

Physico-Mechanical Properties of Rigid Polyurethane Foams Synthesized From Modified Castor Oil Polyols

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Abstract- Using two different formulations with isocyanate/polyol (NCO/OH) ratios of 1/2 and 1/1, rigid castor oil-based polyurethane foams (RCPUFs) were prepared by one-shot method. Foam reaction involved glycerolyzed castor oil containing varying concentrations (10-60 wt.%) of the modifier, and 80:20 mixture of 2,4- and 2,6- toluene diisocyanate (TDI) at room temperature, in presence of stannous octoate and dimethylaminoethanol (DMAE) catalysts, methylene chloride (physical blowing agent) and silicone oil (surfactant). Hydroxyl number range for the modified castor oil polyols (MCOPs) was 168 – 320mgKOH/g. Foams obtained were characterized in terms of their process parameters such as cream time, free-rise time, gel time, tack-free time and foam rise, as well as their physico-mechanical properties namely: density, water absorption, compressive strength and creep recovery. RCPUF density varied over the range 24.50-50.50 kg/m³; water absorption (0.73 – 2.20%); compressive strength (89.20 – 450.20 KN/m²), while creep recovery values were in the range 18.50 – 28.50%. These characteristics were compared with those of the neat castor oil-based polyurethane foams (PUFs) prepared using same formulations. Microstructural imaging using scanning electron microscopy (SEM) indicates rigid, cellular morphology for the RCPUFs, with high modifier-containing RCPUFs exhibiting fibre-like morphology, while morphology for the neat foams was essentially semi-rigid. Rigidity in structure of the glycerol-modified foams (GMFs) produced from hydroxyl-rich polyols was attributed largely to network formation likely resulting from allophanate and urea crosslinking reactions. It was evident especially at NCO/OH ratio of 1/1 that the higher the hydroxyl functionality in polyol, the higher the conversion into allophanate and biuret moieties via secondary polyurethane (PU) reactions, and ultimately the greater the complexity in PUF structure due to higher degree of crosslinking.

Index Terms - Polyurethane foam; castor oil; foam rigidity; physico-mechanical properties.

I. INTRODUCTION

Recent global surge in the quest for renewable natural resources of plant origin stems largely from their suitability and sustainability as chemical feedstock, as a result of the economic and environmental-safety advantages they have over petroleum-based feedstock. These advantages include widespread availability, low cost, non-toxicity, low emission

properties and biodegradability (Sherman, 2007; Petrovic and Cvetkovic, 2012). On the other hand, the use of fossilized carbon-based materials such as coal and petrol in the synthesis of polymeric materials and other products of the chemical industry has resulted in the gradual depletion of these reserves; increased emission of greenhouse gases and accumulation of non-biodegradable waste on earth, among other environmental impacts (Lochab *et al.*, 2012).

Current sustainability research drive therefore is towards developing green source materials as potential replacements for petroleum-based feedstock. Vegetable oils definitely represent an important group of agricultural stock for this purpose. Within this group, soybean oil, castor oil, palm oil and canola oil are the most promising vegetable oils for the industrial development of biobased materials (Husic *et al.*, 2005; Luo *et al.*, 2008; Jose *et al.*, 2008). However, the use of non-edible vegetable oil like castor oil towards realizing this goal obviously has other advantages related to food security (Mazubert *et al.*, 2013).

PUFs are cellular plastics with versatile applications in thermal insulation, packaging, cushioning and floor covering (Brydson, 1999). Rigid PUFs in particular are mainly used as structural and engineering materials especially in construction, insulation, packaging and refrigeration (Chattopadhyay and Raju, 2007; Yamashita *et al.*, 2008). The synthesis of PUFs using polyols derived from vegetable oils (castor, soybean, palm, sunflower, rapeseed etc) has been the subject of many recent studies (Ramirez *et al.*, 2008; Dworakowska *et al.*, 2010; Chian and Gan, 1998; Fan *et al.*, 2012; Yakushin, *et al.*, 2014). Vegetable oils are now fast replacing conventional petroleum-based polyols in PU synthesis (Xu *et al.*, 2008; Badri, 2012). A polyol is a polymeric or oligomeric polyhydroxy compound of the type R(OH)_n (n ≥ 2) that can be used as raw material in PU synthesis. Vegetable oils consist of triglyceride molecules whose complexity and reactivity depend on the nature of fatty acids they contain – their composition, chain length, degree of unsaturation, number, distribution and location of hydroxyl groups etc (Sharmin *et al.*, 2012). Vegetable oils containing secondary hydroxyl groups that are located in the middle of their triglyceride alkyl chains have pendant or “dangling” chains exerting significant steric hindrance to crosslinking (thus incidentally acting as plasticizer) because they do not support stress under load (Guo *et al.*, 2000; Fan *et al.*, 2012). This has the effect of reducing PU rigidity. However, a number of researchers have reported that PU foams produced from natural oil polyols are often rigid or semi-rigid materials, their rigidity being closely associated with the formation of crosslinked structures and urea

linkages (Luo *et al.*, 2008; Kim *et al.*, 2008; Ogguniyi *et al.*, 1998).

Castor oil, a trifunctional vegetable oil, is distinguished from other vegetable oils by its high content (87-90%) of C-18 monounsaturated ricinoleic acid, and relatively high acetyl or hydroxyl value (Ogguniyi, 2006; Conceicao *et al.*, 2007).

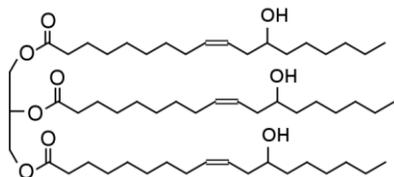


Fig. 1: Structure of castor oil triglyceride

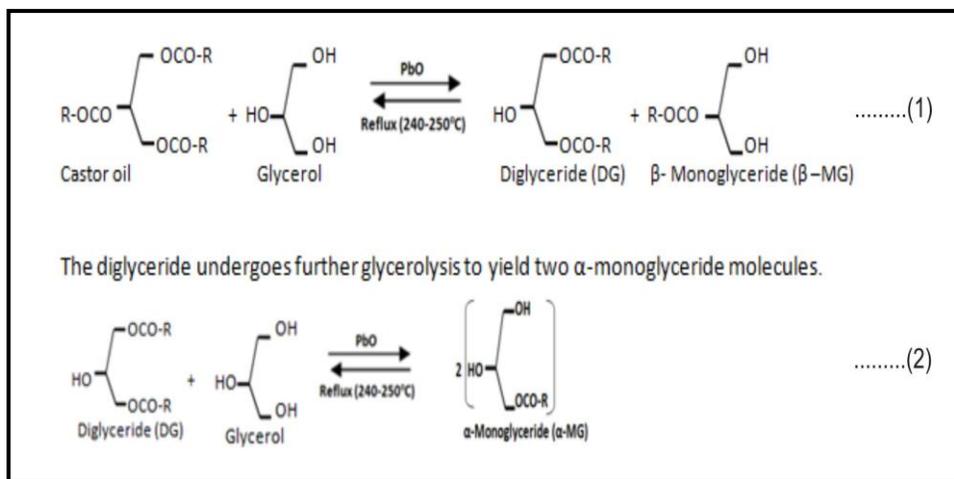
The presence of hydroxyl groups in the oil's fatty acid structure (Fig. 1) is responsible for urethane type reactions with diisocyanate for PU synthesis. The oil's long (C-18) carbon chain confer on it high thermal and hydrolytic stability, with the result that polymers derived from it exhibit high resistance to heat and humidity (Javni *et al.*, 2000; CastorOil.in, 2015). The oil is therefore naturally an excellent biorenewable raw material for

PU development. However, castor oil's hydroxyl number of 160-168 (WHC, 2012) is rather low, and its hydroxyl groups are secondary hydroxyls, which makes them much less reactive than primary hydroxyls (Herington and Hock, 1997). Castor oil is therefore chemically modified to raise its hydroxyl functionality and reactivity, and to enhance its structure and physical properties. Among various methods employed by researchers for the chemical modification of castor oil to generate polyols, the most widely used procedures are:

1. Epoxidation of the oil, followed by oxirane ring opening and subsequent hydroxylation (Sinadinovic-Fiser *et al.*, 2012).
2. Transesterification of the oil using polyhydroxy compounds such as ethanolamine, glycerol, pentaerythritol etc, in presence of acid/base catalyst (Mosiewicki *et al.*, 2009; Islam *et al.*, 2014).

Glycerolysis of castor oil

Scheme 1 depicts the high-temperature catalyzed glycerolysis of castor oil, resulting in the splitting of the triglyceride molecule in the oil to yield polyol fractions bearing additional hydroxyl group(s) (Kimmel, 2004), but with lower average molecular weight compared to castor oil itself.



Scheme 1: Glycerolysis of castor oil

Chemistry of PU synthesis

Polyol and organic polyisocyanate are the most important raw materials in PU synthesis, and the two react (in presence of blowing agents, catalysts and surfactant) according to the generalized PU reaction



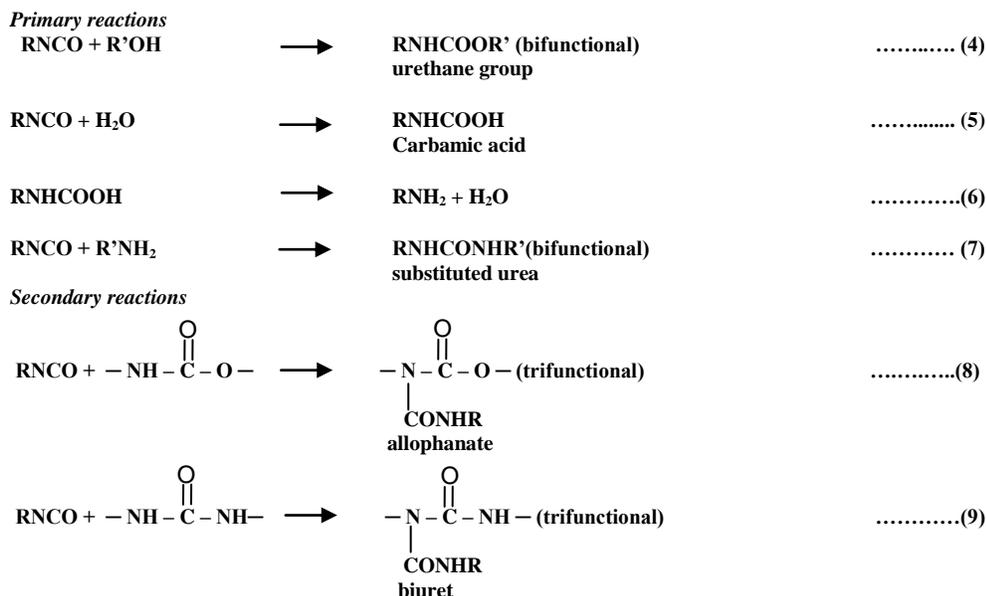
polyol
(where $n \geq 2$)

polyisocyanate

polyurethane

..... (3)

to produce linear product. However, other reactions also take place if there is stoichiometric excess of isocyanate in the formulation. This excess is needed to carry through all the primary and secondary PU reactions leading up to the formation of multifunctional allophanate and biuret moieties (Scheme 2).



Scheme 2: Primary and secondary reactions during PU foam synthesis.

The latter are associated with crosslinking and chain branching reactions that often result in network formation and foam rigidity (Luo *et al.*, 2008; Kim *et al.*, 2008).

Objective of the Study

Since rigid PUFs are mainly used as structural and engineering materials, their physical and mechanical properties are very important in determining their usefulness. This work involved the synthesis and physico-mechanical characterization of rigid PUFs from a chemically modified bio-renewable resource (castor oil); potentially environment-friendly products with other advantages and benefits (low cost, raw material abundance etc) derivable from the use of biobased polymeric materials generally.

II. MATERIALS AND METHODS

Materials

Castor oil was obtained by mechanical (cold-press) extraction from the seeds of wild *Ricinus communis* Linn at ambient temperature. Glycerol-modified castor oil polyols

(GMCOPs) with modifier concentrations of 10-60wt% and hydroxyl number range 168 – 320mgKOH/g were prepared in our laboratory. Other foam-making chemicals made up of TDI (80:20), silicone oil (surfactant), stannous octoate (gelation catalyst), DMAE (amine catalyst) and methylene chloride (physical blowing agent) were all kindly supplied by Vitafoam Nig. Plc, Jos. Distilled water was used as chemical blowing agent.

Methods

Foam Preparation

One-shot method of foam synthesis was used. Accurately measured quantities (as per formulations I and II) of all foam-making chemicals (less TDI) were premixed in a plastic mug for 20 seconds using a high speed (1000 rev/min) mechanical stirrer. This mixture and the required quantity of TDI were then rapidly added together and mixed until reaction mixture creamed. Contents were then quickly poured into an 18x15x9cm³ open cardboard mould with continuous, vigorous stirring, allowing the foaming product to rise freely. Foam was kept in a fume cupboard for 24 hrs to cure completely before demoulding.

Table 1: Foam Formulation I – NCO/OH ratio (1/2)

Component	Actual weight (g)	pph polyol
Neat/modified CO polyol	50.00	100.00
TDI	26.50	53.00
Methylene chloride	6.00	12.00
Stannous octoate	0.10	0.20
DMAE	0.225	0.45
Silicone oil	0.55	1.10
Water	2.25	4.50

Table 2: Foam Formulation II – NCO/OH ratio (1/1)

Component	Actual weight (g)	Pph polyol
Neat/modified CO polyol	50.00	100.00
TDI	49.10	98.20
Methylene chloride	1.50	3.00
Stannous octoate	0.25	0.50
DMAE	0.225	0.45
Silicone oil	0.25	2.50
Water	1.00	2.00

Process Parameters

Process parameters determined during foam synthesis were cream time, free-rise time, gel time and tack-free time. Foam rise was determined post-cure.

Determination of Physical Properties

Density determination

Density (kg/m³) of each foam sample was evaluated at room temperature as average of mass/volume measurement results of 5 specimens (dimension 3x3x3cm³) from the sample, as per ASTM D 1622-98 procedure.

Water absorption test

Water absorption test was performed on 15x7x0.2cm³ foam samples according to ASTM D 570-98 e1 procedure. Water absorption was measured by taking the initial and final weights of foam sample after dipping sample in distilled water in a measuring cylinder at room temperature for 24hrs. Excess water on foam surface was completely mopped up with tissue paper before reweighing. Water absorption of foam was evaluated using the expression.

$$\% \text{ water absorption} = \frac{\text{weight of wet foam} - \text{weight of initial foam}}{\text{weight of initial foam}} \times 100 \dots\dots (10)$$

Determination of mechanical properties

Compressive strength

Foam compressive strength was measured on a computer coupled Instron Universal Testing Machine – TechQuipment Ltd, Nottingham, UK (Model SM 1000). Instrument load capacity was 100KN (10 tons). Crosshead speed was 3.0 mm/min. ASTM D 1621-10 procedure was followed. Foam samples were punched out from the bulk foam in cylinders of 30mm diameter and

25mm length. Test specimen was placed between two metal plates parallel to the surface and compressive load applied. The maximum load (along with stress-strain data) was automatically recorded by the computer attached to the instrument. For each foam sample, 3 specimens were tested in compression and their results averaged. Compressive strength was taken as the force required at 10% deformation based on the original specimen thickness.

$$\text{Compressive strength} = \frac{\text{maximum compressive load (N)}}{\text{minimum cross-sectional area (m}^2\text{)}} \dots\dots (11)$$

Creep recovery

Creep recovery test was performed on a TecQuipment SM 1006 creep machine with a cell load of 250N and equipped with an SM 1006 CK thermocouple transmitter. Specimen shape of dimension 63.5mm x 4.8mm x 1.8mm was cut from the bulk foam. Specimen was fitted and gripped between steel support clips in the machine and subjected to a tensile force of 20N at a speed of 60 mm/min at ambient temperature, using the method of constant rate of extension. The maximum extension (mm) of the specimen was noted on removal of the applied load after 5 seconds. The amount of relaxation (mm) per specimen was also noted.

$$\% \text{ creep recovery} = \frac{\text{creep recovery or resilience}}{\text{extension on application of load}} \times 100 \dots\dots (12)$$

SEM

Cell morphology for 1mm thick specimens of RCPUFs and the neat foams was observed under a Phenom (Pro) scanning electron microscope. Dimensions of foam pores (pore diameter and strut thickness) were measured from SEM images obtained and arithmetic mean determined in each case.

III. RESULTS AND DISCUSSION

Table 3: Observed general features for GMF and neat CPUFs with NCO/OH ratio 1/1 in formulation

PU foam	Colour	Texture	Post-cure state
Neat foam	Pale yellow	Soft to spongy	No shrinkage
GMF*	White	Rigid	No shrinkage

* 10- 60 wt. % modifier concentration

Foam Process Parameters

Cream or initiation time is related to the beginning of foaming reaction between polyol, isocyanate and other raw material ingredients in foam formulation. Cream time generally decreased with increasing modifier concentration and NCO/OH

ratio (Table 4), indicating the influence of raising the amount of both hydroxyl and isocyanate components on lowering the thresh-hold or activation energy of foam reaction, as well as raising the reaction rate.

Table 4: Physical characteristics of GMFs at room temperature

Parameter	Modifier concentration (% w/w) in polyol													
	NCO/OH (1/2)							NCO/OH (1/1)						
	0	10	20	30	40	50	60	0	10	20	30	40	50	60
Cream time(s)	45	40	39.50	39	38	38	37	40	38	34	30	26	20	19
Free-rise time (s)	180	178	180	172	165	150	148	167	174	168	162	157	140	136
Foam rise (cm)	8	8.20	8.50	9.30	9.38	9.40	9.42	9	9.10	9.30	9.40	9.60	9.90	10.20
Gel time (s)	220	210	190	180	180	173	169	210	205	184	175	170	166	162
Tack-free time (s)	240	235	232	230	225	220	210	250	245	242	240	236	230	225
Density (Kg/m ³)	23.60	24.50	26.80	30.40	34	39.20	45.80	24.30	25.80	26.90	33.50	36.70	44.20	50.50
Water absorption (%w/w)	2.20	1.90	1.70	1.22	1.15	0.94	0.81	2	1.80	1.60	1.20	1.02	0.82	0.73

The latter is evident from generally shorter free-rise times and higher foam rise (Table 4) observed for GMFs with higher modifier concentrations and at the higher NCO/OH ratio of 1/1. Higher NCO/OH ratio appears to promote early and enhanced foaming and gelation reactions during foam synthesis. However, delayed cream time observed for the control (neat) foam generally is an indication of the lower reactivity of castor oil with organic isocyanate compared to conventional polyether polyols with hydroxyl numbers as high as 400-500mgKOH/g (Narine *et al.*, 2007).

During foam synthesis, gel time represents the onset of stable network formation through allophanate crosslinkings and urea linkages (Kim *et al.*, 2008). Later, the foam curing stage allows for crosslinking reactions in the foam to complete, resulting in increased foam stiffness (Rampf *et al.*, 2012). In the GMFs, added hydroxyl functionality (via glycerolysis) in the

modified polyol tended to enhance the formation of allophanate crosslinks and urea linkages (hard segments) resulting in rigid foams. This confirms the role of glycerol in this system essentially as that of a crosslinker. The control foam had fairly good cell structure, felt soft to spongy on touch and did not show signs of shrinkage. Foam shrinkage is associated with cell collapse as a result of pressure differences between the entrapped gas in closed cell foams, and the high external air pressure (Rampf *et al.*, 2012). Generally, the produced foams exhibited no shrinkage at room temperature (30-36°C), suggesting that the CPUFs are of good dimensional stability within this temperature range.

In Fig. 2, it is observed that GMFs exhibited relatively higher densities than the control/neat foam, with foam density increasing with modifier concentration and NCO/OH ratio.

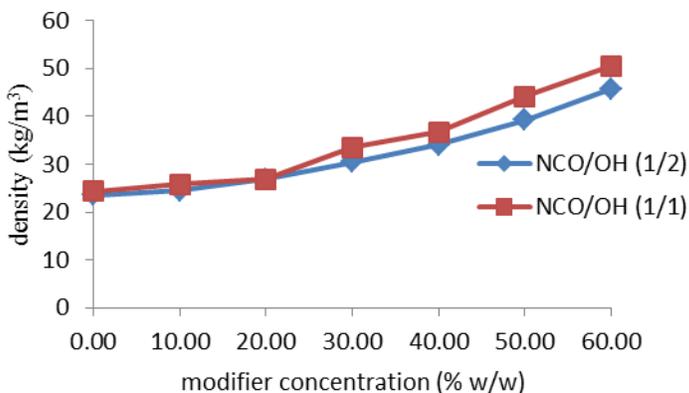


Fig. 2: Density versus concentration of CO modifier in GMF

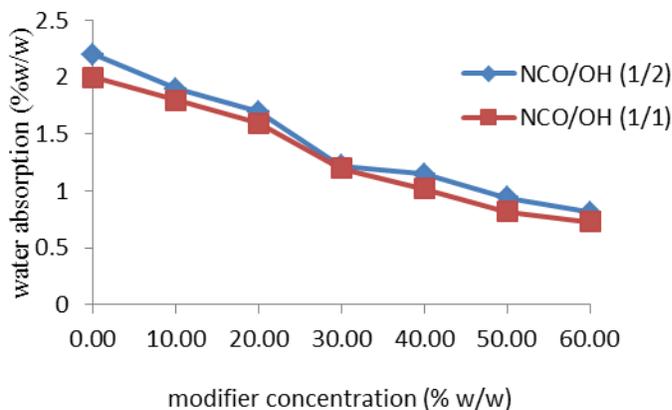


Fig. 3: Water absorption versus concentration of CO modifier in GMF foams

Highest densities were observed for GMFs containing 60wt% modifier at NCO/OH ratio 1/1. High density of GMFs is directly related to network formation and foam rigidity.

Foam water absorption

Fig. 3 depicts rapid fall in water absorption of GMFs with increased modifier concentration and NCO/OH ratio. This is as a result of the formation of more rigid, crosslinked structures at higher hydroxyl content in polyol, and at higher NCO/OH ratio in formulation as discussed earlier. In other words, water absorption of foam is inversely related to foam crosslink density. Water absorption is also related to foam dimensional stability, as well as its hydrolysis resistance (Vashisht and Kaushal, 2013). Rapid water uptake has the ability to cause dimensional instability and property deterioration in foams. Resistance to moisture permeability is therefore an important quality of PU foams especially those meant for outdoor application.

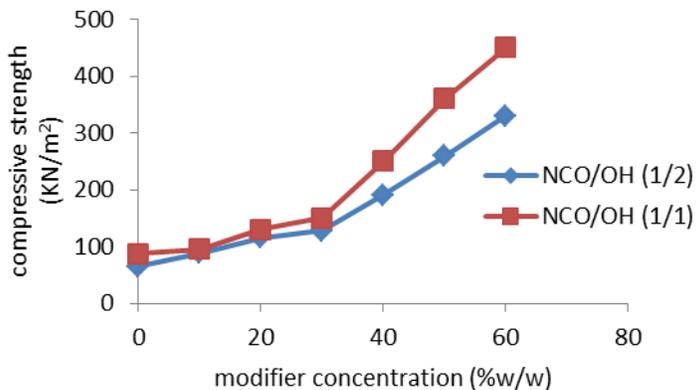


Fig. 4: Compressive strength versus modifier concentration in GMF foams

Mechanical properties of foam

Compressive strength

In Fig. 4 compressive strength of GMFs increased steadily up to about 30% modifier concentration, followed by a sharp, steep rise thereafter up to 60%, with foams prepared using formulation II (NCO/OH ratio of 1/1) yielding higher values. GMFs showed highest compressive strength value of up to 450KN/m². Higher isocyanate content resulted in increased hard segment content (through allophanate and urea linkages) in the foam matrix. Similarly, higher hydroxyl functionality in polyol also resulted in increased crosslinking reactions and formation of interchain network (Lim *et al.*, 2008). Both could result in increased foam crosslink density and greater rigidity in foam structure, making foam harder to compress.

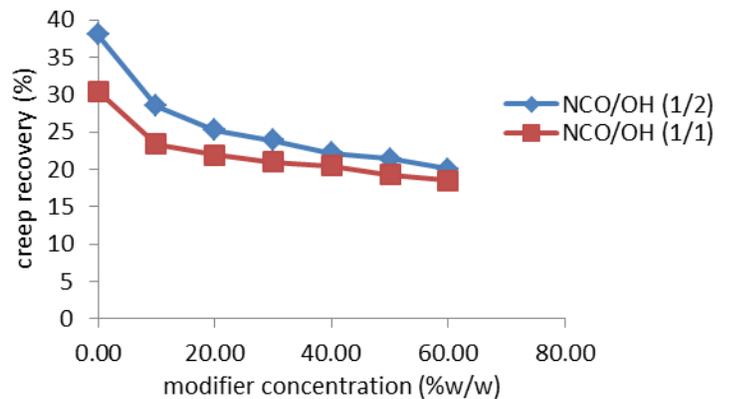


Fig.5: Creep recovery versus modifier concentration in GMF foams

Creep recovery

Foam creep recovery describes the extent to which a foamed polymer under plastic deformation recovers its original shape over time, when the stress/load applied on it is removed. In other words, creep recovery is a measure of foam resilience. Creep recovery of GMFs (Fig.5) decreases steadily with increase in modifier concentration.

Rigid GMFs containing 60wt% modifier gave the lowest % creep recovery of 18.50 and 20.00 respectively for NCO/OH ratios of 1/1 and 1/2 respectively.

Effect of foam density on mechanical properties

Mechanical properties of PU foams such as tensile strength, compressive strength, creep recovery etc are known to depend strongly on density (Saint-Michel *et al.*; 2006), as well as on material composition. Compressive strength is a “support” factor

that is related to load-bearing capacity, while creep recovery is an indicator of foam resilience. Both parameters are very important especially in foam applications that require high-energy impact absorption such as packaging, sporting footwears etc (Linul *et al.*; 2013).

This study has investigated the relationship between foam density and mechanical properties. In particular, the close relationship between foam density and compressive strength of GMFs has been noted. In Fig. 6, there is a steady increase in compressive strength of GMFs with increase in foam density. This is mainly because density of GMFs increases with increasing foam rigidity, the latter raising foam compressive strength.

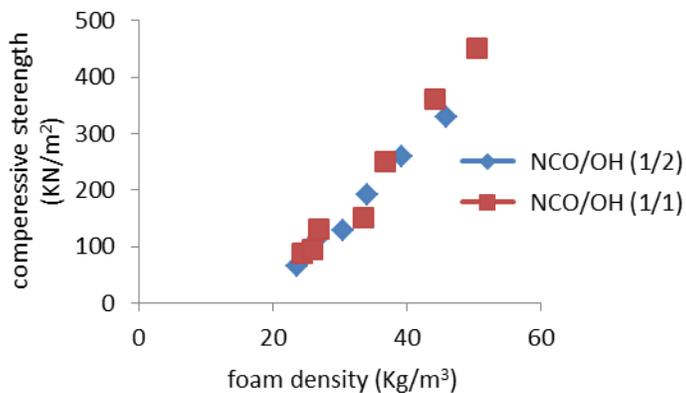


Fig. 6: Compressive strength versus foam density for the GMFs

For GMFs, whose densities are directly related to the hydroxyl functionality in the MCOPs, a plot of compressive strength against hydroxyl number of polyol (Fig. 7) also shows a direct relationship. Hydroxyl number in polyol is directly related to the extent of gelling reaction between polyol and isocyanate, and by extension, to the density of the resulting PU foam. This is in agreement with the works of Kanner and Decker (1969), Firdaus (2010) and Chan (2008) on soybean oil-based PUFs.

SEM analysis

Cellular morphology using SEM has revealed wide variation in pore size (0.10 - 0.25mm) and shape (mainly spherical and polyhedral), while strut thickness ranged from 25-50µm. The control or neat foam (Fig. 8a) shows a semi-rigid morphology with thick struts and almost even closed and open cell content.

GMF SEM micrographs (Figs 8b-d) are characterized by increasing solid content morphology with increasing modifier concentration, confirming the rigid structure of these foams. SEM micrograph of the 60wt% GMF foam (Fig. 8d) shows a fibre-like morphology, suggesting heavy network formation, due to extensive crosslinking and hydrogen bonding within the foam matrix.

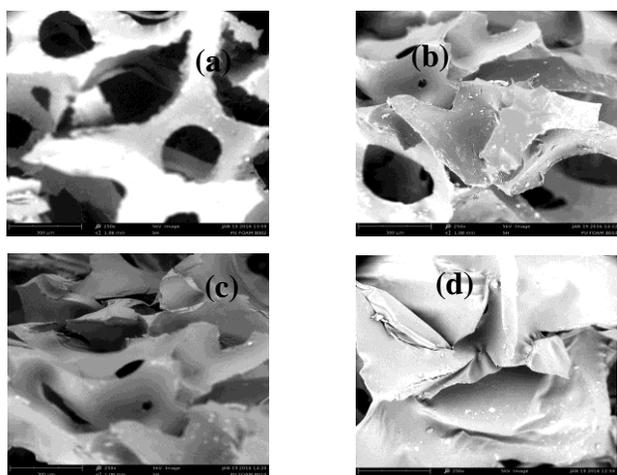


Fig. 8: CPUF (NCO/OH 1/1) SEM images
(a) control/neat foam; (b) GMF-20;
(c) GMF- 40; (d) GMF- 60

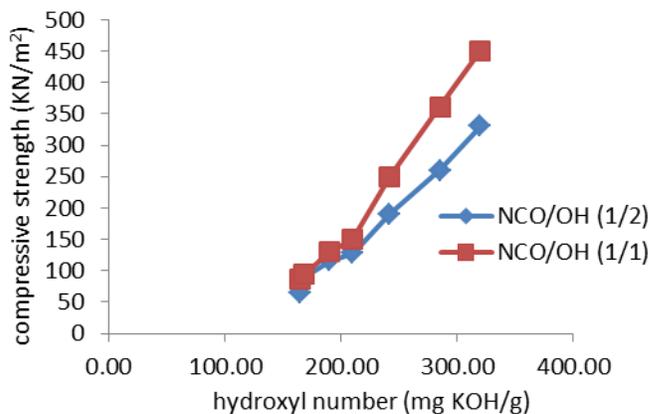


Fig. 7: Compressive strength of GMF foam versus hydroxyl number of GMCOP

IV. CONCLUSION

This study has investigated the physico-mechanical properties of rigid PUFs prepared from glycerol-modified castor oil polyols containing 10-60wt% of the modifier, using two different formulations with NCO/OH ratios of 1/2 and 1/1. The determined foam properties were wide-ranging in value. Foam rigidity, which increased with higher modifier concentration and NCO/OH ratio, was found to enhance density and compressive strength, the latter a measure of foam load-bearing capacity. On the other hand, rigidity adversely limited foam creep recovery, as foam lacked needed resilience to recover its original shape and foam on release of applied force/load. High resistance to water permeability shown by the GMFs (very low water absorption values) and their high solid content morphology (compared to the control/neat foam), as revealed by their SEM micrographs, are further evidences of heavily crosslinked, complex foam structures. With rigid PUFs generally used as insulation, packaging, refrigeration, flotation etc materials, wide-ranging physico-mechanical properties of the GMFs are potentials of their applicability across the entire utility spectrum of the RPUFs.

ACKNOWLEDGEMENT

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