

## **Isolation and Characterization of Castor Seed Oil and Its Utilization Potential in the Production of Polyurethane Foam**

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### **Abstract**

Firm polyurethane (PU) foams were prepared using Nigerian grown brown and white castor seed oil starting materials extracted at ambient temperature. Polyol with terminal primary hydroxyl groups synthesized from crude castor oil were reacted with aromatic diphenylmethane diisocyanate to prepare the foams. Castor seeds were decorticated and milled, after which they were weighed into filter bags for expression at ambient temperature, 50, 100 and 150 °C respectively at a constant pressure of 2 ton. Evaluation of the oil yield shows that the brown seeds with lower weight at a temperature of 150 °C gave a high yield of 54.79 %, compared to high weight at ambient temperature, which yielded 29.45 %. The white seeds with lower weight at a temperature of 150 °C gave high yields of 52.75 %, compared to higher weight at ambient temperature yielding 30.06 %. The oil was characterized in terms of moisture content, volatile content, acid value, free fatty acid and saponification value. The results are within the range reported in literature. In-situ polymerization was used in the production of polyurethane foam using the extracted oil as polyol. The results of the foam characterization in terms of compression set and density conform to standard foams.

**Keywords:** Castor seeds, polyurethane foam, oil

### **Introduction**

One of the most interesting features in scientific research is the development of new and exciting materials for a wide variety of applications. Thus, the renewed interest in natural materials has resulted in a large number of modifications to bring it to a level at a par and even superior to synthetic materials. The development of commodities derived from petrochemical polymers has brought many benefits to mankind. However, it is becoming more evident that the ecosystem is considerably disturbed and damaged as a result of pollution occasioned by discharge of heavy metals and the non-degradable materials used in disposable items. Therefore, the interest in polymers from renewable resources has recently gained exponential momentum and the use of biodegradable and renewable materials to replace conventional petroleum materials for disposable and other industrial applications are becoming popular and necessary [1,2]. Rigid polyurethane (PU) foams are used in engineering applications, such as insulation materials, automotive parts, and structural materials [3,4]. The basic production step of PU foams is based on the reaction of organic isocyanates with polyols.

In polymer and chemical industry, seed oils which represent a major potential source of chemicals have been utilized as an alternative feedstock for monomers. Oils such as soybean oil- and rapeseed oil-based polyols have been used to make PU foams as well [5,6]. Due to the hydrophobic nature of the triacylglycerols (TAG), the main component in seed oils, the polymers so produced have some excellent

chemical and physical properties, such as enhanced hydrolytic and thermal stability [7]. However, most seed oil-based polyols currently utilized to produce PU foams have their hydroxyl groups located in the middle of the TAG's alkyl chains. Upon crosslinking these polyols, the pendant, or dangling chains, are unsupported, which significantly limits the rigidity of the PU polymers [8]. Significant steric hindrance to cross-linking (especially by bulky aromatic diisocyanates) is introduced by the –OH groups when located in the middle of the fatty-acid moieties. Moreover, these dangling chains, which are imperfections in the final polymer network, do not support stress if the network is under load, and can act as a plasticizer, thereby reducing polymer rigidity while increasing its flexibility.

This present communication examines the isolation of castor oil from the brown and white seed varieties and oil yield at varying temperatures and its characterization, as well as its utilization potential in the production of polyurethane foam for storage of items at controlled temperature.

## Materials and methods

### Materials

Castor seeds were obtained from Ekpoma, Edo State, Nigeria. The chemicals used; Acetone, Phenolphthalein, sodium hydroxide, ethanol, diethyl ether, hydrochloric acid, potassium hydroxide, N,N-cyclohexylamine, N,N-dimethylethanolamine, silicon surfactant, methylene chloride, di-isocyanate-diphenyl methane (MDI), and Freon II (Trichlorofluoromethane), were of analytical grade and supplied by BDH, England.

### Extraction of the Castor oil by mechanical hydraulic pressing (Expression)

One kg of the decorticated milled castor beam was weighed and wrapped in a filter cloth and was placed in a perforated steel box. The box and content were filtered between the fixed and movable heads of a vertical hydraulic press, pressure was applied slowly up to 2 tons and there was a flow of viscous oil through the outlet of the collecting pan into a clean beaker. The process lasted for 24 h before the oil and cake were removed from the press [9].

For the hot press, the samples temperature was maintained at 50, 100 and 150 °C respectively for both the brown and white coated seeds used. The weights of the oil produced were recorded and stored in a clean container for further analysis.

### Characterization of the seed oil

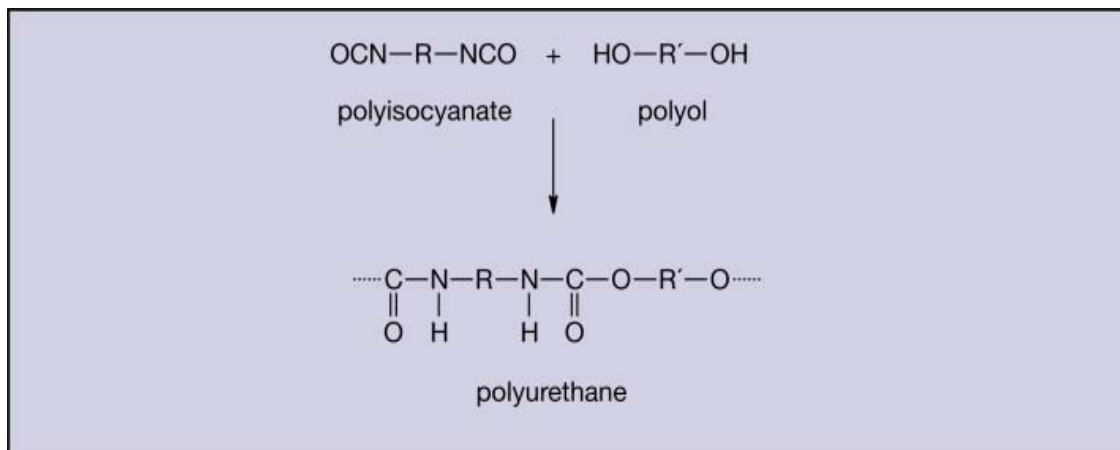
Samples of the various seed oil isolated were characterized in terms of their physico-chemical properties such as moisture content, volatile content, acid value, saponification value and free fatty acid value according to standard methods AOAC (1998) [10] and loss on ignition, ASTM D1509 [11].

### Preparation of the polyurethane foam as precursor for cooler production

The formulation to prepare the foams was chosen so that the final hydroxyl number was between 450 and 500 mg KOH/g, in order to obtain a rigidity that is close to what was commonly used for foams prepared from vegetable oils based polyols and found in the literature [12]. Because the hydroxyl number of the starting materials was too low, glycerin, a hydroxyl containing crosslinker, and water were added to attain the desired hydroxyl number. Twelve parts of glycerin and 3 parts of water were added in castor seed oil based PU foams.

The detailed foam formulation is shown in **Table 1**. The polyol was first mixed during 2 min in a plastic container with suitable amounts of crosslinkers, catalyst, and surfactant. MDI was added and the mixture was stirred vigorously at 1,500 rpm for 40 s. The mixture was then poured into a home-made Teflon mold which was previously greased with a silicon release agent and sealed with a hand-tightened clamp. After the completion of the reaction, the sample was post cured at room temperature for 4 days. Cream time, rising time and gel time are reported in **Table 4**.

The produced PU foams is referred to as castor-PU [13].



**Figure 1** Polyurethane reaction formula.



**Figure 2** In situ polyurethane foam production.

**Table 1** Formulation table for polyurethane foam.

Ingredient	Part per hundred
Castor oil	100
Distilled water	1.0
N,N-cyclohexylamine	0.3
N,N-dimethylethanolamine	0.3
Silicon surfactant	1.0
Methylene chloride	0.98
MDI	45
Freon II (Blowing agent) (Trichlorofluoromethane)	50

For the block samples the ingredients were weighed in similar manner as above into the plastic mould, and the reaction proceeded as above until a semi-rigid cellular mass was obtained after about 15 min. Samples of the polyurethane foam were collected and characterized using standard methods.

**Characterization of the polyurethane foam**

The compressive properties of the foams were measured on an Instron universal testing machine (model 4202) according to the ASTM D1621-00 standard [14]. Samples were prepared in cylindrical Teflon molds of 60 mm diameter and 36 mm length. The cross-head speed was 3.54 mm/min with a load cell of 500 kg. The load was applied until the foam was compressed to approximately 15 % of its original thickness and the compressive strengths were calculated based on the “10 % deformation” method according to the standard. The strengths of identical specimens per sample were tested and the results were averaged.

The density of the PU foam was determined by averaging the mass/volume measurement results of 5 specimens per sample following the ASTM D1622-98 standard [15]. The results are listed in **Table 4**.

The closed-cell content was determined following the ASTM D2856-94 standard.

**Results and discussion**

**Table 2** shows the results of the evaluation of percentage oil yield from castor seeds of 2 different colours (brown and white). From the table, the brown seeds with lower weight at a temperature of 150 °C gave a high yield of 54.79 % compared to higher weight at ambient temperature yielding 29.45 %, suggesting that a lower quantity of brown seeds yields a higher quantity of oil, which is profitable economically.

**Table 2** Percentage of oil yield from castor seeds.

Colour of seeds	Brown seeds	Brown seeds	Brown Seeds	Brown seeds	White seeds	White Seeds	White seeds	White seeds
Wt of milled bean (g)	1924.3	1604.1	663.27	1236.1	1389.4	700.00	700.00	600.00
Temperature (°C)	Ambient	50	100	150	Ambient	50	100	150
Pressure force (ton)	2	2	2	2	2	2	2	2
Oil yield (g)	566.4	539.52	227.22	677.31	417.6	262.10	349.2	317.5
% Yield	29.43	33.62	34.22	54.79	30.06	37.44	49.89	52.75

From the characterization, the percentage for moisture and volatile content, acid, and free fatty acid (FFA) values ranges between 0.1 - 0.2, for % volatile, 1.72 - 2.12 for acid value, and 0.83 - 1.06, for %FFA, as shown in **Table 3**.

**Table 3** Results of seed oil characterization.

Seed oil	Wt. of oil (g)	Acid value	% FFA	Saponification value	Loss on ignition	% Moisture/volatile
Brown Exp. At ambient	10	2.12	1.06	171.4	0.18	0.2
White Exp. At ambient	10	2.10	1.05	175.6	0.17	0.2
Brown Exp. At 50 °C	10	2.02	0.86	181.8	0.11	0.1
White Exp. At 50 °C	10	1.98	0.83	183.6	0.12	0.1
Brown Exp. At 100 °C	10	1.75	0.87	181.2	0.06	0.1
White Exp. At 100 °C	10	1.72	0.89	180.4	0.05	0.1
Brown Exp. At 150 °C	10	1.85	0.93	177.9	0.09	0.1
White Exp. At 150 °C	10	1.84	0.90	179.1	0.07	0.1

The saponification value is as low as 180, indicating that the oil can be used in numerous applications as in the in situ polymerization for the coolers produced [16]. Castor oil was very effective, as the reaction proceeded freely, yielding a semi-rigid cellular mass at minimum time with a high compression set, as well as a low density of 0.634 g/cm<sup>3</sup> [17].

The processing parameters (cream time, rising time and gel time), measured with an uncertainty lower than 1 s and listed in **Table 4**, illustrate the reactivity of the PU foams. Glycerin played a major role in the reaction, but its presence does not explain the differences in reactivity. Castor oil PU has a cream time 50 % larger, a rising time 35 % larger and a gel time 25 % larger than those of Canola and rapeseed PUs reported in literature [18]. This was therefore attributed to the difference in polyol structure, particularly the dangling chains content and their location.

Canola based polyol contained only primary terminal hydroxyl groups located at carbon 9, and castor oil contained secondary functional hydroxyl groups all located in the middle of the fatty acid chains which resulted in a significantly higher steric hindrance to further crosslinking. Note that even if canola polyol was constituted of 30 % (on a molar basis) pendant chains, in the castor oil, every molecule with hydroxyl functionality provided a portion of the fatty acid chain as a dangling chain.

**Table 4** Result of polyurethane foam characterization (Mechanical properties).

Properties	Brown-castor PU	White-castor PU
Compression set (kPa)	1,170 ± 138	1650 ± 125
Density (Kg/m <sup>3</sup> )	168 ± 2	154 ± 5
Modulus (Mpa)	32 ± 3	25 ± 9
Cream time (S)	16	18
Gel time (S)	21	20
Rising time (S)	52	48

The mechanical properties of the foams were characterized by compressive stress-strain measurements and the results are shown in **Table 4**.

With a density of 154 kg/m<sup>3</sup>, the white castor-PU foam has a compressive strength of 1650 ± 125 kPa and a modulus of 25 ± 9 MPa. The brown castor-PU foam yields the highest compressive strength (1,170 ± 138 kPa) and modulus (32 ± 3 MPa).

The compressive strength and modulus depend not only on the cellular structure of the foam, i.e. the material of the cell walls (strut) and the size and shape of the cells, but also on the type of the cells (which could be closed or open). The results of the characteristics of all the PU foams are listed in **Table 4**. As can be seen, the content of brown castor-PU foams is much higher than that of white castor-PU foams,

except for the compressive set. It is known that the strength of an open-cell foam is greater than that of a closed-cell material which has had its walls ruptured, because the broken walls are unable to contribute any reinforcement to support stress when the network is under load [19].

The compressive strength and modulus of brown castor-PU foams were the highest, mainly because it had the lowest closed-cell content and the thickest cell walls. The low compressive strength of white castor-PU samples was the result of the plasticizing effect of the dangling chains combined with a smaller amount of hard segment, even with less closed-cell content. The plasticizer weakens the network under load and lowers the compressive strength and Young's modulus. The hard segments confer to the PU foams high modulus, especially when they are of non-uniform size and therefore more difficult to disrupt.

The seemingly poor quality of the castor-PU foam microstructure might be attributed to its inadequate optimization of the catalyst and surfactant used in its formulation. When the amounts of catalysts are reduced to 0.5 parts, finer cells with narrow distribution were obtained (data not reported). It is established that the role of the surfactant is to stabilize the cell walls by lowering the surface tension between the cells and prevent their coalescence, resulting in smaller cells uniformly distributed over the network. Meanwhile, catalysts are added to accelerate reactions according to the requirement. The final cellular structure is a balance between the network formation and the blowing reaction [3].

### Conclusions

It has been shown that the use of castor oil from renewable materials for polyurethane foam production is technically feasible, eco-friendly, and has a low cost and with high efficiency. Besides that, being composed of agricultural waste, it helps in the reduction of waste generation and gives added value to the waste. This oil can be a good candidate for production, not only for these polyurethane foam, but also other products of industrial applications.

### References

- [1] JPH van Wyk, Biotechnology and the utilization of biowaste as a resource for bioproduct development. *Trends Bio. Technol.* 2001; **19**, 172-7.
- [2] AK Mohanty. Biofibres, biodegradable polymers and biocomposites: An overview. *Macromol. Mater. Eng.* 2000; **276-277**, 1-24.
- [3] M Szycher. *Szycher's Handbook of Polyurethanes*. In: J Devine and PN William. The Chemistry and Technology of Edible Oils and Fats. CRC Press, Boca Raton, New York, 1999, p. 198-222.
- [4] YL Melzer. *Urethane Foams Technology and Applications*. Noyes Data Corporation, Park Ridge, 1971, p. 1-448.
- [5] YH Hu, Y Gao, DN Wang, CP Hu, S Zu, L Vanoverloop and D Randall. Rigid polyurethane foam prepared from a rape seed oil based polyol. *J. Appl. Polym. Sci.* 2002; **84**, 591-7.
- [6] A Guo, YJ Cho and ZS Petrovic. Structure and properties of halogenated and nonhalogenated soy-based polyols. *J. Polym. Sci. Pol. Chem.* 2000; **38**, 3900-10.
- [7] A Zlatanic, ZS Petrovic and K Dusek. Structure and properties of triolein-based polyurethane networks. *Biomacromolecules* 2002; **3**, 1048-56.
- [8] A Guo, I Javni and Z Petrovic. Rigid polyurethane foams based on soybean oil. *J. Appl. Polym. Sci.* 2000; **77**, 467-73.
- [9] D Ruys, A Crosky and WJ Evans. Natural bast fibre structure. *Int. J. Mater. Product Technol.* 2002; **17**, 2-10.
- [10] D Firestone. *Official Methods and Recommended Practices of the American oil Chemists Society*. 5<sup>th</sup> ed. AOCS Press, Champaign, Illinois, 1998, p. 1-54.
- [11] ASTM 1509. *Standard Method of Testing Heat Loss*. 1983.
- [12] A Guo, D Demydov, W Zhang and ZS Petrovic. Polyols and polyurethanes from hydroformylation of soybean oil. *J. Polym. Environ.* 2002; **10**, 49-52.
- [13] JA Brydson. *Plastic Materials*. 7<sup>th</sup> ed. Butterworth-Heinemann, London, 1999, p 1-920.

- [14] Annual Handbook of ASTM Standards. *Section Eight, Plastics, 08:01*. ASTM Intern West Conshohochem, P.A. USA, 2005.
- [15] ASTM 1622. *Standard Method of Testing Density*. 1983.
- [16] J Devine and PN William. *The Chemistry and Technology of Edible Oils and Fats*. Pergamon Press, New York, 1982, p. 1-22.
- [17] RW Dyson. *Specialty Polymers*. 2<sup>nd</sup> ed. Blackie Academic & Professional, London, 1988, p. 1-255.
- [18] S Narine, X Kong, L Bouzidi and P Sporns. Physical properties of polyurethanes produced from polyols from seed oils: II. Foams. *J. Amer. Oil Chem. Soc.* 2007; 84, 65-72.
- [19] EA Meinecke and RC Clark. *Mechanical Properties of Polymeric Foams*. Technomic Publishing Company Inc., Lancaster, 1973, p. 1-105.