of polyurethane foams. These became necessary because of the insistence on sustainability and the need to save the environment. Some natural oils can be produced in small scale and they must compete between food industrials and petrochemical industrials.. Vegetable oils have been successfully used for polyols in the polyurethane industry. Oils such as soybean rape seed, sunflower, have been converted into hydroxyl groups in order to make them capable to react with isocyanate molecules.

Polyol can be produced by two consecutive reactions, namely epoxidation and hydroxylation (Petrovic *et al.*, 2003). During the epoxidation stage, the double bonds in the vegetable oils are converted into epoxide (oxirane) groups whereas in the hydroxylation stage, the epoxide groups are converted to hydroxyl groups. The resulting product is a polyol as it contains more than one hydroxyl groups. The recent trend in the research world is to replace the petrochemical polyols with bio-based polyols in the production of different polyurethane products. A lot of scientific and technical papers have worked on these different vegetable oils locally available in their locality.

Polyurethane foam production involves the use of about 50% of polyol, therefore the use of bio-polyols affects adversely the properties of the polyurethane produced. Mostly affected properties are the, compressive ability of the foam produced, tensile properties, elongation at break and the density of the foam which apparently increases, reducing the surface tension causing an increase in cell number production which automatically leads to changes in the mechanical properties of

the foam (Patwardhan and Pradhan, 2006). Although with the level of research carried out on bio-polyols, vegetable oil polyols are not yet produced on a large scale on an industrial scale. Therefore, this research selected the natural oil-based polyol that is available in locally and not yet exploited industrially for this purpose, to study their effect on properties of PUFs. This research aims to study the effect of natural oil based polyols from *Ximenia americana* seed oil (Tsdaseed) on the characteristic times, foam density, tensile and compression properties as well as compression set of PUFs.

Materials and Methods

Materials

Ximenia americana seed oil polyol, was used to replace the petroleum based polyol. Toluene diisocyanate was supplied by Sigma Aldrich. Company. Distilled water and methylene chloride was used as a chemical blowing agent.

Preparation of flexible polyurethane foam

One-shot method was used to produce the polyurethane foam. It was synthesized by all chemicals including the seed oil Polyol. The blowing agent and surfactant were mixed in a plastic cup for 5 min using mechanical stirrer at 2,000 rpm. TDI-80 was then quickly added into the mixture and mixed further for 5 sec at the same rate. After that, the mixture was emptied into an open mold with dimension of (200 x 240 x 40 mm³) an allowed to cure undisturbed overnight.

The NCO index (NCO equivalent/OH equivalent) was fixed at 1.00 (Okoye *et al.*, 2018).

Characterization

Density

Density of PUF was measured according to ASTM D3574-11 test A with sample size of 50 x 50 x 25 mm³ (width x length x thickness). Measurements were proceed five times per sample and average value was reported.

(Support factor and Hardness) properties

Compression properties of PUFs were investigated according to ASTM D3574-11 test C with sample size 50 x 50 x 25 mm³ (width x length x thickness). The samples were compressed to 50% of its original height at a speed of 50 ± 5 mm/min by UTM machine.

Tensile properties

Tensile properties of PUFs were investigated according to ASTM D3574-11 test E. Samples were stamped by UTM machine (Fig. 1). The test was run at a speed of 500 ± 50 mm/min.

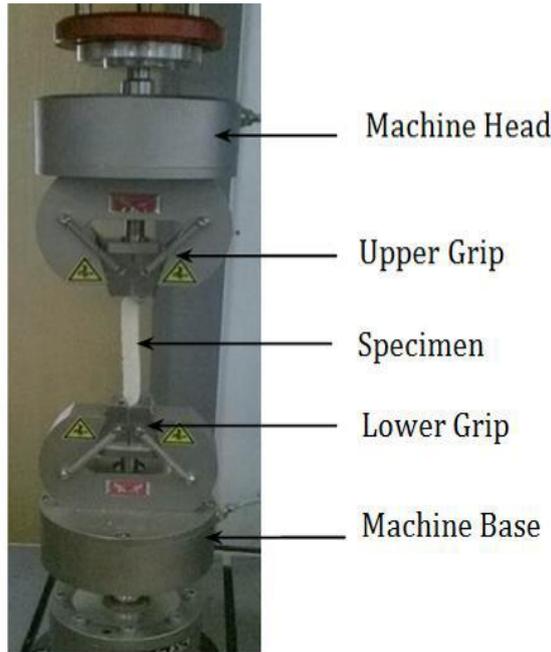


Fig. 1: Tensile testing using Instron E-3000

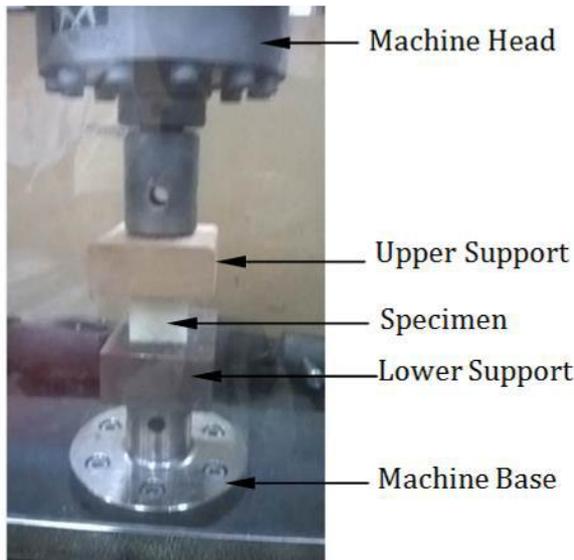


Fig. 2: Compressive testing using Instron3382

Compression set

Compression set of PUFs were investigated according to ASTM D3574-11 test D with sample size of $50 \times 50 \times 25$ mm³ (width x length x thickness). Samples were placed in the apparatus and compressed it to $50 \pm 1\%$ of its original height (Fig. 2). Then, apparatus was kept in a hot air oven at 70°C for 22 h. After, the samples were cooled down.

Results and Discussion

Effect of polyol concentration on some physical properties of *X. americana* biobasedPu foam

Foam density is a specific measurement of how much weight in kilograms polyurethane foam can handle per cubic meter.

Simply put, the higher the density the longer the foam will last (the density rating tells the strength of the foam).

Figure 3 presents the effect of polyol concentration on the density of foam. The initial increase is as result of the cell size decrease which increases the density automatically. But with further increase in polyol (soft segment) the cell size begins to expand which explains the reduction of density as shown in the second phase of the graph. A sudden fall may also be associated with polyol/TDI ratio especially for biobasedpolyol (Blanchemain *et al.*, 2005).

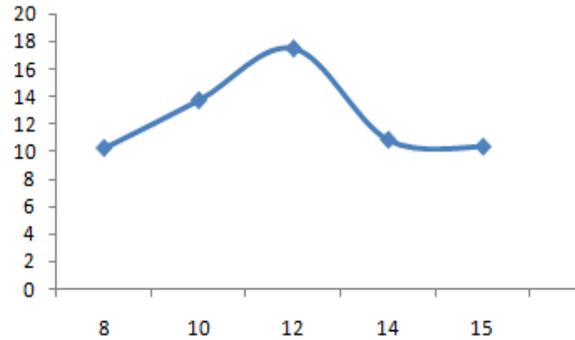


Fig. 3: Graph showing the effect of polyol on foam density

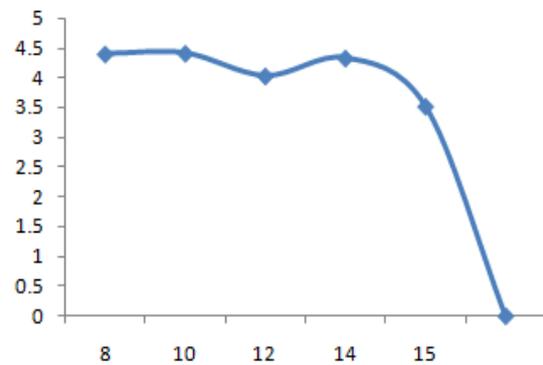


Fig. 4: Graph showing the effect of polyol on support factor of foam

Effect of polyol concentration on the support factor of *X. americana* biobasedPu foam

The support factor is the ratio of 65% IFD (indentation force deflection) divided by the 35% IFD (indentation force deflection). The support factor in a grade of foam is one of the most important measures because it indicates how much weight or load factor the foam will support. Support factor is a measure of the cushioning ability of foam.

From Fig. 4, it was observed that, the support factor slightly increased with an increase in polyol concentration. The support factor decreased a little and with more polyol in the formulation it began to drop. the initial rise may be because of a little rise in molecular weight of the foam produced leading to a rise in density of foam .The initial decrease is caused by a reduction in the molecular weight, while the later increase may be due to the mixing ratio at that point. The decrease in support factor (cushioning effect) is caused by a reduction in the density of the foam which leads to a decrease in the cushioning effect (Narayan, 2005). The higher the number of support factor, the greater the difference between the surface firmness and deep support. Higher support factors allow desirable softness a firm inner support

This foam sample fell slightly above the standard range; this implies that the foam have the ability to provide support, The

support factor according to the NIS and ASTM D-3574 is expected to have a range of 2.0 – 3.5. It then indicates that these foam are better in terms of support factor.

Effect of polyol concentration on the indentation hardness of *X. americana* biobasedPu foam

Indentation hardness test

The indentation hardness index of foam is measurement of its load-bearing properties. In real terms, the index is the force required to depress by 25, 40 and 65% a small circular plate into the foam. The testing machine is capable of indenting the test-piece between a supporting surface and an indenter which has a uniform relative motion in a vertical direction (Groud, 2006).

Figure 5 shows a little increase in the hardness of the biobased foam, after which the degree of hardness started decreasing. The initial increase in the biobased foam hardness is caused by the high isocyanate index which when it is high it increases the hardness of the foam. The gradual decrease is caused by a low isocyanate index which causes foam crack, poor resilience and poor strength leading to a reduction in the hardness of the foam.

The result of indentation hardness shows that the formulation of biobased foam with polyol value at 12 ml gave the best indentation value. That is, its maximum load carrying capacity was the highest among all the foam sample. However, the hardness property of all the foam samples fell out of the NIS 295 and ASTM D-3574 range of 147 – 170N expected for good foam.

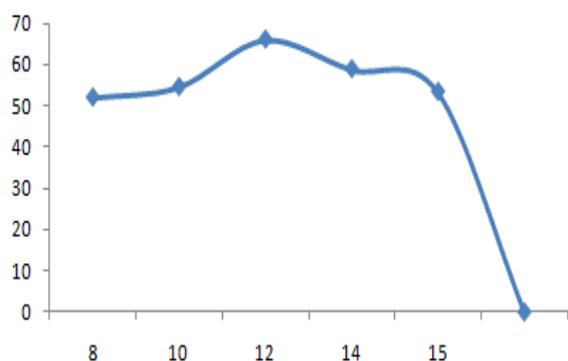


Fig. 5: Graph showing the effect of polyol on the indentation hardness of biobased foam

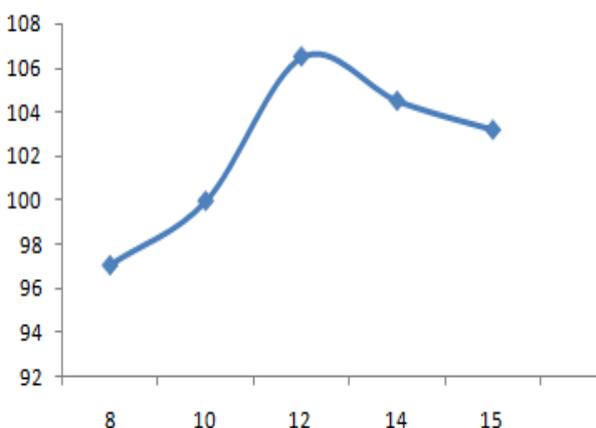


Fig. 6: Graph showing the effect of polyol on the tensile strength of biobased foam

Effect of polyol concentration on the tensile strength of *X. americana* biobasedPu foam

Tensile test

A tensile test gives information about the elasticity of foam and also indicates the strength of the foam under tension. By definition therefore, tensile strength is the maximum force required to break a test-piece, divided by the original cross-sectional area

As can be seen from Fig. 6, the tensile strength of the biobased foams increased initially with increase in polyol concentration in water (in-situ blowing agent). As more polyol is added, the foam tensile strength begins to drop. This development can be explained as follows; at the initial stage of the graph, the molecular weight of the TDI/polyol copolymer increases with increase in polyol concentration a corresponding increase in crosslinking density of the biobased foam. This increase in crosslink density led to a decrease in the cell volume of the foam thereby giving rise to the observed increase in tensile strength of the foam (Ajiwe *et al.*, 2005); as more and more polyol is added, the crosslink density of the copolymer (foam) approaches its optimum and hence the gradual decrease in foam density is observed in the second regime of this experiment, leading to a decline in the strength of the foam (Groud, 2006).

Effect of polyol concentration on the elongation at break *X. americana* biobasedPu foam

The elongation at break (defined as the extent to which a foam sample can be stretched before it breaks expressed as a percentage of its original length). The elongation at break is the change in gauge length of the test piece, determined at the time of break, and expressed as percentage of its original gauge length. The elongation at break as a percentage is given by the equation below;

$$\text{Elongation at break} = \frac{L1 - L0}{L0} \times 100 \text{ (Odeomelam, 2005)}$$

Figure 7 reflects an initial increase the elongation of the foam as the polyol concentration increases. After reaching an optimum point, the elongation of the biobased foam begins to drop as more polyol is added to the formulation. The initial rise in elongation values is due to the fact that the cells formed were not very porous; but as the polyol concentration increases, the foams formed becomes less dense; causing increase in porosity therefore leading to increase in the strain of the foam. These characteristics produces decrease in the elongation property of foams produced (Ekpa and Ekpa, 1996).

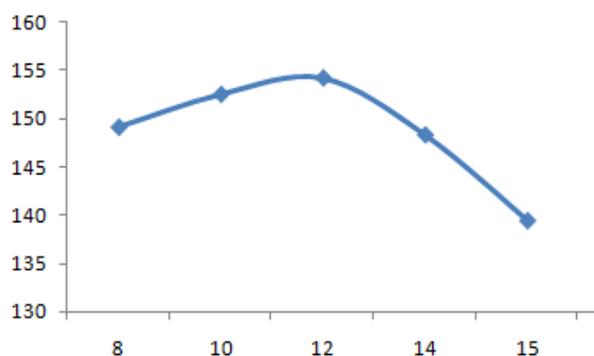


Fig. 7: Graph showing the effect of polyol on the elongation of biobased foam

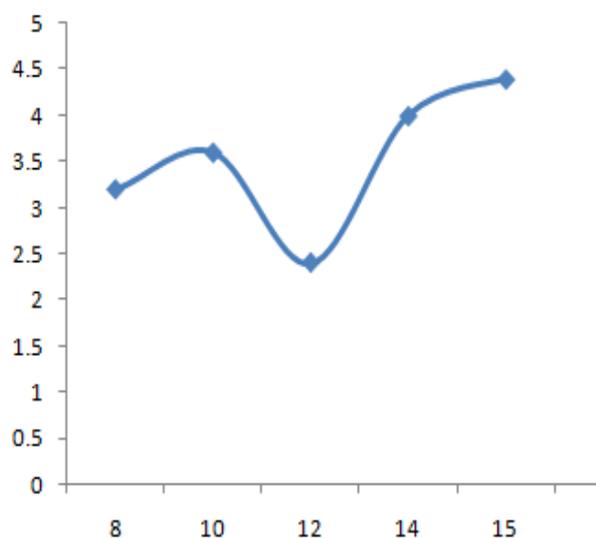


Fig. 8: Graph showing the effect of polyol on the compression of the biobased foam

Effect of polyol concentration on the compression set of *X. americana* biobased Pu foam

Compressibility test

The compression set measures the difference in dimension before and after compression. The value obtained from this test is a measurement of the ability of foam to recover after subjected to constant deflection compression. The compression set can simply be defined as the difference between the initial thickness and final thickness of foam as a percentage of its original thickness.

Compression set = $(T_o - T_f) \times 100 / T_o$ (Eromosele *et al.*, 1994).

From Figure 8, it was observed that, the compression set value increased slightly with an increase in polyol concentration; then the compression value drops sharply with an increase of polyol concentration, but again there is a sharp rise in the values, after which a continuous rise in the values is observed. To explain this; initially the increase in compression may be caused by a collapse of the foam cells, which may be due to the irregular bonding (irregular mixing, materials not properly dispersed) that occurred as the polyol concentration increased. But in the second phase the sharp decline in the compression set values is caused by the concentration of amine might have been responsible for the decrease in porosity of the cells formed during the reaction thereby increasing the density of foam which implies that the compression would also decrease giving rise to better foams in the process (Kaszynski *et al.*, 2003). Later an increase in the compression set values is observed as the polyol concentration is further increased, this might be due to the decrease in the crosslinking effect which is caused by the addition of more polyol into the formulation thereby increasing the softer segment of the foam matrix. With low cross-linkers the foam becomes more porous and tends towards brittling (Alper *et al.*, 2002).

Conclusion

Polyol from gotten by the epoxidation and hydrolysis of *Ximenia americana* seed oil was produced. It was used to successfully replace the originally used Petroleum based polyol. The natural- based polyol however affected physical properties of the foam. The following properties were similar with that of a polyester based foam properties such as tensile modulus, compressive modulus and compressive strength were related to foam density. The foam density decreased with increasing of *X. americana* seed oil polyol. Both the tensile strength and elongation at break increased with the increased of *X. americana* seed oil. These properties were dependent on the balance between urethane linkages contents and the generated urea micro domain (Odeomelam, 2005).

Conflict of Interest

The authors declare that there is no conflict of interest related to this work.

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