



Effects of Low Castor Oil on Mechanical Properties of Polyurethane Foams

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Authors' contributions

This work was carried out in collaboration between all authors. Author MBD designed the study, carried out the determination and analyses of mechanical properties and wrote the final manuscript. Author AQI carried out the extraction and determination of physico-chemical properties of castor oil. Author HMA interpreted the infra-red spectras of castor oil and physico- chemical properties of CPO and PPO. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

The polyurethane foam industry in Nigeria depends largely on imported feedstocks based on fossil sources at exorbitant cost and high foreign exchange. Furthermore, emissions from some of these chemicals during processing have been reported to cause negative environmental impact effects and also carcinogenic to both animal and humans. It is for these reasons that this present research explores and exploits alternative non-conventional or supplement local sources of raw materials such as castor oil (CO) for the commercial manufacture of polyurethane foams in our quest for local content development. Mechanically extracted (CO) was characterized for physico-chemical properties such as refractive index, relative viscosity, pH, specific gravity, boiling point and acid, hydroxyl, saponification and iodine values by conventional and titrimetric methods were found to be within the ASTM D 1639 – 90, 1994 standard specifications. IR spectral analysis of the oil shows characteristic absorption bands of hydroxyl, carbonyl and olefinic groups. These results show that CO properties compare reasonably with those of conventional (CPO) and polymer (PPO) polyols. Foam formulations based on CO and various blend compositions with CPO and PPO were investigated for physico-

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mechanical properties such as density, tensile stress, tensile strain, elongation at break, compression set, and creep recovery (resilience). The results obtained show a critical blend composition at CPO/CO (90/10, % w/w) and PPO/CO (90/10, % w/w). This blend composition displays a good balance of density, tensile strength, elongation at break and creep recovery compared to other blend compositions. It also shows higher values than those of 100% CPO or PPO, for instance, tensile strength at CPO/CO (90%:10%) displayed a value of 11.06N/cm² as against 6.81 N/cm² at CPO/CO (100%:0%), while tensile strength value at PPO/CO (90%:10%) showed 9.49 N/cm² as against 6.03 N/cm² at 100% PPO. Similarly, values for elongations at break, indicate 49.99mm at CPO/CO (90%:10%) as against 73.98mm for 100% CPO, while at PPO/CO (90%:10%), the value was 37.05mm compared to 44.75mm for 100%: PPO. However, 100% CO shows a low tensile strength of 2.04 N/cm² with a high elongation at break of 89.95mm. Furthermore, results of creep recovery indicate a value of 30.21% at CPO/CO (90%:10%) compared to 21.52% at 100% CPO, while the corresponding value for PPO/CO (90%:10%) was 25.49% as against 14.65%. for 100% PPO. Similar trends were observed for mechanical testing of factory trials of Iso-block foams.

Keywords: Conventional Polyol (CPO); Polymer Polyol (PPO); Castor Oil (CO); Mechanical properties; Blends.

1. INTRODUCTION

At present, the bulk of industrial raw materials are derived from non-renewable sources, essentially from fossils. The development of cost-effective, readily available, eco-friendly alternatives or supplements especially from renewable sources is desirable and points to many commercial opportunities that would reduce the growing concerns about environmental degradation and protect our ecosystem in the long run [1]. One of the development forces in economic theory of production is availability and distribution of scarce raw materials for the manufacturing industry. Generally, industrial raw materials whether organic or inorganic have been grouped into three classes; Agricultural, Fossil and Inorganic sources [2-3].

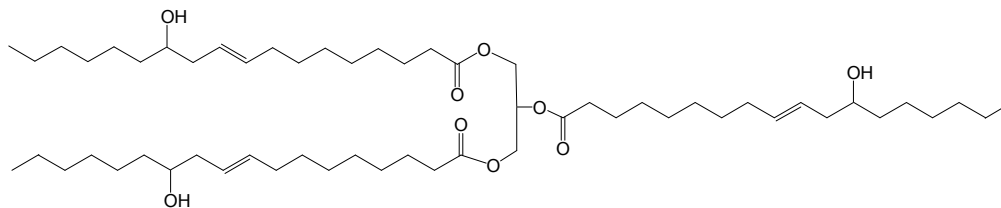
The Agricultural sources of raw materials include carbohydrates, proteins, lipids(fats and oils), resins, gums, phytochemicals and so on. These constitute the renewable resources while the fossils sources of industrial raw materials are petroleum, natural gas and coal from which various chemicals and petrochemicals are obtained as feed-stocks for the industries [4-5]. Furthermore, the inorganic sources of industrial raw materials are the mineral elements and their compounds obtained from the earth crust such as iron, copper, tin, columbite, aluminum and their compounds including the gases from the atmosphere such as N₂, O₂, CO₂, [6]. The agricultural and the fossil sources of raw materials provide the bulk of raw materials for the process and manufacturing industries [7-8]. However, both the fossil and earth crust inorganic sources are exhaustible while the agro-based sources are renewable. Vegetable oils have contributed immensely to the growth of the economies of many developing nations, for instance, olive oil remains a factor in the agricultural economies of Greece, Spain and Italy just as palm oil in the domestic and export economies of West Africa (Nigeria) and Malaysia as well as castor oil in Brazil and India [9-11].

The castor plant *Ricinus communis* belongs to the family *Euphorbiace*, genus *ricinus*, and species *communis*. *Ricinus* means 'tick' in latin, 'Communis' means 'common' or 'general'. The castor plant is widely distributed in tropical countries. Essentially, it is a native of Africa

and India, however, it is practically found in all the continents [12]. It can be cultivated on practically any type of soil provided the soil is well drained [13].

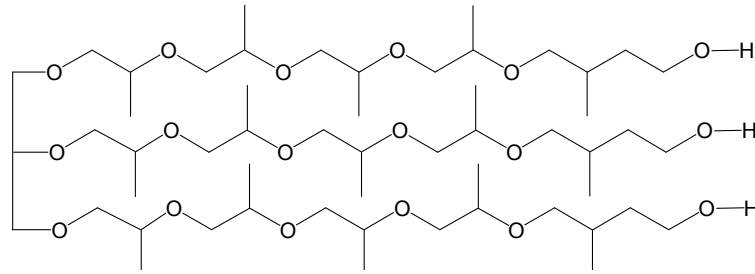
In Nigeria, apart from Kogi state where it is being cultivated, the plant grows in the wild as weed. This shows the ability of the plant to grow under different climatic conditions especially in the Guinea Savannah [14]. The oil which is obtained from the seeds either by mechanical expression or solvent extraction has been known since antiquity and was used by the Egyptians as a constituent of embalming fluid [15]. Earlier, in Mesopotamia (in present day Iraq), the Sumerians of Ur used the oil along with palm oil to produce a crude soap by boiling with alkali [16]. Although, most widely known for its medical properties, such use accounts for only a minute fraction of the total [12]. It has long been known as an article of commerce and its industrial uses are many and varied including protective coatings, greases, fatliquors, and soaps, to mention a few [4]. Castor oil is one of the few naturally occurring glycerides that approaches being a pure compound as the fatty acid portion is 90% ricinoleic acid, 7% oleic acid and 3% linolenic acid, however, the oil is non-drying [4,17]. It has been reported that the seed contains three potent poisons: ricin, a protein active in concentrations of 1.0×10^4 ppm or less, a powerful allergenic material which is active in concentrations as low as 1 ppm and ricinine, a mildly toxic alkaloid [18]. This makes the harvest of castor seeds a health risk, however, researches are ongoing to genetically modify the plant to prevent the synthesis of ricin. The good news is all these toxins are denatured by heating during oil extraction [19].

Castor oil is readily distinguishable from other oils by its high specific gravity, viscosity and acetyl value and by the presence of -OH group on the main fatty acid. The double bond and -COOH group are the functional groups responsible for the large number of reactions of industrial importance [12]. It is a colorless to very pale yellow liquid with mild or no odour or taste. Its boiling point is 330°C (595 °F) and its density is 961 kg/m³ [20]. It is a triglyceride in which approximately 90 percent of fatty acid chains are ricinoleic acid. Oleic and linoleic acids are the other significant components [21]. Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the 12th carbon, (structure (i)).

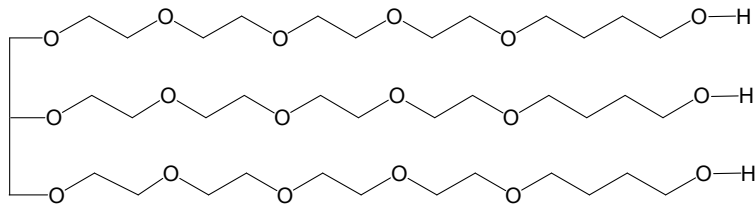


Structure of castor oil triglyceride (i)

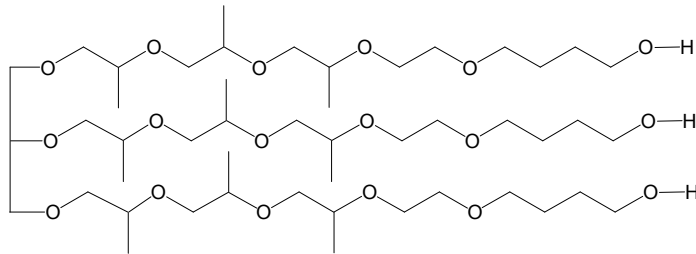
The hydroxyl functional group causes ricinoleic acid (and castor oil) to be unusually polar, and also allows chemical derivatization that is not practical with most other seed oils. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feedstocks. Compared to other seed oils which lack the hydroxyl group, castor oil commands a higher price. For a example, in July 2007, Indian castor oil sold for about US\$0.90 per kilogram, while U.S. soybean, sunflower and canola oil was sold for about US\$0.30 per kilogram [22]. Industry uses account for about 600-800 million metric tons of castor oil per year. Castor oil and its derivatives have found applications in the manufacturing of soaps, lubricants, hydraulic and brake fluids, paints, dyes, coatings, inks, cold resistant plastics, waxes and polishes, nylon, pharmaceuticals and perfumes [23].



An idealized structure for a 960 Mw all – propylene oxide triol based on glycerin
 (ii)



An idealized structure for a 750 Mw all – ethylene oxide triol based on glycerin
 (iii)



An idealized structure for a triol made by reacting glycerin with nine molar equivalent of propylene glycol and capping with six equivalents of ethylene oxide
 (iv)

Castor oil has also been used to formulate rigid polyurethane foams due to the presence of secondary hydroxyl groups as reactive sites, through the “prepolymer technique”. The prepolymer formed further reacts with catalyst, water and stabilizer to produce a polyurethane foam [30]. The current “one shot” technique has made possible to prepare flexible polyurethane foams by a batch mixture of all the ingredients used in foam preparation [30]. The potential for polyols derived from vegetable oils to replace chemical-based polyol began garnering attention in 2004, partly due to the cost of petrochemical feedstocks and partially due to an enhanced public campaigns for environmentally friendly green products [31]. One of the most vocal supporters’ of these polyurethanes made using natural oil is Ford Motor Company [32]. Makanjuola et al. (1999) stated that the chemical structure of natural oils such as the length and size branching of the hydroxyl bearing group plays an important role on the properties of the final foam products [33]. Short chain length

compounds with di and trifunctional alcohols are used to produce more rigid foams while long chain length compounds with trifunctional alcohols are used to produce more flexible foams [32].

Among all vegetable oils, castor oil that occurs in the seed of castor plant is distinctive because of its high level of ricinoleic acid which is over 80%. The oil is essentially a triglyceride which contains almost 90% of triricinoleate. The oil quality depends on the ricinoleic triglyceride used for chemical reactions. The oil is characterized by higher density, viscosity and reactivity than common triglycerides found in other vegetable oils [12]. Castor oil can also be used industrially for adhesives, brake fluids, dyes, in textiles, nylon-11 plastics apart from being used as a substitute for petrochemicals especially in the manufacture of polyurethane foams. Several chemicals can be produced from castor oil, notably, sebacic acid, undecylenic acid, and nylon [34].

The objective of this present study is to incorporate castor oil, a renewable natural resource to 10% parts per hundred resin in polyurethane formulation and evaluate its effects on physico-mechanical properties.

2. MATERIALS AND METHODS

2.1 Sample Collection

One metric ton of castor seed pods was locally collected in Rukuba village in Jos, Plateau state and Korai village in Zaria, Kaduna state. The pods were deshelled to obtain the seeds and the oil was extracted by mechanical expression and also by solvent extraction for yields comparison. Industrial chemicals which include PPO, CPO, toluene diisocyanate (TDI) (80/20), stannous octanoate, dimethyl ethanolamine, polysilicone methylene dichloride (MC), and CaCO_3 were gratefully obtained from Vitafoam Nig. Plc, Jos Mega Factory.

2.1.1 Sample Treatment

The castor seed pods were deshelled using the National Research Institute for Chemical Technology (NARICT) castor deshelling machine to obtain the seeds. The castor seeds were fed into the NARICT Mosanto Expeller machine in 50Kg batches which ground it into a slurry and thereafter the slurry was mechanically pressed by NARICT hydraulic press to obtain the oil and cake. This gives an oil yield of about 30% which was collected into plastic containers. Similarly, solvent extraction was carried using n-hexane in a Soxhlet extractor to obtain an oil yield of 35-40%. However, the mechanical expression was adopted in this work, for bulk extraction.

2.2 Materials and Industrial Chemicals

Castor oil (CO), de-ionised water, CaCO_3 and all the industrial chemicals are products of Korean Fire Chemicals Ltd or BASF or Dupont.

2.3 Laboratory Reagents (AR grades, BDH chemicals)

Potassium hydroxide, potassium iodine, sodium hydroxide, carbon tetrachloride, chloroform, ethanol, methanol, diethyl ether, hydrochloric acid, nitric acid, sulphuric acid, acetic anhydride, Hannus Reagent, pyridine, sodium thiosulphate, benzene, indicators, di-n-

ethylamine, toluene, isopropyl alcohol, antimony trioxide, 2% and 10% starch indicators, calcium hypochlorate ($\text{CaOCl}_2 \cdot \text{H}_2\text{O}$), Wij's Reagent, nitrogen gas, distilled water, etc were supplied by Medilab Chemicals, Ltd, Jos and used as received.

2.4 Equipment /Glasswares/ Moulds

Motorised mechanical stirrer and aluminum moulds of dimensions, 21.5x13.145cm were fabricated locally. Soxhlet extractors, toploading balances, Ubbelohde viscometer, refractometer, and other glasswares were obtained in our laboratory. Automated Mosanto Tensometric Testing Machine obtained from Standard Organisation of Nigeria Laboratory, Kaduna, while Automated FTIR spectrometer, Mosanto Expellers/hydraulic press, castor seed pods deshelling machine were facilities utilized from NARICT – Zaria. Band knives, Isol-block machine, digital thermometers and cutting knives/meter rules were facilities utilized from Vitafoam Nig. Plc, Jos Mega Factory.

2.5 Physical and Chemical Characterization of CO, CPO and PPO

The specific gravities, relative viscosities, refractive indices, colour, boiling points and acid, hydroxyl, saponification and iodine values of CO, CPO and PPO were determined by Conventional methods [35]. Furthermore, IR spectral analysis of castor oil samples were carried out neat on NARICT FTIR spectrometer [36].

2.6 Foam Formulation (Table 1)

One-shot technique of urethane foam formulation was used. The ingredients were measured accurately using syringes, micro-syringes, pipettes and measuring cylinders into moulds of dimensions (21.5cm x 13.7cm x 14.5cm), using the recipes on Table 1 The components were thoroughly stirred and TDI added with continuous stirring until the systems creamed. The foams were then allowed to rise undisturbed and left to cure for 24 hrs after which physico-mechanical properties were determined.

2.7 Determination of Density Foams [37]

The rises (h), widths, breadths and the weights of the foams were measured and their volumes and densities were calculated using the equation (2);

$$\text{Density} = \frac{\text{weight of foam (w)}}{\text{volume of foam (v)}} \quad \text{----- (2)}$$

Volume (v) = base area of mould x foam rise (h)

Where base area = base of mould (breadth) x width of mould

2.8 Determination of Stress and Strain [37]

Each foam was trimmed and cut into 3 pieces using band knife splitter CV-02 at Vitafoam Nigeria Plc Jos mega factory. From each cut piece, three test samples measuring 10cm x 5cm x 1cm were cut randomly using a special knife and their extensions (mm) (elongation at break) with loadings were read from a computer coupled Tensometric Testing Machine with a cell load of 500kgf (5000N), at a speed of 60mm/min at constant rate of extension method at Standard, Organization of Nigeria (SON) Laboratory Kaduna. Mechanical properties were calculated from equations, 3a,b,c,d.

$$\text{Tensile strain} = \frac{\text{extension (mm)}}{\text{original length (mm)}} = \frac{l - l_0}{l_0} \quad \text{----- (3a)}$$

$$\text{Tensile stress} = \frac{\text{force (load at break) Ncm}^{-2}}{\text{cross sectional area (cm}^2\text{)}} \quad \text{----- (3b)}$$

$$\text{Tensile Strength} = \frac{\text{Tensile stress (Ncm}^{-2}\text{)}}{\text{Tensile strain}} \quad \text{----- (3c)}$$

$$\% \text{ Elongation at break} = \frac{l - l_0}{l_0} \times 100 \quad \text{----- (3d)}$$

Where l = extended length, l₀ = original length, cross sectional area = length x thickness.

2.9 Determination of Creep Recovery/Resilience [37]

From the trimmed samples, tests samples measuring 10cm x 5cm x 1cm were cut and subjected to a tensile force of 20N using a computer coupled Universal Tensile testing machine with a cell load of 250 N at a speed of 60mm/min under ambient condition (67±2% Relative Humidity and 27°C) using the method of constant rate of extension. The total extension (mm) on application of load (20N) and the relaxation (mm) on removal of load after 5 seconds of each test piece were noted and the percentage recovery of each sample was calculated using the expression:

$$\% \text{ creep recovery} = \frac{\text{creep recovery or resilience}}{\text{extension on application of load}} \times 100 \quad \text{----- (4)}$$

Where creep recovery/resilience = Total extension (mm) on application of load – Relaxation (mm) on removal of load after 5 seconds.

2.10 Determination of % Compression Set [37]

The test pieces were cut into dimensions. The samples were placed in the compression device which consisted of two flat plates parallel to each other and the space between plates was adjusted to the required deflected height. The test piece was compressed by 50%, maintained at ambient temperature of 27°C for 22 hours. At the end of the 22 hours, the test piece was removed from the device and placed on a wooden surface since wood is of low thermal conductivity. The test piece was allowed to recover for 30mins after which its thickness was measured as (Tr)

$$\% \text{ Compression Set} = \frac{T_0 - Tr}{T_0} \times 100 \quad \text{----- (5)}$$

Where T₀ = initial thickness, Tr = thickness after removal of load after 30 mins.

3. RESULTS AND DISCUSSION

3.1 Chemical and Physical characteristics of CO, CPO and PPO

Table 2 shows the results of the physical and chemical characteristics of castor oil and the polyols. CO compares favorably with CPO and PPO especially, the hydroxyl and acid values which are within the ASTM D (1994) values [39]. The OH group is very important in the foam

or urethane reaction as shown in equations 6 – 10. The low acid value indicates high stability to hydrolytic rancidity. Castor oil being a triglyceride, offers other advantages, such as soap making because of the high saponification value which is a good source for creamy white soaps. Its iodine value is far higher compared to CPO and PPO which means it can easily be converted from a non-drying oil to a drying oil [4].

The above considerations suggested that oils and fats or their fatty acids possess functional groups that could be involved in chemical reactions, namely; the ester linkage, the carboxylic acid (COOH) group and the double bonds. Thus, the ester linkage and/or COOH group undergo such reactions as hydrolysis, esterification, saponification, amidation, halogenation etc, while double bonds undergo reactions such as oxidative polymerization, hydrogenation, epoxidation, halogenations, sulphonation and so on. Depending on the degree of unsaturation, vegetable oils have been classified into non-drying, semi drying, and drying oils. Those with iodine values (level of unsaturation) less than 100 are non-drying, between 100 – 130 are semi drying while above 130 are termed drying oils. In fact the film – forming properties of an oil or fatty acid depend on its level of unsaturation. Oils with high level of unsaturation (iodine value > 130) are film – forming, because they undergo oxidative polymerization [12].

Table 3 shows Infrared spectral analysis of CO which indicates a broad absorption band for hydrogen bonded OH (V) at 3450 cm^{-1} with sharp bands of CH (V) at 3100 cm^{-1} , C=O(V) for carboxylic acids at 1710 cm^{-1} and olefinic C=C(V) at 1700 cm^{-1} antisymmetric stretching vibration which is in agreement with the findings by Dalen et al. [40]. The IR spectral analysis shown on Table 3 indicates well defined peaks for hydroxyl, carbonyl, olefinic and CH (stretching vibration) absorptions bands for CO. The OH for CO absorption band is broad indicating the presence of hydrogen bonded OH groups and the large band area suggests high concentration of OH groups [36].

Infra-red spectroscopy is of particular value in the recognition of usual functional groups and in the study of fatty acids with trans double bonds. This method has been used to recognize certain functional groups in most oils containing usual mixtures of saturated and unsaturated acids. Such functional groups includes: OH, C = C, -COOH, NH_2 , CONH_2 etc. [40]. However, the absorption frequencies for these groups are not absolute as they are affected by other parameters such as H – bonding, neighboring groups, vibrational couplings, molecular associations, conjugation of multiple bonds, and the solvents in which these samples are dissolved. For instance, H – bonding and other molecular association, conjugation tend to lower vibrational frequencies especially for alcohols, carboxylic acids and diene, triene conjugated acids in that order [41].

Table 4 shows the results of density variations with PPO/CO blend concentration. The density of a material varies under different conditions. It is dependent on temperature and pressure. Materials expand and contract as they experience changes in their temperature, and changes in density are also experienced. Ikeh [40] reported that foam density is a rating applied to polyurethane which may be based in part on the chemical composition of the polyurethane and in part on the additives such as fillers, incorporated in the foam formulations and it is not an exclusive measure of durability or comfort. Polyurethane foam density depends on structure and composition of starting materials, degree of cross links in the polymer, types of blowing agent, functionality of the polyols [42].

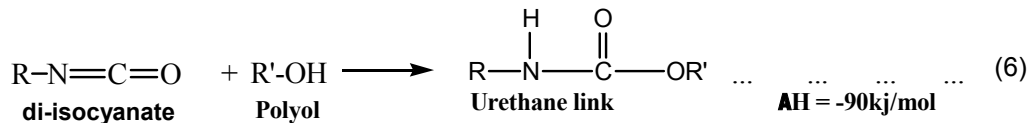
Density first decreases with increase in CO and reaches a value of 2.7 g/cm^3 at PPO/CO (90:10) which compares reasonably with the value at 100% PPO. This indicates that 10%

CO incorporation displays characteristics synergy with the polyol. This further suggests that 10% CO is a threshold concentration for which it shows favourable interactions with polyols [33a]. It was also observed that foams samples at PPO/CO(100:0), (97.5/2.5), (95.0/5.0), (92.5/7.5) and (90:10) compositions showed little or no shrinkage after aging for 24hrs while samples from PPO/CO (80:20), (60/40), (40/60), (20/80), and PPO/CO (0:100) showed high progressive degree of shrinkages far above the 4% degree of shrinkage expected for normal formulations after aging with increases in foam densities [33b].

The shrinkages have been linked to cell collapse as a result of pressure differences between the entrapped gas in the closed cell castor oil (CO) foams and the high external air pressure. These observations are both in agreement and disagreement with the findings of Yeadon, Masherry and Goldbatt (1959) who studied the properties of castor oil polyurethane foams by increasing the concentration of castor oil from 50% to 80%, and observed that foaming time increased from 20 – 45 mins and foam density increased from 1.7 to 6.4kg/m³ and shrinkage decreases from 21% to 1% [42]. The results on Table 4 indicate decreases in foam densities with increases in heights compared to the standard 100% PPO. However, the foam heights displayed peaks at 2.5% CO and depressions at 10% CO and above with consequent increases in densities. Comparing the standard formulations at PPO (100:0) and CO (100:0) show that density for CO>>PPO because the polyol is a linear chain polymer which exhibits weak interchain attraction, while CO is a branched hydroxyl compound with secondary OH groups that increase interchain networks with slight rigidity due to C = C bond which restricts bond rotations (Structure i). It was also observed that a critical blend concentration of PPO/CO (90.0/10.0) which compares favourably with the standard 100% PPO both in terms of physical properties such as density and height showed little or no shrinkage with high degree of reproducibility was adopted as a working formulation for subsequent investigations.

3.2 Mechanical Properties of Foams

In the preparation of urethane foams, the reactions profiles (cream, gel, rise and tack-free times) are primarily controlled by the choice of catalyst. The main reactions are those of isocyanate with polyol or castor oil and water.



The reaction of di-isocyanates with water gives an unstable carbamic acid which decomposes to carbon dioxide and a primary amine. The reaction shown in equation (7) is a nucleophilic addition of HOH across CN. It is highly exothermic, fire retardants are usually added to the formulations to control the exotherms.

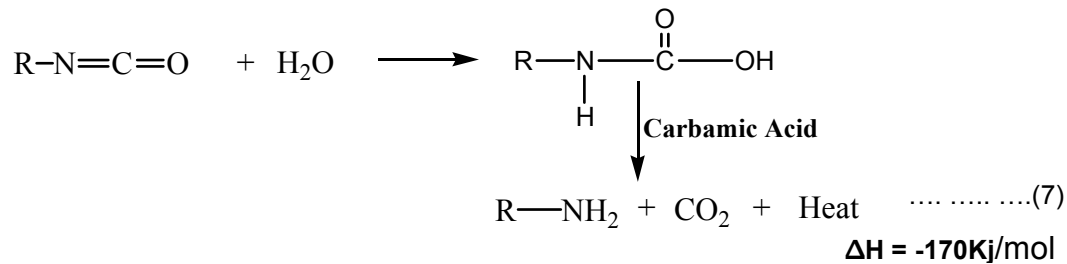


Table 1. Recipe for foam formulations

CPO or PPO (g)	100.00	97.50	95.00	92.50	90.00	80.00	60.00	40.00	20.00	0.00
CO (g)	0.00	2.50	5.00	7.50	10.00	20.00	40.00	60.00	80.00	100.00
TDI(g)	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Water(g)	4.30	4.30	4.30	4.30	4.30	4.30	4.30	4.30	4.30	4.30
Diethyl ethanolamine(g)	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
Stannous Octanoate(g)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Silicone polymer(g)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
CaCO ₃ (g)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00

Key: CPO = Conventional polyol, PPO = Polymer polyol, CO = Castor oil

Table 2. Results of physical and chemical characterizations of CO, CPO and PPO

Characteristics	CO	CPO	PPO	ASTM D1959. 1986, 1639-90, 1994
Specific gravity (25°C)	0.96	1.02	1.03	0.95 – 0.96
Refractive index (30°C)	1.47	1.44	Opaque	1.47 – 1.48
Relative viscosity (30°C) in Toluene	5.70	10.97	11.66	6.30 – 8.90stokes
pH	6.50	10.30	5.50	6.40
Acid value (mgKOH/g)	3.16	1.12	2.23	2.0 max
Hydroxyl value (mgKOH/g)	161.42	187.20	169.19	160 – 168
Iodine value(g /100g)	83.75	66.94	60.60	83 – 88
Saponification value mgKOH/g)	181.25	129.21	107.56	176 – 184
Colour (levibond comparator scale at pH 6.2-6.4)	Pale yellow	Clear	Milk cream	Pale yellow
State at ambient temperatures	Liquid	Liquid	Liquid	Liquid
Solubility in alcohol (30°C)	Complete	Complete	Complete	Complete
Bpt (°C)	220	145	182	330

Key: CO = Castor oil, CPO = Conventional polyol, PPO = Polymer polyol

Table 3. Analysis of IR spectrum of castor oil

Functional group	frequency	% Transmittance	Absorbance	Sharp	Remarks
-O-H (v)	3450.60	14.95	0.8254	Broad	OH group is bonded through H-bonding large band area suggests high concentration of OH groups.
-O-H (δ)	966.27	27.26	0.5645	Sharp	OH bending vibration
C-H (v)	3100.84	5.94	1.2262	Sharp	Presence of olefinic double bonds.
	3000-2840	0.33	2.4815	Sharp	Presence of long chain hydrocarbon linkages.
C-H (δ)	1462.63	5.28	1.2774	Sharp	Bending vibration
-C=O (v)	1710.0	0.99	2.004	Sharp	Carbonyl absorption frequency reduced due to the positive inductive effects of OH groups
-C-O (v)	1378.1	11.98	0.9215	Sharp	Carbonyl of fatty acids.
-C=C- (v)	1700	0.66	2.1805	Sharp	Antisymmetric stretching of C=C
Complement-ary Band	1410.86	10.99	0.9590	Sharp	
	1184.11	4.95	1.3054	Sharp	

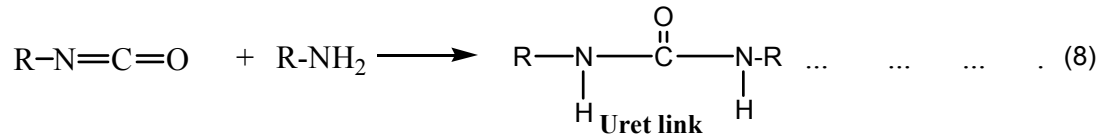
Key: V = Stretching vibration, δ = Bending vibration

Table 4. Results of trial foam formulations with variations in CO concentration

PPO/ CO(g)	Density (g/cm ³)x10 ⁻²	Physical observation
100.00/0.00	2.74	
97.50/2.50	2.41	Little or no shrinkage after aging for 24hrs
95.00/5.00	2.49	
92.50/7.50	2.65	
90.00/10.00	2.70	
80.00/20.00	3.23	
60.00/40.00	3.57	Increasing degree of Shrinkage ↓
40.00/60.00	3.52	
20.00/80.00	4.47	
0.00/100.00	4.84	

Increasing degree of softness to touch ↓

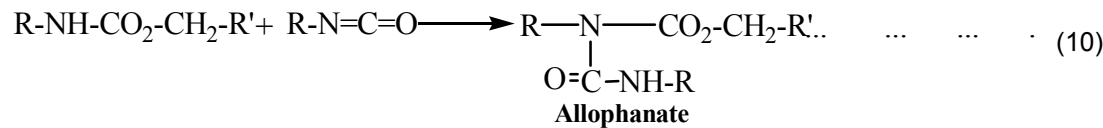
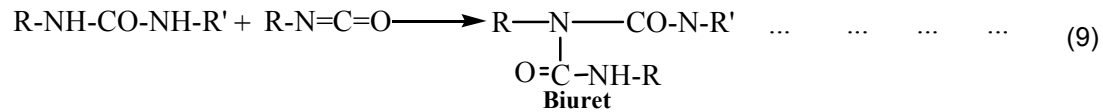
The primary amine then reacts with more isocyanate to form a urea (uret) linkage.



These reactions are responsible for the rise of flexible foam. The reaction of the isocyanate with the polyol forms a urethane and is responsible for extending the polymer. Cross-linking of the polymer occurs from the use of multi-functional isocyanates and polyols.

This is due to the fact that the nature of the polyol and isocyanate components can be widely varied to give different compositions with attendant physico-mechanical property variations [38].

The urea formed from equation (8) reacts with a molecule of Isocyanate to form biuret linkage. Additional Cross linking results from the side reactions of the isocyanate with the urea and urethane with another molecules of isocyanate to form bi-uret and allophanate linkages respectively (equations 9 and 10).



If the condensation reaction is carried out without blowing agents, hard (thermosetting) polyurethane plastics would be formed. In foam manufacture, a range of additives are blended with the raw materials to stabilize the foam while a few amines are added to control the extent of cross-linking and the rate of reaction. Dyes are also added to distinguish between different batches and grades of foams as well as fire retardants are added to reduce the heat generated during the exothermic reactions shown in equations (6) and (7). Control of the reaction profile is achieved by controlling the rate of reaction of each of the above equations. The catalysts used to control reaction rates primarily are tertiary amines and metallic salts (mainly tin) of carboxylic acids. The blowing reaction is catalysed by the tertiary amine, while the gelation reaction is controlled by the metallic salt. The amine and the metallic salt affect both blowing and gelation reactions to some degree [38].

Figs. 1, 2, 3, 4 and 5 compare and contrast some mechanical properties such as tensile strength (N/cm²), % elongation, % creep recovery and compression test (mm) of CPO and PPO blends with CO in concentrations of 0, 2.5, 5.0, 7.5, 10 and 100% (pure oil only).

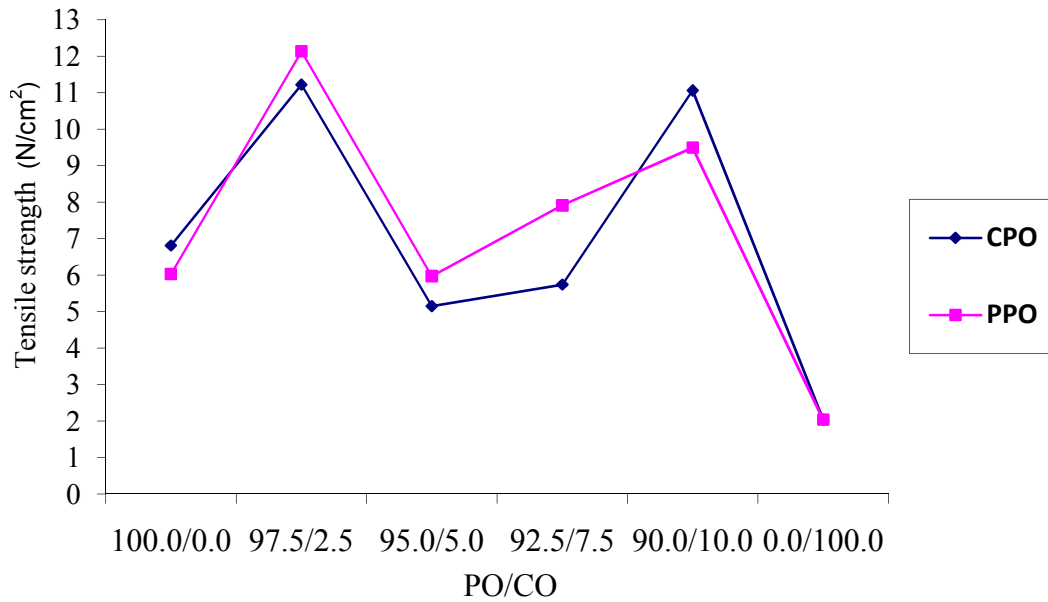


Fig. 1. Results of variations of tensile strength of CPO and PPO with CO blends
 Where CO = Castor oil, CPO = Conventional polyol, PPO = Polymer polyol

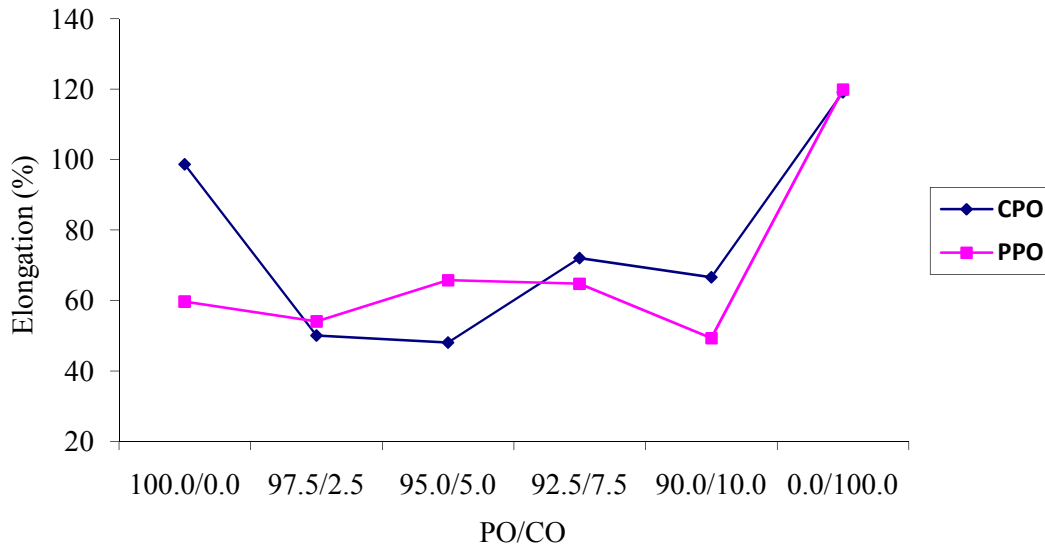


Fig. 2. Results of variations of elongation of CPO and PPO with CO blends

Fig. 1 indicates values for tensile strength with peaks observed at; CPO/CO (97.5/2.5) = 11.22 N/cm², PPO/CO (97.5/2.5) = 12.35N/cm², CPO/CO (90.0/10.0) = 11.06 N/cm² and PPO/CO (90.0/10.0) = 9.49 N/cm² as against 100% CPO = 6.81N/cm², 100% PPO = 6.03N/cm² and 100% CO = 2.04N/cm² while the tensile strength values at; CPO/CO (92.5/7.5) =5.74N/cm², PPO/CO (92.5/7.5) =7.91N/cm², CPO/CO (95.0/5.0) =5.15N/cm² and PPO/CO (95.0/5.0) =5.97N/cm² in each case showed depressions compared to other

blends. Arinze et al. [42] observed in their report on establishing polymer-polymer interactions asserted that polyblends reduce compositional non-uniformity often seen in homopolymers. Blending is concerned with the mechanical, physical, chemical and optical properties hence there must be compatibility between component mix. It is desired that the correct molar ratios are established that give properties such as modulus, surface hardness, melting temperature, specific gravity, elasticity, viscosity etc [42b]. Therefore, the peaks observed are due to molar ratio compatibilities (reinforcement) in the use of CO while the low tensile strength values are due to little or no compatibility. This observation is further corroborated by Madufor and Iheonye [44] in their studies on influence of composition on deformation behavior of HDPE/LLDPE blends in which they reported that deficient mechanical properties are due to poor or incompatibility of materials [44]. Furthermore, Ikeh (1991) reported that incorporation of low CO concentration in polyols decreases density, tensile strength and modulus of elasticity while foam heights, yield stress, % elongation, and creep recovery increase [43]. Our findings partially disagree with this trend in terms of tensile strength but however, agree with the rest of the parameters mentioned.

Fig. 2 shows % elongations at break which generally increases with decrease in tensile strength which show peaks at 100% CPO, PPO and CO. However, values for 100% CO and 100% CPO peaks are higher than that of 100% PPO. It indicates that 100% CPO, PPO & CO have higher % elongation than the values for blends. Elongation at break is a measure of ductility of the material. It has been reported that plasticizers lower tensile strength of film but increase % elongation as it is observed here where the incorporation of low CO introduces depressions of low tensile strengths because of this plasticizing effects. This observation is in agreement with findings of Okafor and Chukwu [42] in which they reported that tensile strength inversely correlates with the magnitude of % elongation [43].

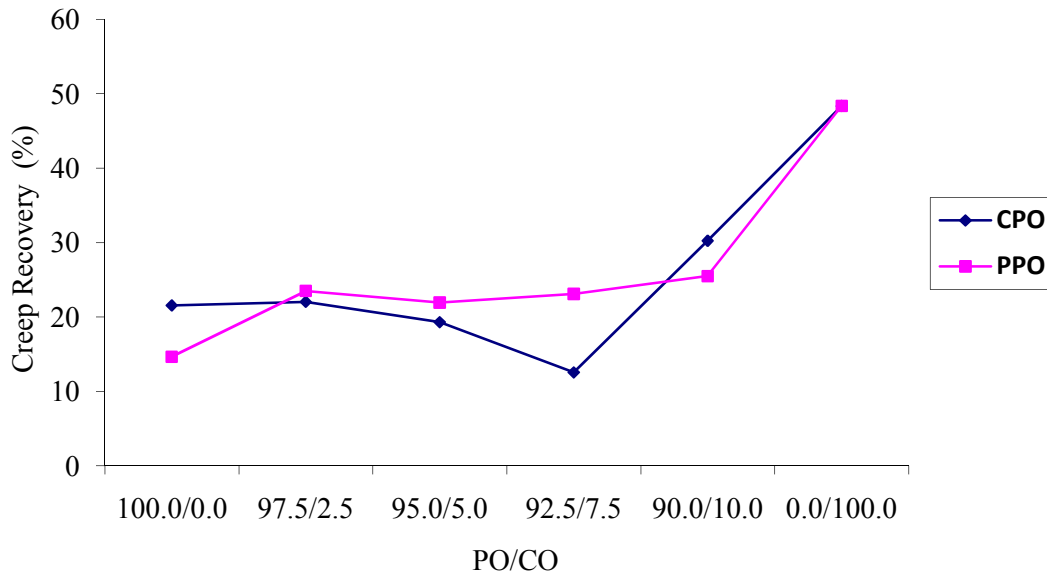


Fig. 3. Results of variations of creep recovery of CPO and PPO with CO blends

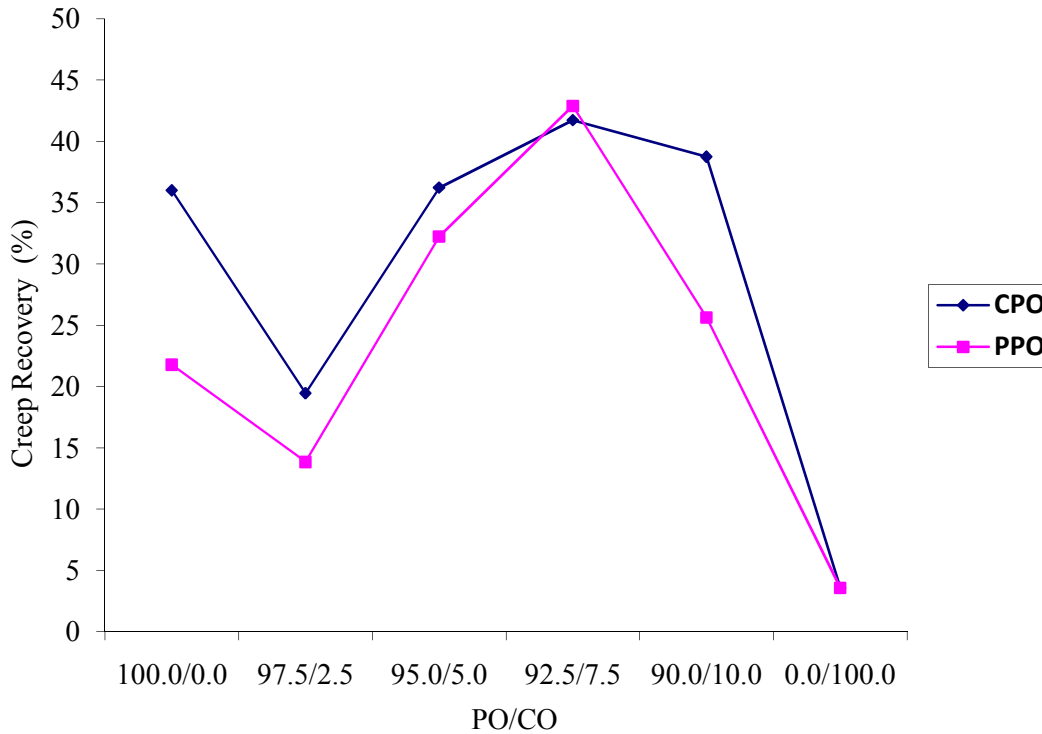


Fig. 4. Results of variations of creep recovery of CPO and PPO with CO blends at 20N applied Compression Load

Fig. 3 shows % creep recovery which surprisingly peaks at 100% CO = 48.30% as against 21.5% for 100% CPO and 14.65% for 100% PPO while CPO/CO blend (90.0/10.0) gives 30.20% and PPO (90.0/10.0) gives 25.49%. Both CPO and PPO blends at (90.0/10.0) have higher values than values at 100% CPO and PPO. It also indicates that blending with CO improves both tensile strength and creep recovery. This observation is in agreement with the findings of Ikeh [43], however, the magnitude of the increase of % creep recovery for the CPO/CO (90.0/10.0) shows great disparity whereby a value of 2036% was reported while in this present study, a value of 30.20% was observed. Furthermore, creep recoveries for 100% CPO (=722.5%) and 100% CO (=825%) were reported by this researcher while 21.5% and 48.30% were observed for 100% CPO and 100%CO in that order, in the present study.

Fig. 4 shows values of % creep recovery at 20 N applied load. Peaks were observed at CPO/CO (92.5/7.5)= 41.74% and PPO/CO (92.5/7.5)= 42.88%. However, values for 5.0%, 7.5% and 10.0% CO blends with CPO and PPO are higher than the corresponding values for 100% CPO =36.0% and 100% PPO =21.78% in that order. Furthermore, for this applied load, 100% CO has the lowest creep recovery of 3.58% compared to the value of 48.34% creep recovery earlier observed on Fig. 3. This is due to differences in the applied load or cell load in which the former employs an applied load of 500N or due to experimental error since other blends showed higher increases in % creep recoveries.

Fig. 5 shows the results of variations of compression tests (mm) at 20N applied compression load. Peaks of 17.94mm and 18.15mm were observed at (92.5/7.5) for both CPO and PPO blends in that order. Again, increases were observed generally between 5 – 10% CO blends

with the polyols compared to the 100% CPO = 15.15mm and 100% PPO = 9.61mm. Again, 100% CO shows a very low value of 1.83mm. These values compliment very well with the values of % creep recovery shown on Fig. 4 and to some extent the trends of creep recovery display on Fig. 3. It means creep recovery on compression and relaxation is a foam characteristic property. The % creep recovery values at (92.5/7.5) composition blends for both CPO and PPO shown on Fig. 4 are in agreement with the values of compression tests on Fig. 5. The peaks of compression at (92.5/7.5) for both CPO and PPO blend compositions have the highest % creep recovery of 41.73% and 42.80% respectively compared to other blends. This again is in agreement with the results of Ikeh [42].

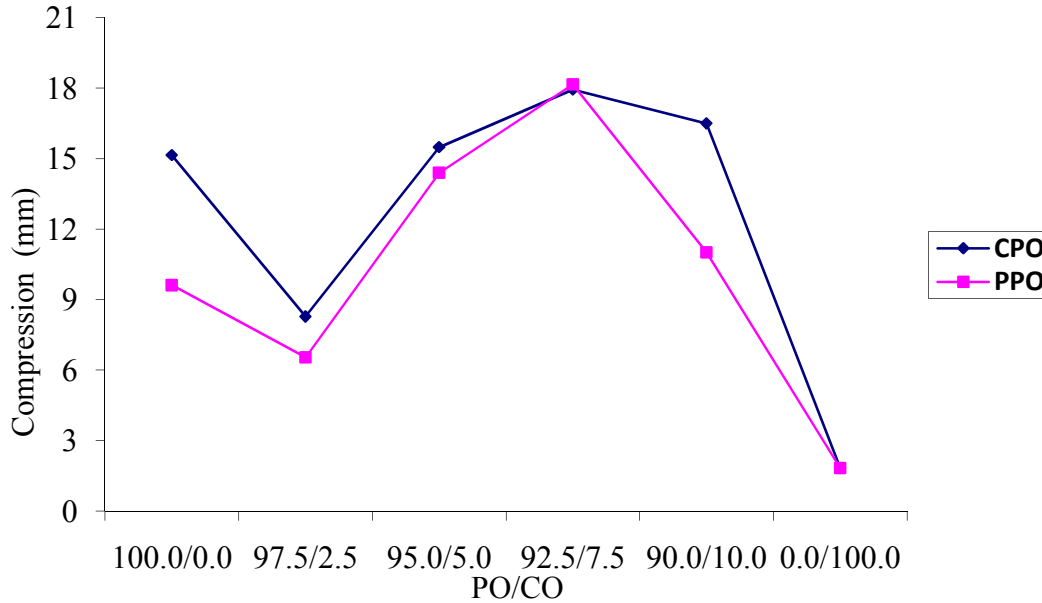


Fig. 5. Results of variations of compression testing of CPO and PPO with CO blends at 20N applied compression Load

Figs. 6 and 7 show the variations of tensile strength and % elongations at break for factory trials of CPO blends with CO. Isol-block foam formulation is a semi-automated (semi-batch) process where the polyols and additives are charged in a flow process into a static mould, while calculated amount of toluene diisocyanate (TDI) is added manually and the mould is toggled and allowed to cool before it is opened. Again, tensile strength generally display peaks at CPO/CO (92.5/7.5) = 46.41 N/cm² and CPO/CO (90.0/10.0) = 57.51N/cm² over above the values at 100% CPO = 40.40N/cm² and 100% CO = 18.36 N/cm². These values are in agreement with the results of laboratory formulations shown on Fig. 1. These observations confirm our earlier results and explanations earlier advanced.

The results of % elongation shown on Fig. 7 indicate an inverse relationship with tensile strength. The higher the % elongation, the lower the tensile strength and vice versa. Elongation increases with CO blend composition, but depresses at CPO/CO (90.0/10.0) = 51.76% with a corresponding highest tensile strength of 57.51N/cm² shown on Fig. 6. Similarly, the 100% CO has the highest % elongation of 119.93% with the corresponding lowest tensile strength of 18.36N/cm² which in agreement with the results on Fig. 2 for the laboratory formulations. This again confirms earlier statements made on this trend above.

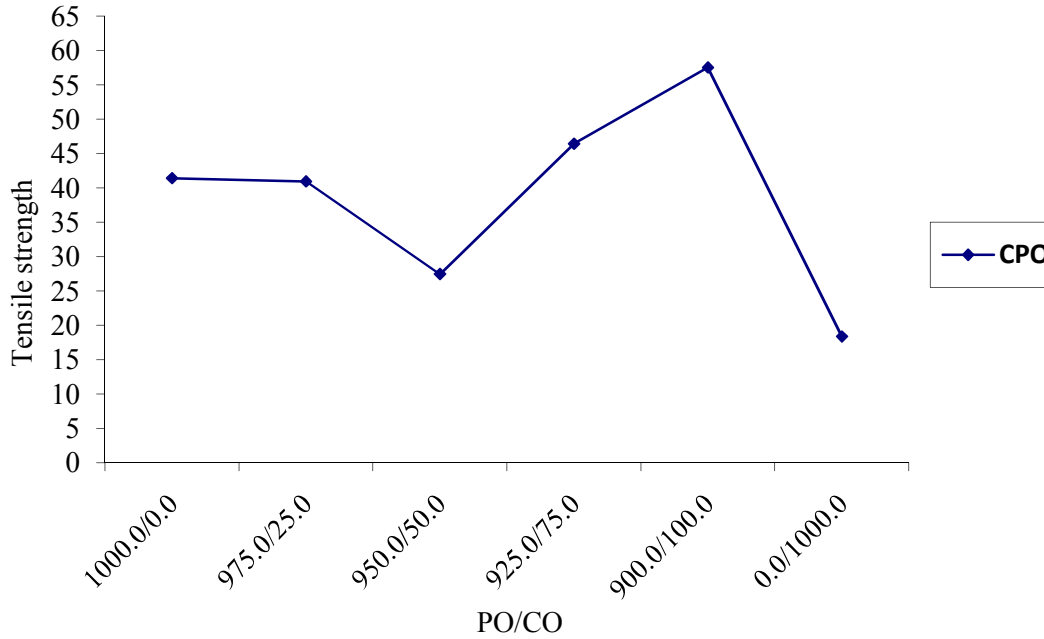


Fig. 6. Results of variations of tensile strength of factory trials of CPO Isol-block foams

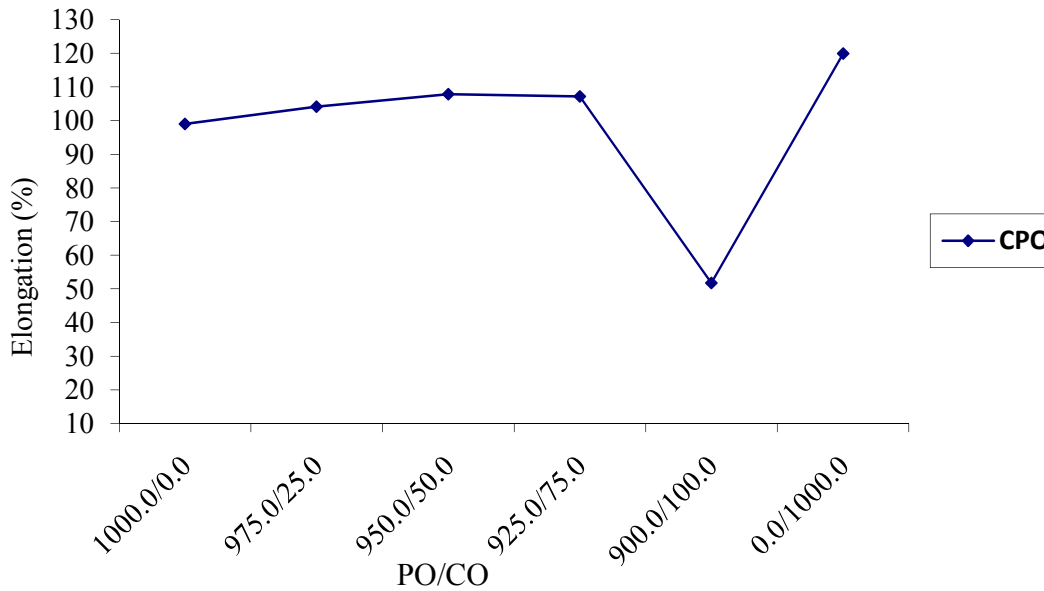


Fig. 7. Results of variations of elongation of factory trials of CPO Isol-block foams

Figs. 8, 9 and 10 show variations of tensile strength, % compression set and % elongation with mean density of Vitafoam Jos factory 14 Density batches. The results show batch to batch variations in the production of Isol-block foams. Fig. 8 shows that tensile strength increases linearly with increase in mean density. Similarly, % compression set

shown on Fig. 9 increases with mean density, as Fig. 10 shows that % elongations decreases with increase in mean density which is in agreement with the fact that tensile strength has an inverse relationship with elongation as earlier mentioned. Both the laboratory and the factory results are in agreement with this observation.

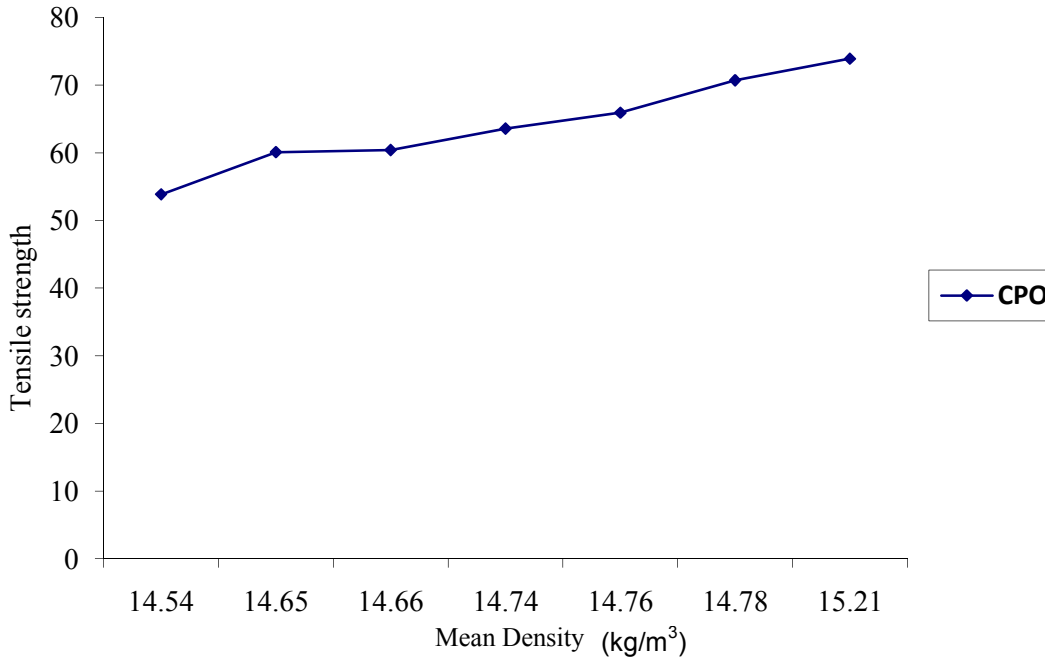


Fig. 8. Results of variations of tensile strength of Vitafoam 100% CPO Isol-block factory batches of 14 Density

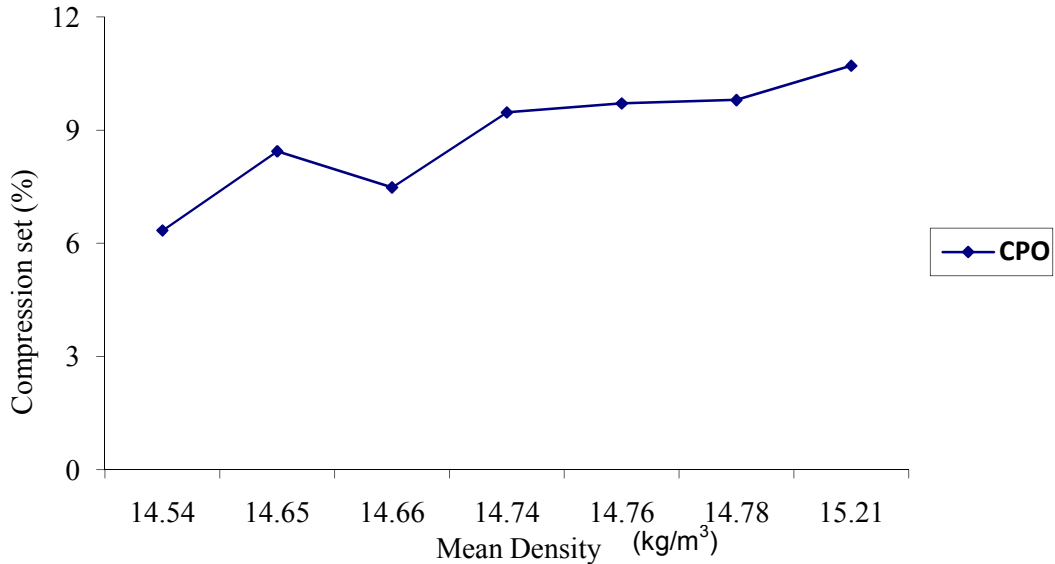


Fig. 9. Results of variations of compression set of Vitafoam 100% CPO Isol-block factory batches of 14 Density

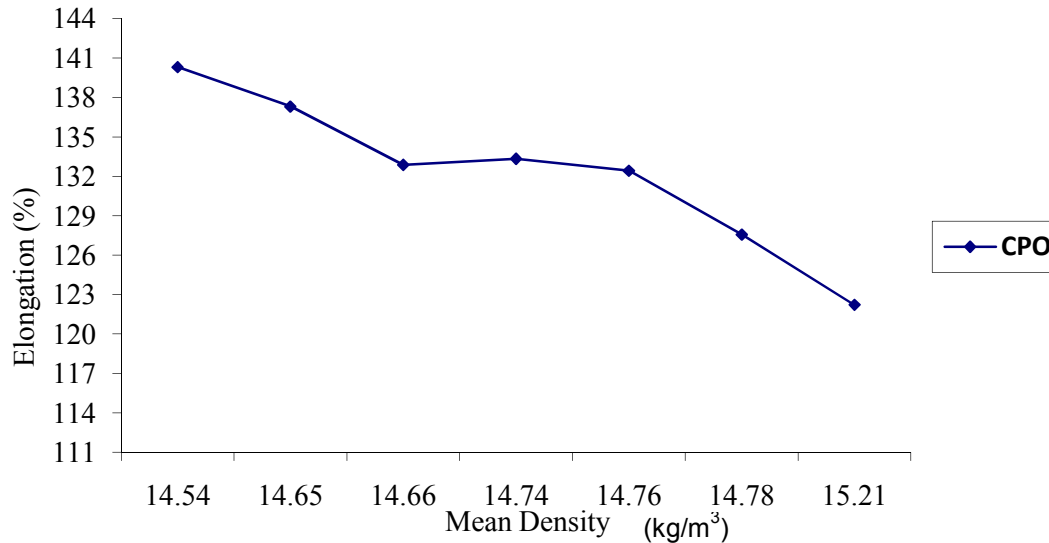


Fig. 10. Results of variations of elongation of Vitafoam 100% CPO Isol-block factory batches of 14 Density

4. CONCLUSION

Nigeria is greatly endowed with abundant natural resources that can kick start an industrial chemical revolution. The foam industries depend largely on imported raw materials. Therefore, agro- based raw materials and their likes that are abundant can be explored and exploited with little or no-value-addition. The potential for local production of industrial raw materials and intermediates from agricultural products as well as the explorations and exploitations of industrial minerals have not been fully embarked upon. This is because of the over and ever dependence on fossil based raw material gingered by huge foreign exchange earnings that made Nigeria to easily finance imports of industrial raw materials to feed our local industries at the expense of locally available, but untapped resources. However, the recent global economic meltdown and food crisis, many of the chemical industries could no longer import their raw materials due to lack of foreign exchange and general cash crunch. This has led to many of them closing down out rightly while others could not produce at their installed capacity [45].

It is however heartening to note that there is still hope for the revival of ailing chemical industries in Nigeria, if there is a concerted effort towards backward integration by all the stakeholders. This involves intensive drive towards local sourcing of raw materials for sustainable development, conservation of scarce foreign exchange and to achieve the vision 2020:20 of the Federal Government [46]. It has been established in this research that incorporation of castor oil (CO) up to 10% produces open-cell foams with improved tensile strength, creep recovery and compression set properties over and above 100% CPO and PPO Physico-mechanical properties of low CO in formulations are in agreement with the factory trial batch productions. Generally, open-cell foams are suitable for cushioning and insulating applications because they are easily compressed and allowing air flow between cells, while the closed-cell foams consist of discrete gas pockets completely surrounded by

polymer with higher compression strength due to the structure and high density usually for high load bearing applications [42].

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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