STRUCTURE-PROPERTY RELATIONSHIPS OF CASTOR OIL-BASED POLYURETHANE FOAMS

BY

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B.Sc. (Hons) Chemistry (ABU), 1980; M.Sc. Polymer Science and Technology (ABU), 1985
Ph.D/SCIE/9886/2010-2011

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Department of Chemistry,

Ahmadu Bello University,

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DECLARATION

I hereby declare that this thesis titled " Structure-Property Relationships of Castor Oil-Based Polyurethane Foams" has been written by me, and that it is a record of my own research work.

As far as I know, no part of this thesis has been presented in any previous application for a higher degree at any university. All information derived from the literature has been duly acknowledged in the text and a list of references provided.

Name of Student	**Signature**	**Date**

CERTIFICATION

This thesis entitled " Structure-Property Relationships of Castor Oil Based Polyurethane Foams" by Yusuf, Abdulazeez Kankia, meets the regulation governing the award of degree of Doctor of Philosophy (Ph.D) of Ahmadu Bello University, Zaria, Nigeria, and is approved for its contribution to knowledge and literary presentation.

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Dean, School of Postgraduate Studies (Prof. Kabir Bala)	Date

DEDICATION

To the memory of my late father (Yusuf Magaji Kankia) and my late mother (Halima Yusuf Kankia).

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Yusuf, Abdulazeez Kankia

ABSTRACT

Mechanically extracted castor oil (CO) from the seeds of Nigerian wild castor plant (*Ricinus communis* Linn) was used after purification and chemical modification by PCl_5-chlorination and by lead (II) oxide (PbO)-catalysed glycerolysis. FTIR and GC-MS techniques were used for the structural characterisation of the neat and modified polyols, while titrimetric methods were used to determine their physico-chemical characteristics. Using two different formulations of isocyanate/polyol (NCO/OH) ratios of 1/2 and 1/1, rigid, semi-rigid and flexible CO-based polyurethane foams (COPUFs) were prepared by one-shot method. Foam reaction involved either neat CO or its modified polyols 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 (30-35^{0}C). Foam reaction took place in presence of stannous octoate and dimethylaminoethanol (DMAE) catalysts, methylene chloride (physical blowing agent) and silicone oil (surfactant). In addition to the basic foam formulation, $CaCO_3$-filler (2-20 wt%) was incorporated in selected sample preparations. Heptachlorotetradecane (HCTD) and heptachloroheptadecane (HCHD), two medium (straight)-chain chlorinated paraffins, were also incorporated in selected preparations as plasticisers and flame retardants (FRs) either singly or as blends of different weight ratios. All foams obtained were characterised in terms of their process parameters such as cream time, free-rise time, gel time, tack-free time and foam rise (ASTM D7487) as well as their physico-mechanical properties namely: density (ASTM D1622-08), water absorption (ASTM D570-98/D2842-12), compressive strength (ASTM D1621-10) and creep recovery (ASTM D2990-09). The structure-property relationships of COPUFs were established through process; physico-chemical, mechanical, morphology and flammability parameters. Glycerol-modified foams (GMFs) were found to be rigid and

moisture resistant, with their densities varying from 24.50-50.50 kg/m^3; water absorption (0.73-2.20 wt%); compressive strength (89.20-450.20 KN/m^2) and creep recovery (18.5-28.5%). Rigidity in the structure of GMFs increased with modifier concentration and at higher NCO/OH ratios. GMF rigidity was attributed to network formation likely resulting from allophanate and urea crosslinking reactions during foam synthesis. $CaCO_3$-filled foams (CFFs) have shown improvement in moisture resistance, density and compressive strength, but reduction in creep recovery compared to the control (neat) COPUF, with further property enhancements as filler loading was increased from 2-20 wt%. HCTD/HCHD plasticised COPUFs were found to be soft, flexible foams, especially at the lower NCO/OH ratio of 1/2, and at 50:50 (HCTD: HCHD) weight ratios. Foams were also characterised in terms of their flammability properties. Flame properties studied were ignition time (IT), flame propagation rate (FPR) and after-glow time (AGT). Results indicate that IT is closely related to the density of COPUF matrix. Additives (other than plasticisers) generally improved the density, compressive strength or fire retardancy characteristics of the COPUFs. FR treatment of COPUFs has revealed HCTD as a more effective individual FR than HCHD. This is explained in part in terms of greater absorbability (higher add-on) of HCTD in the COPUF system, and also in terms of a vapour phase radical quenching mechanism of action by which the shorter chain and more thermally unstable HCTD released more chlorine radicals per mole than HCHD, thus giving the former early and greater arrestive power of COPUF combustion processes. Microstructural imaging of foams using scanning electron microscopy (SEM) has revealed wide variation in pore size (0.10-0.35 mm) and shape (spherical, oblong and polyhedral), while wall thicknesses ranged from 18-50 μm.

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LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
AGT	After-glow time
AN	Acid number
ASTM	American Society for Testing and Materials
BD	1,4-Butadiene
BTPP	Butylated triphenyl phosphate
CFFs	$CaCO_3$-filled foams
CO	Castor oil
COP	Castor oil polyol
COPUF	Castor oil-based polyurethane foam
CP	Chlorinated paraffin
CT	Computer tomography
DEG	Diethylene glycol
DMAE	Dimethylaminoethanol
DOP	Dioctyl phthalate
DSC	Differential scanning calorimetry
EG	Ethylene glycol

FA	Fatty acid
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FPR	Flame propagation rate
FR	Flame (or fire) retardant
FRP	Fibre reinforced plastics/polymers
FTIR	Fourier transform infra-red (spectroscopy)
GC-MS	Gas chromatography-mass spectrometry
GMCOP	Glycerol-modified castor oil polyol
GMFs	Glycerol-modified foams
HCHD	Heptachloroheptadecane
HCTD	Heptachlorotetradecane
HN	Hydroxyl number
HS	Hard segment
IN	Iodine number
IPNs	Interpenetrating polymer networks
ISO	International Organisation for Standardisation
IT	Ignition time

LOI	Limiting oxygen index
MCOP	Modified castor oil polyol
MDI	4,4 -Diphenylmethane diisocyanate
Micro-CT	Micro-computer tomography
MPS	Mean pore size
MUFA	Mono-unsaturated fatty acid
MWT	Mean wall thickness
NCO/OH	Isocyanate/polyol ratio
NCOP	Neat castor oil polyol
NOPs	Natural oil polyols
OI	Oxygen index
OM	Optical microscopy
PEG	Polyethylene glycol
PMCOP	PCl_5-modified castor oil polyol
PMFs	PCl_5-modified foams
PN	Peroxide number
PPHP	Parts per hundred polyol
PS	Pore size
PU	Polyurethane

PUF	Polyurethane foam
PUFA	Poly-unsaturated fatty acid
RI	Refractive index
RPUF	Rigid polyurethane foam
RV	Relative viscosity
SAXS	Small angle X-ray scattering
SBOP	Soybean oil polyol
SEM	Scanning electron microscopy
SFA	Saturated fatty acid
SG	Specific gravity
SIPS	Structural insulating panels
SLCO	Sulphated castor oil
SN	Saponification number
SS	Soft segment
SSC	Soft segment concentration
TDI	Toluene diisocyanate
TEM	Transmission electron microscopy
Tg	Glass transition temperature
TIC	Total ion content

TPU	Thermoplastic polyurethane
UFA	Unsaturated fatty acid
UHS	Urea hard segment
WAXS	Wide angle X-ray scattering
WT	Wall thickness
X-ray CT	X-ray computer tomography
XRD	X-ray diffraction

CHAPTER ONE

INTRODUCTION

1.1 Preamble

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; Gupta *et al.*, 2010; Petrovic and Cvetkovic, 2012). On the other hand, the use of fossilised 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 bio-based materials (Husic *et al*., 2005; Luo *et al*., 2008; Jose *et al*; 2008). In terms of availability though, soybean, palm, rapeseed and sunflower oils are the most abundant (Zhang *et al*., 2007; Genova *et al*., 2008; Prociak, 2008). However, the use of non-edible vegetable oil like castor oil towards realising this goal obviously has other advantages related to food security. Moreover, world consumption of edible vegetable oils from 1995/1996 - 2014/2015, for

instance, has been on a steady rise, reaching 173.27 million metric tons in 2014/2015 (Fig.1.1) (Statistica, 2015). Focus, therefore, ought to be more on the exploitation of the non-edible stock (such as castor and jatropha oils), while preserving the edible ones mainly for human consumption. Even then, there could still arise the problem of vast land areas needed to cultivate large plantations of the non-edible stock, which could otherwise have been used for the edibles (Mazubert *et al.*, 2013).

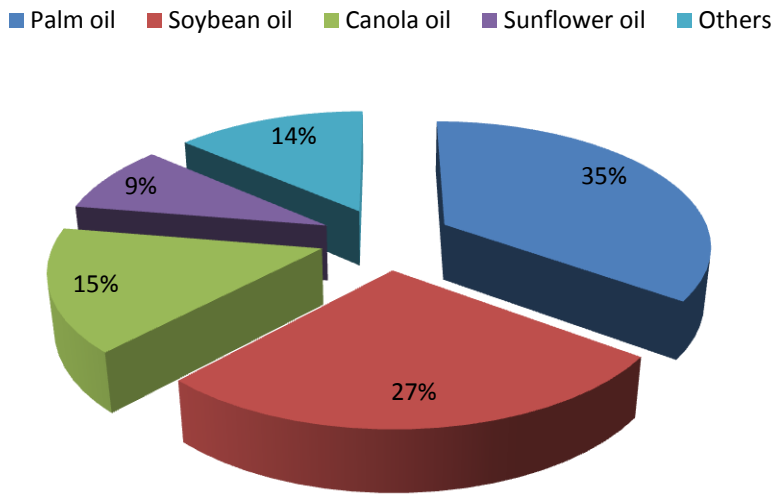


Fig.1.1: Global vegetable oil consumption by type (2014/2015)

Source: Statistica (2015)

This work represents a modest contribution, and an added impetus to the growing search for viable and sustainable options for replacing petroleum-based chemical feedstocks from among the more palatable and renewable bioresources of plant origin available. In Nigeria, the polyurethane (PU) foam industry is still stitched in mass importation of petro-polyols for PU foam production. This is costing the country large amounts of foreign exchange needed in other (more essential) sectors. Castor oil, non-edible and with its numerous advantages over other vegetable oils, is focused upon as a potential candidate for this replacement, especially in commercial PU development.

1.2 Polymers Based on Vegetable Oils

Vegetable oils and fats belong to a large family of hydrophobic chemical compounds called lipids. The oils are made up of triglyceride molecules, each molecule comprising three fatty acids attached to a glycerol backbone. According to Stenberg (2013), fatty acids make up about 94 - 96% of the total weight of triglycerides. Therefore, the properties and reactivity of triglycerides strongly depend on their composition, chain length, degree of unsaturation, number, distribution and location of hydroxyl groups etc (Sharmin *et al.*, 2012). In other words, vegetable oils are heterogeneous entities, with overall compositions and properties varying from oil to oil. Polymers can be synthesised from vegetable oils because the triglyceride molecules in the latter contain polymerisable sites or functional groups - usually double bonds, hydroxyl or epoxy groups. Various polymerisation reactions, including cationic, condensation, and radical copolymerisation reactions, have been used to produce different types of polymers such as polyesters, polyamides, epoxies and polyurethanes (PUs) (Del Rio, 2011).

Studies have shown that typical drying oils characterised by high unsaturation levels (notably linseed and tung oils) are transformed into hard, solid film-like materials on exposure to air for some time, because of the crosslinking between fatty acid (FA) chains through the atmospheric oxygen molecule (Taylor, 1950). For a very long time, drying oils have been used in oil paints and as surface-coating materials because of this property (Del Rio, 2011). However, for most vegetable oils, double bonds in triglycerides are not sufficiently reactive for any viable polymerisation process. Again, with the exception of castor and lesquerella oils, natural oils do not contain hydroxyls inherently (Appelqvist, 1989; Carlson *et al.*, 1990). Therefore, chemical modification is needed to add hydroxyls to natural oils to produce so called natural oil polyols (NOPs).

A polyol is a polymeric or oligomeric polyhydroxy compound of the type R $(OH)_n$ ($n \geq 2$) that can be used as raw material in PU synthesis. High molecular weight polyols with low hydroxyl functionality yield flexible PUs with lower glass transition temperatures (Tgs) than those synthesised with lower molecular weight and high functionality polyols (Del Rio, 2011). Compared to petroleum-based polyols such as polyether and polyester polyols with hydroxyl numbers of up to 400-500mgKOH/g (Narine *et al.*, 2007), NOPs typically have low hydroxyl functionalities and relatively high equivalent weights (Sherman, 2007).

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 plasticiser) because they do not support stress under load (Guo *et al.*, 2000; Xu *et al*., 2008; Fan *et al.*, 2012). This has the effect of reducing PU rigidity (Zlatanic, 2002). Thus, although such vegetable oils (e.g. castor oil) can be polymerized directly by reacting their secondary hydroxyls with diisocyanate to yield PUs, or with carboxylates to obtain thermosetting polyesters (Guner, 2006; Petrovic, 2008), the PU products were found to be of low compressive strengths, low modulus, low resilience and high Tg (Ramirez *et al.*,2008; Del Rio, 2011; Bleys, 2012). Chemical modification has provided substantial remedy to all these. Recent efforts have been directed towards chemical modification of vegetable oils to produce useful, cheaper and environmentally friendly polymers compared to petro-polyols (Saremi *et al.*, 2012). The modification introduces reactive groups into the FA chains to enhance polymerisability. This can be achieved by:

(1) Epoxidation, followed by oxirane ring opening (Okieimen *et al*., 2002;Tayde *et al*., 2011; Dworakowska *et al.*, 2012).

(2) Transesterification/alcoholysis using polyhydroxy compounds like glycerol, pentaerythritol etc (Schuchardt *et al*., 1998; Chakrabarti and Rafiq, 2008).

(3) Hydroformylation or ozonolysis, and subsequent hydrogenation (Narine *et al*., 2007).

(4) Halogen addition and nucleophilic substitution (Guo *et al*., 2000).

(5) Treatment with maleic anhydride to attach maleates (Eren *et al*., 2003).

(6) Enzymatic/microbial conversion (McNeil and Berger, 1993).

Chemical modifications make vegetable oils polymerisable because of the introduction of new and usually more reactive functional groups such as hydroxyls, epoxies or carboxyls (Del Rio, 2011). They also confer on the synthesised polymers enhanced structure and physical properties, in addition to imparting other desired characteristics on them. Many research studies on vegetable oil-based PUs have been performed in the last few decades. Vegetable oils, as renewable bioresources, are fast replacing conventional petroleum-based polyols in PU synthesis (Petrovic, 2008; Babb, 2012; Zhang *et al*., 2013).

In the polymer and chemical industry, vegetable oils which represent a major potential source of chemicals have been utilised as alternative feedstock for monomers in the production of biopolymers with diverse properties and applications. As polymers are widely used both in industry and daily life, they are quantitatively the most important products of the chemical industry. However, while most petroleum-based polymers are non-recyclable, polymers based on vegetable oils largely are (Fig. 1.2).

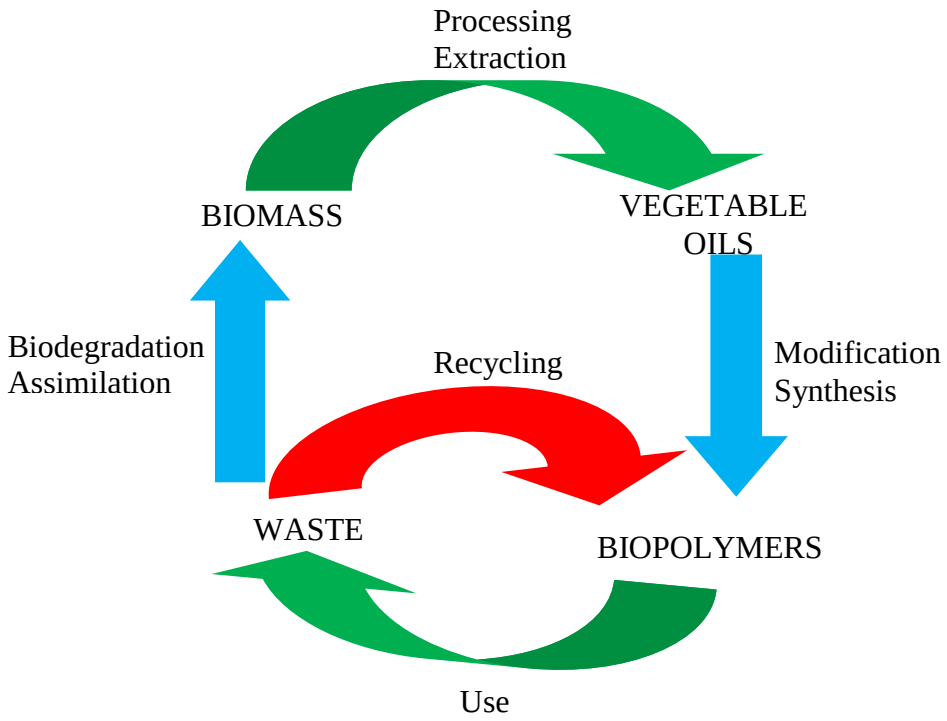


Fig.1.2: Life cycle of vegetable oil-based biopolymers

1.3 Castor Oil

Castor oil (CO) is a colourless to pale yellow vegetable oil derived from the castor plant (*Ricinus communis* Linn) belonging to the family *Euphorbiaceae*. The plant thrives well in tropical, subtropical and even warm temperate regions of the world (Salunke and Desai, 1992; Ogunniyi, 2006; Salihu *et al*., 2014), in addition to being drought and pest resistant. Global castor seed production is over one million tons per annum, with India, China and Brazil as major producers. In Nigeria, the castor plant is widely available throughout the country- but largely as uncultivated weed growing wild on marginal lands. The only reported (small scale) cultivation of the crop was in Kogi State, Nigeria (Dalen *et al.*, 2014), and in the eastern part of the country where the castor seed is popularly used as food condiment called *ogiri* after treatment and detoxification by fermentation (Achi, 2005).

Castor seed oil is extracted from dehulled and processed castor beans by mechanical expression (usually by hydraulic pressing or continuous screw pressing), solvent extraction or both. Mechanically extracted castor oil may be cold- or hot- pressed. Processing of castor beans involves a sequence of operations that may include pod or seed coat removal, winnowing, sorting, cleaning, grinding or milling, pre-heating etc. (Akpan *et al*., 2006; Alirezalu *et al.*, 2011; CastorOil.in, 2015). Average oil content for all castor seed varieties is about 46-55% (Ogunniyi, 2006). Oil yield, oil composition and quality will depend on seed variety and quality, as well as geographic origin and climatic conditions around the resource castor crop (Ogunniyi, 2006; Alirezalu *et al.*, 2011; Oluwole *et al.*, 2015). Oil yield and recovery will also depend on the extraction method (s) used and the prevailing extraction conditions (Olaniyan, 2010).

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 (Ogunniyi, 2006; Conceicao *et al.*, 2007).

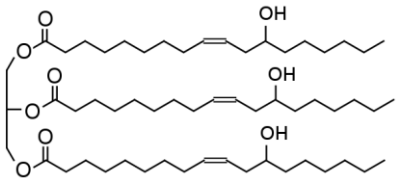
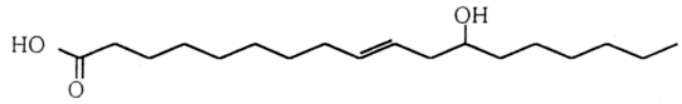
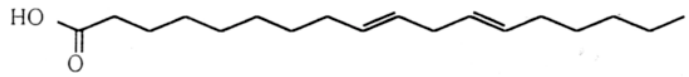
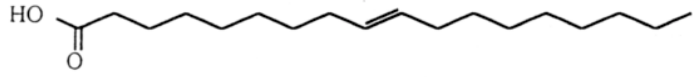
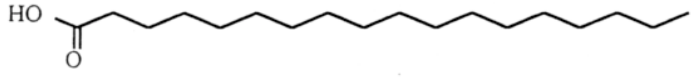
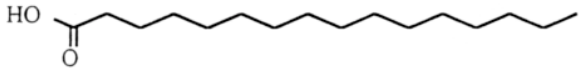
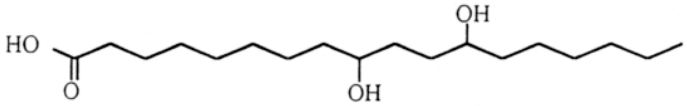
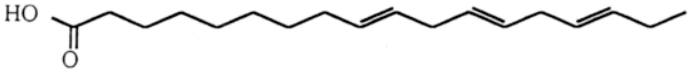
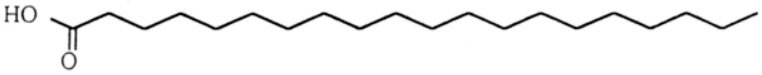


Fig.1. 3: Structure of castor oil triglyceride

The oil also contains other fatty acids that include oleic, linoleic, stearic, palmitic and linolenic acids (Table 1.1).

Table 1.1: Fatty acid composition in castor oil (Dave, 2002)

Weight% Fatty acid	Structure
89.5 % Ricinoleic Acid	
4.2% Linoleic Acid	
3.0% Oleic Acid	
1.0% Stearic Acid	
1.0% Palmitic Acid	
0.7 % Dihydroxystearic Acid	
0.3% Linolenic Acid	
0.3% Eicosanoic Acid	

High ricinoleic acid content gives castor oil high degree of purity. The chemistry of castor oil is centred on its high ricinoleic acid content, and the three main reaction sites or functional groups in the triglyceride molecules. Specifically, the ester linkages, the double bonds and hydroxyl groups in the oil provide reaction sites for the preparation of many useful castor oil derivatives. The presence of hydroxyl groups in the oil's fatty acid structure (Fig. 1.3) is responsible for urethane type reactions with diisocynate 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; Zlatanic *et al.*, 2002; CastorOil.in, 2015). The oil is therefore naturally an excellent biorenewable raw material for PU development. Castor oil has a growing international market assured by

more than 700 uses ranging from medicines to cosmetics, to substituting petroleum in the production of biodiesel, plastics and lubricants (Weiss, 2000; CIREP, 2007). This makes the oil versatile seed oil with very high utilitarian value compared to other vegetable oils.

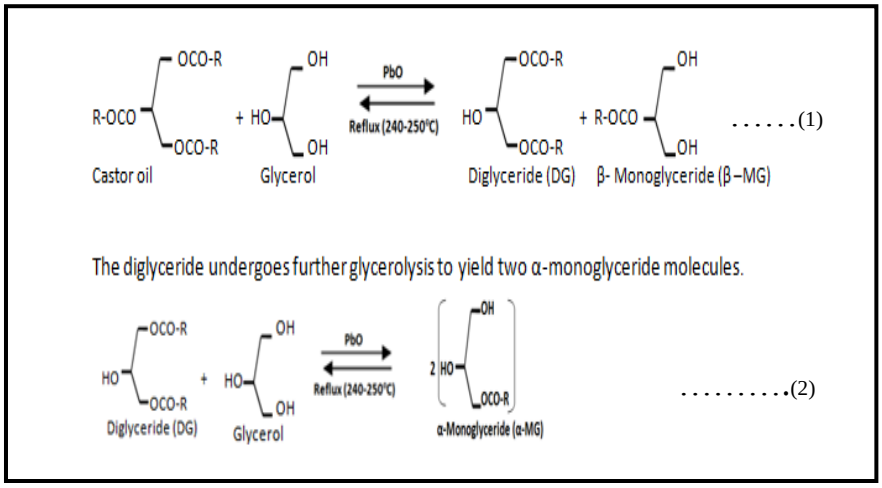
However, castor oil's hydroxyl number of 160-168 (WHC, 2012) is rather low, and its hydroxyl groups are secondary hydroxyls. It is known that isocyanate reacts faster with primary hydroxyl groups than with secondary hydroxyls (Ionescu, 2005). It is estimated that the reactivity of secondary hydroxyls is only about one-third that of primary hydroxyls (Herington and Hock, 1997). Furthermore, attaching hydroxyl groups to castor oil especially on primary carbon atoms not only increases the hydroxyl functionality of the oil, but also enhances its thermal stability (Liu *et al*., 2014). Consequently, PUs from polyols with primary hydroxyls are more stable than those with secondary hydroxyls (Tassie, 2014). 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:

(i) Epoxidation of the oil, followed by oxirane ring opening and subsequent hydroxylation (Sinadinovic-Fiser *et al.*, 2012).

(ii) 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).

1.4 Glycerolysis of Castor Oil

Scheme 1 depicts the high-temperature, PbO-catalysed 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

However, partial glycerolysis of castor oil yields a mixture of mono- and diglycerides (Equation 1), with some free hydroxyl groups in the reaction mixture.

1.5 Polyurethanes (PUs)

Polyurethanes are polymers containing the urethane or carbamate linkage (-NHCO-O-) as repeat unit in their molecular backbones. It was the pioneering work of Dr. Otto Bayer and his co-workers that not only produced the first PUs in 1937 (work actually published in 1947), but also provided the fundamental chemistry for the PU industry. Later, the first PU elastomers were produced in 1940 as a World War II programme to develop viable alternatives to rubber. Production of flexible PUs only came on stream

in 1954. In 1967, urethane modified polyisocyanurate rigid foams were introduced to offer better thermal stability and flammability resistance.

PUs generally are chemically diverse materials with corresponding diverse physical and chemical properties. As a result, PUs can be tailored to meet diversified demands of various applications such as coatings, adhesives, fibres, thermoplastic elastomers and foams. However, the advent of bio-based PUs was the result of increasing costs of petrochemicals, as well as rising and sustained environmental concerns on the negative impacts of petroleum-based polymers.

1.6 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 generalised PU reaction

$$\mathbf{R(OH)n} + \mathbf{R^1\text{-}(N{=}C{=}O)n} \rightarrow \mathbf{R - (NH.CO\text{-}O)_n\text{-}R^1} \qquad \mathbf{(3)}$$

polyol polyisocyanate polyurethane

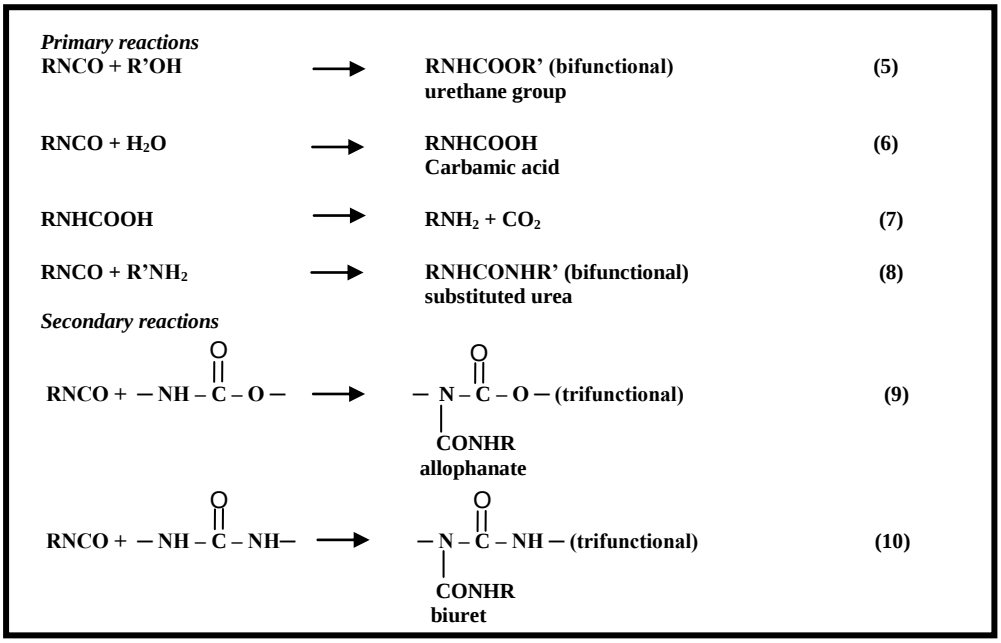
(where $n \geq 2$)

to produce linear product. Isocyanate functionality is the foundation of PU chemistry. The reactivity of the isocyanate group towards active-hydrogen compounds is largely due to the ability of this group to form resonance structures (below).

$$\mathbf{-N^{\ominus}\text{-}C{=}O^{\oplus} \longleftrightarrow -N{=}C{=}O \longleftrightarrow -N^{\oplus}{=}C\text{-}O^{\ominus}} \qquad \mathbf{(4)}$$

Attack of nucleophilic centres on the electrophilic carbon atom by active-hydrogen compounds (electron donors) is responsible for initiating chemical reaction between the two species (Sykes, 1999) to produce activated complex as intermediate.

However, other reactions also take place if there is a 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). Consequently, most PU products obtained from vegetable oil polyols have been found to be crosslinked materials or thermosets (Guo *et al.*, 2000; Zlatanic *et al.*, 2002; Petrovic *et al.*, 2005).

The association of three isocyanate groups into cyclic trimer units (isocyanurates) that are capable of chain branching and crosslinking is another possibility (Wirpsza, 1993) (Fig. 1.4).

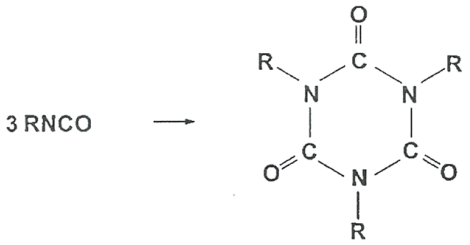


Fig. 1.4: Structure of isocyanurate trimer

This also leads to network formation to yield rigid polyisocyanurates (Del Rio, 2011), the latter more heavily crosslinked than rigid polyurethanes. In other words, two types of rigid foams are derivable from this system - rigid polyurethanes and rigid polyisocyanurates.

1.7 Polyurethane Foams (PUFs)

PUFs are cellular plastics with versatile applications in thermal insulation, packaging, cushioning and floor covering (Brydson, 1999). Rigid PUFs are used as structural and engineering materials especially in construction, thermal insulation, buoyancy and refrigeration, while flexible PUFs are mainly used as cushioning, seating and packaging materials (Woods, 1990). Use of rigid foams is as a result of their low heat conduction coefficient (very low heat transfer), low water absorption and relatively good mechanical strength (Randall and Lee, 2002). However, any foamed material is a good insulator by virtue of the low conductivity of the gas (air) contained in the system.

Polyurethane foams differ from unfoamed polyurethanes in that their production requires the incorporation of a gas that will expand or blow the polymer into a foam.

This confers on the former greater impact absorption capacity than the latter. The basic principle of foaming is the dispersion of the gas phase in a liquid to obtain a liquid foam which later solidifies into solid cellular product in contact with air. The reaction between isocyanate group and water generates amine and carbon dioxide gas, the latter starting or initiating a blowing process that is aided by heat generated due to the exothermic nature of the reaction, and thus giving the foam its cellular structure. The density of foam largely depends on the amount of carbon dioxide gas produced (Bhatnagar, 1992). The amine reacts with other diisocyanates, resulting in urea-linkages in the foam. The polyol (soft) phase, on reacting with isocyanate groups, covalently bonds with urea hard segments through urethane linkages (Aneja, 2002).

PU foams are cellular structured polyurethanes consisting of a network of spherical, quasi-spherical, octahedral or pentagonal dodecahedral cells which behave as micro-springs (Herrington and Hock, 1998). Each cell may be completely enclosed by a membrane (impermeable) or it may be inter-connected with its neighbours (permeable or porous). By nature of cells, two main types of foams exist namely, rigid and flexible foams (Fig.1.5).

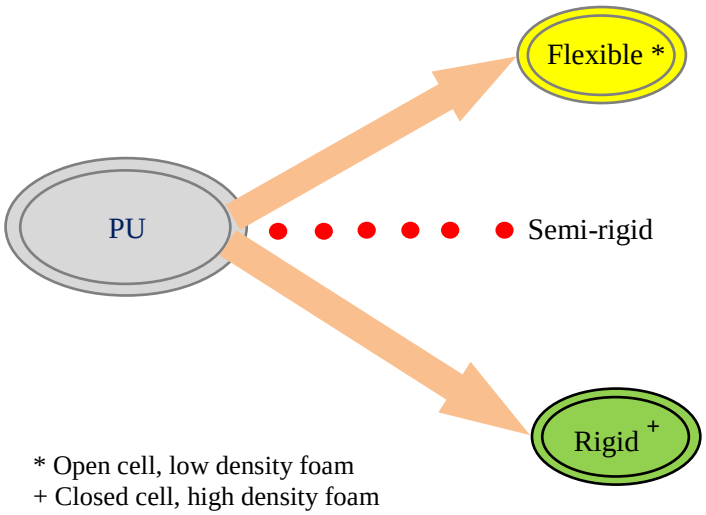


Fig.1.5: Types of polyurethane (PU) foams

However, by appropriate selection of reactants and controlling conditions for the foaming process, it is possible to produce rigid, semi-rigid or flexible foams (Bhatnagar, 2004). The semi-rigid foams may be used in specialty applications where some load bearing and impact resistance properties are required at the same time (Northstar Polymers, 2000- 2007).

1.7.1 Cell structure

The presence or absence of windows in the cells or the number of windows per cell, which constitutes the cell structure, is a function of the process by which the foam is made. Rigid foams are high density, closed-cell foams. The closed cells (spherical) are small, tightly walled individual cells, that do not allow air or liquid permeability, and in which heat transfer is very low. This makes rigid foams good thermal insulators, with a high degree of buoyancy (Sivertsen, 2007). Flexible foams on the other hand are low density, open cell foams. They are made up of larger, loosely or incompletely walled inter-connected cells that are porous. Such cells will act as a sponge, sucking up liquid by capillary action (Aneja, 2002). Cellular morphologies of PU foams can be captured and probed using various microscopic techniques that include optical microscopy (OM), scanning electron microscopy (SEM), small angle x-ray scattering (SAXS), atomic force microscopy (AFM) etc. (Tyagi *et al*., 1986; Kaushiva *et al*., 2000; Aneja and Wilkes, 2002).

1.8 Castor Oil-Based PUFs (COPUFs)

PUFs produced from castor oil polyols are known to have some excellent chemical and physical properties such as enhanced hydrolytic and thermal stability due largely to the

hydrophobic nature of their triglycerides (Zlatanic *et al.*, 2002; CastorOil.in, 2015), in addition to their environment-friendly nature. However, most PU products obtained from vegetable oil polyols (including castor oil polyols) have been found to be crosslinked materials or thermosets (Guo *et al*., 2000; Zlatanic *et al*., 2002; Petrovic *et al.*, 2005). This has constituted a serious problem especially with regards to the production of soft, flexible PUFs that are widely used both in industry and daily life as cushioning, packaging and adhesive materials. In order to obtain soft, flexible PUFs based on renewable castor oil polyol, many researchers resorted to blending conventional petroleum-based polyether polyols with varying proportions of castor oil as replacement of the base polyol (Ogunniyi *et al*., 1998; Xu *et al.*, 2008; Zhang, 2008; Chan, 2008; Xing, 2014). Although cost-benefit analysis of blending polyether polyol and castor oil has indicated some level of cost effectiveness (Ogunfeyitimi *et al*., 2012; Thorat and Patil, 2015), these mixed polyol recipes were not quite successful, as the castor oil proportion needed to produce soft, flexible foams was no more than 20 - 25% (Ogunniyi *et al.*, 1998; Ogunfeyitimi *et al*., 2012; Dalen *et al.*, 2014). Moreover, in such mixed polyol formulations, the compatibility question between castor oil and conventional polyether polyol is a very important one. Current challenges therefore are on how to make or produce soft, flexible PU foams from 100% castor oil content as polyol component in foam formulation. This could lead to substantial reduction in production cost and the maximal exploitation of castor oil as raw material for flexible PUF production. Consistent with this, the present work has sought to produce soft, flexible castor oil-based PUFs by the use of two moderately long, straight-chain chlorinated paraffins (CPs) (formulae $C_{14}H_{23}Cl_7$ and $C_{17}H_{29}Cl_7$) as internal liquid plasticizers introduced *in-situ* in castor oil polyol component of foam formulation during foam synthesis. These CPs, whose physico-chemical properties depend largely

on their chain length and chlorine content (Houghton, 2003), are compatible with oils generally, and are reported to have advantage over conventional plasticisers by both increasing the flexibility of a material, as well as enhancing its fire retardancy and low temperature strength (Klorfin, 2012). Details on this novel application are discussed in later chapters of this work.

1.9 Polymer Foam Formulations

In foam making, the desired end-properties of the foam dictate the choice of specific components along with their required quantities (Aneja, 2002). Major components needed to synthesise PU foam are diisocyanate, polyol, water, physical blowing agents, catalysts, surfactants and cross-linking agents. However, the most important components are polyol and diisocyanate. Hence their unique functionalities, polarities and symmetries must be considered in working out foam making recipes. PU formulations can be tailored and/or controlled to produce a wide range of materials with varied properties and end-uses. The materials include:

(i) Low density flexible foam

(ii) High density rigid foam

(iii) Soft solid elastomers

(iv) Hard solid plastics

(v) Coatings, adhesives, fibres and sealants.

Stiffness and elastic behavior of foam, for instance, can be adjusted by controlling the hard segment (HS) to soft segment (SS) ratio in the formulation (Aneja, 2002).

In PU foam formulations, two types of diisocyanates (both aromatic) are used namely, toluene diisocyanate (TDI) and methylene diphenyl isocyanate (MDI). The diisocyanate is a mixture of two isomers which differ slightly in reaction rate.

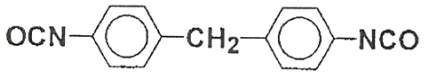


Fig.1.6: 4,4'-Diphenylmethane diisocyanate (MDI)

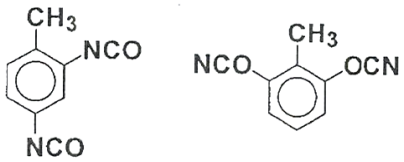


Fig.1.7: 2,4- and 2,6-Toluene diisocyanate (TDI)

The major advantage of the aromatic diisocyanates in PU systems is that they react faster, while their aliphatic counterparts are more UV-stable, and do not undergo yellowing on exposure to light (Sykes, 1999). Isocyanates constitute the hard segment of foamed PUs. Isocyanate added to the formulation is usually reported by an index number. An isocyanate index of 100 indicates that there is a stoichiometric amount of isocyanate added to react with functional groups from the polyol, water and cross-linkers in the formulation. Polyols on the other hand, constitute the soft phase or soft segment of PU foam. Two kinds of polyols commercially available for PU foam production are the polyesters and polyethers. However, almost 90% of the PU foam market utilises polyether polyols based on polypropylene oxide in comparison to

polyester polyol. Advantages of the polyether polyols include low cost, better hydrolysis resistance, better resilience and better ease of handling (Aneja, 2002).

Polyols used in flexible foam formulation are higher molecular weight compounds (3000-6000gmol^{-1}) compounds, with average functionalities of 2.5-3.0 (Herrington and Hock, 1998). Flexible foams are formed by a process of simultaneous polymerisation and expansion. The gas for expansion is primarily carbon dioxide produced by the reaction of isocyanate and water. The reaction with water also produces substituted urea cross-links, which stabilizes the expanding foam. To prevent serious foam shrinkage, the cells must be open to allow air to penetrate. Rigid urethane foams, however, are made from more highly branched lower molecular weight polyols with functionalities as high as 8.0 (Aneja, 2002). The increased branching and shorter aliphatic chains contribute to more rigid molecular structures. Because of the lower hydroxyl equivalent weight of the polyol, a higher concentration of aromatic polyisocyanate is needed to obtain the same equivalent ratio. Rigidity of PU is closely associated with the formation of cross-linked structures and urea linkages (Luo *et al*., 2008; Kim *et al*., 2008; Ogunniyi *et al.*, 1998).

The basis for the formulation of rigid PU foams is the same as that used for flexible foams, with the exception that rigid foams are highly cross-linked structures. This would imply among others, greater isocyanate/polyol (NCO/OH) ratio, i.e. stoichiometric excess of isocyanate, less amount of water and use of a polyol with hydroxyl functionality not less than 3 in foam formulation. Isocyanate and polyol are the most basic ingredients. An organotin compound catalyses the reaction, especially in the presence of small amount of tertiary amine. Silicone surfactant regulates the cell size uniformity and also controls the viscosity and surface tension of the cell membranes as they are stretched during foaming. Physical blowing agent is also

introduced and this increases the total volume without itself participating in the chemical reactions that are occurring. Water is not an essential ingredient. Table 1.2 represents formulation basics for flexible PU foams, while Table 1.3 gives a recipe for rigid polyurethane foam synthesis.

Table 1.2: Formulation basics for flexible polyurethane foams (Herrington and Hock, 1998).

Component	Parts by weight
Polyol	100
Inorganic Fillers	0 -150
Water	1.5 - 7.5
Silicone Copolymer Surfactant	0.5 - 2.5
Amine Catalyst	0.1-1.0
Tin Catalyst	0.0- 0.5
Chain-Extender	0 - 10
Cross-Linker	0 - 5
Additive	Variable
Auxiliary Blowing Agent	0 - 35
Diisocyanate	25- 85

Table 1.3: Typical formulation for rigid polyurethane foam synthesis (Chanda and Roy, 2006).

Component	Parts by weight
Polyol ($f \geq 3$)	100
Catalyst 1 (N,N-cyclohexylamine)	0.3
Catalyst 2 (N,N-dimethylethanolamine)	0.3
Freon II ($CFCl_3$)	50
Water	1
Surfactant (block copolymer of polyether and silicone)	1
4,4-diphenylmethane diisocyanate (MDI) (index = 100)	100

Two reactions (blow and gelation) go on simultaneously in the foaming process. Hence catalysts are chosen for each reaction such that there is balancing of the reactions to avoid collapsing of product, and ensuring expansion of the foam structure. Also, uniform mixing of reactants is necessary to produce a homogeneous foam. It has been

observed that adequate, uniform mixing enhances both the gas blowing and cross-linking reactions, while improper mixing results in foams with relatively big cell size and low resilience (Adogbo and Atiwurcha, 2014). Because foaming reaction takes place very rapidly, large scale production of foam demands automatic mixing equipment.

1.10 Structure-Property Relationship in Polymers

Natural and synthetic polymers are known to exhibit wide diversity of properties. Some are rigid, hard, strong and dimensionally stable, while others appear soft, flexible or largely extensible under the influence of stress. Some show ready solubility and fusibility, while others appear more resistant to heat and solvents. In many biological macromolecules such as polynucleic acids (e.g. ribonucleic acid, RNA, and deoxyribonucleic acid, DNA), proteins, celluloses, lipids etc, structure-property relationships are strongly influenced by hydrogen bonding and crystallisation (Jeffrey and Saenger, 1994; Alper, 2002; Vogel, 2002). However, synthetic polymers are produced on an industrial scale primarily for use as structural materials. Their physical properties are particularly important in determining their usefulness, be they rubbers, plastics or fibres. According to Ghosh (2006), factors that influence polymer properties in general are: molar cohesion, polarity, molecular weight, crystallinity, overall molecular symmetry (both recurrence symmetry and architectural symmetry), linearity and non-linearity of chain molecules. Higher molecular weight permits greater degree of chain entanglements, thus resulting in higher melting temperature (T_M) and tensile strength (TS). Branching will make the polymer less resistant to solvents, chemicals and heat owing to increased mobility manifested through the branch units or pendant

groups. But high degrees of branching with enhanced branch lengths and ultimate crosslinking render the polymer relatively stiff, arising from greater degrees of chain entanglement and leading to the formation of giant molecules with a network structure. This restrains large scale molecular mobility or chain slippage, thus improving dimensional stability and resistances to thermal and mechanical loading.

Crosslinking causes basic structural changes in polymers, with attendant changes in polymer properties. Crosslinks are very important in determining physical properties because they increase molecular weight and limit translational motions of polymer chains with respect to one another. Presence of a few crosslinks is enough to greatly reduce solubility of a polymer and produce a gel polymer (Ghosh, 2006). Thus, the tendency to absorb solvents decreases as the degree of crosslinking is increased because the chains cannot move enough to allow the solvent molecules to penetrate between the chains. But polymers that are not highly crosslinked have properties that depend greatly on the forces that act between the chains.

1.11 Effect of Filler Incorporation on Morphology and Structure of PUFs

The use of reinforcing fillers in PU foam formulations produces composite materials with modified morphology and structure, and enhanced performance (Lees, 2013). However, satisfactory performance of such composites depends to a large extent on the degree of dispersion of the reinforcing filler in the polymer matrix, and strong interfacial filler-matrix interaction and adhesion. In PU foams, mechanical properties are primarily controlled by the cellular structure of the PU, as well as the nature of chemicals that constitute the hard and soft segment phases in the foam structure. In flexible PU foams, fillers fill voids in the open-cell porous structure of the polymer

matrix, to promote among others an increase in density and resistance to compression, with attendant improvement in mechanical strength (Latinwo *et al.*, 2010). They however reduce resilience, and contribute to an increase in permanent deformation (Usman *et al.*, 2012). Many studies have shown that modification in the properties of flexible PU foams is achieved by the dispersion of the filler particles across the polymer matrix along with polyurea hard segments. In this way, shape, size and mobility of hard domains, mobility of soft segments, load bearing characteristics and overall flexibility and modulus of the polymer matrix can be affected (Agarry *et al.*, 2015). This means that compatibility between the reinforcing filler and the polymer matrix is a very important issue.

Reinforcing fillers used in flexible PU foam formulations include inorganic fillers (e.g. calcium carbonate, dolomite, aluminium silica, talc etc) and organic materials (carbon black, natural fibres such as wood and non-wood fibres) (Mothe and Araujo, 2000; Mothe *et al.*, 2002). However, calcium carbonate and glass fibre are the most commonly used (Lees, 2013). Calcium carbonate (whether micro- or macro-sized) is known to improve significantly, load-bearing properties and modulus characteristics of PUs (Nunes *et al.*, 2000; Chen *et al.*, 2002; Latinwo *et al.*, 2010); while glass generally confers high strength and high modulus to the reinforced polymer (John, 2001). The need for filler reinforced plastic composites generally arises because conventional materials cannot meet many desired property requirements of modern technology. Hence the use of metallic/mineral particles as well as glass or fibre to achieve material property requirement in plastics and other engineering materials is a well known practice (Cotgreave and Shortall, 1977; Javni *et al.*, 2011).

1.12 Flammability Characteristics of PUFs

Polymer foams are very flammable on account of their high hydrocarbon content as organic polymers, as well as their predominantly cellular structure (Wilde, 1980). The latter allows for a lot of air permeability within the foam matrix. With regard to air permeability, flexible or open cell foams are less dense and more porous than rigid foams, and therefore more flammable (Sivertsen, 2007). Ease of ignitability and high combustibility tend to limit the application of foamed polymers as mattresses, cushioning and seating materials, packaging materials, insulators in building and construction etc. The flammability of PUFs is therefore an important industrial issue.

A major challenge in the use of PUFs both in domestic and industrial applications is how to reduce the flammability of these materials to enhance their safety of application. Flame retardants (FRs) are chemicals used to lower the ignitability and combustibility of polymers, thereby reducing the risk associated with incident fires that have become regular occurrences in everyday life (Eboatu *et al*., 1995).

From literature, FR chemicals usually incorporated into PUFs to reduce their flammability include phosphorus-containing compounds, halogen-containing compounds, nitrogen-containing additives, silicone-containing products etc. (Pearce, 1986; Weil and Levchik, 2004; Singh and Jain, 2008; Papazoglou, 1994; Jurs, 2004; Wang *et al*., 2012). Halogen-containing FRs in particular have been used either singly or as mixtures with synergists like Sb_4O_6, Fe_2O_3, ZnO etc. (Lyons, 1970; Kurt and Reegen, 1975). However, a major disadvantage of some halogenated FRs in PU foams is that they are not only potential toxicants at moderately low to high temperatures, but that they are also susceptible to hydrolysis (Singh and Jain, 2008).

The thermal degradation of PU foams and its relation to foam ignition have been studied with a variety of analytical and existing fire-test methods (Tang *et al*., 2002; Hager *et al*., 2004; Lefebvre *et al*., 2004). Among major parameters studied in these systems are ignition time, flame propagation rate, after-glow time, heat release rate, mass loss rate, smoke density etc. The thermal stability and ignition of conventional PU foam depends on the composition (Lefebvre *et al*., 2005). When PU foam is subjected to heat, various PU linkages are broken at different temperatures (Singh and Jain, 2008). The dissociation of PU foam linkages at different temperatures is shown in Table 1.4.

Table 1.4: Dissociation of Polyurethane Foam Linkages at Different Temperatures (Singh and Jain, 2008).

Linkage	Dissociation temperature (^{0}C)
Allophanate	100–120
Biuret	115–125
Urea	160–200
Urethane	180–200
Disubstituted urea	235–250
Carbodiimide	250–280
Isocyanurate	270–300

Halogen-containing FRs, for instance, have been reported as acting chemically by radical quenching in the vapour phase to interfere at particular stages of the polymer combustion process (Dufton, 2003; Weil and Levchik, 2009; Laoutid *et al*., 2009).

Flammability testing is essentially an assessment of how easily a material will ignite or burn, causing fire or combustion. In this study, flammability testing of castor oil-based PUFs will be carried out as an assessment of material fire safety and a basis for its enhancement, given the immense domestic and industrial application of these foams.

1.13 Mechanical Properties of Polymer Foams

The mechanical properties of a polymer are those properties that are manifested when the polymer is subjected to mechanical stresses, and they collectively determine the applicability or end use of the polymer. The response of a polymer to mechanical stresses will depend upon its gross morphology and the behaviour of its molecules. Size or molecular weight, flexibility/rigidity and intermolecular interactions are very important characteristics that can influence mechanical properties generally (Meijer and Govaert, 2005). According to Alexandre and Dubois (2000), mechanical properties of polymeric materials are largely determined by their molecular structure, morphology and processing methods. Mechanical properties of foams differ from those of un-foamed solid polymers. The former generally have greater impact-absorption capacity than the latter. Flexible foams compress more than rigid foams because in an open-cell structure, the gas phase is not held together. Since gas has the least mechanical strength, open cell (flexible) foams have lower Young's modulus, compressive and tensile strengths (Sivertsen, 2007). Moreover, since these mechanical properties are substantially anisotropic because the strength of foam is always better along the direction of foaming, geometry of foams could have more to say for the strength than density, chemistry and the amount of open cells in the structure (Chan and Nakamura, 1969).

1.14 Polymer Foam Geometry

In the making of polymer foam, mixed starting materials react, expand and flow, increasing in molecular weight and viscosity and eventually forming cross-linked structures after curing. But on a microscopic scale, cells nucleate, grow in size, coalesce, stabilise and open in case of flexible foam. In polymer foam, it is not only

polymer molecules in the polymer matrix that determine the properties of the foam, but also the gas-filled space between them. Intercellular gas interacts with the polymer matrix, affecting its properties and behaviours over time (Sivertson, 2007). Specifically, the properties of foamed polyurethanes will depend on:

(i) The chemical composition and thickness of the cell walls.

(ii) The volume-solid matter/air ratio.

(iii) The concentration of the cell membranes (air permeability/ open cell structure).

Size and shape of cells or pores in polymer foam are very disperse, since the packing of spherical cells in a foam are never regular. Consequently, adequate description of foam structure would require detailed statistical procedures (Sivertson, 2007).

1.15 Research Objectives of the Study

Aim or main objective of the study was to investigate the structure-property relationships of castor oil-based polyurethane foams (COPUFs).

The specific objectives of the study were to:

(i) Extract/prepare castor oil and castor oil polyols (COPs) for polyurethane foam production.

(ii) Produce COPUFs using different formulations.

(iii) Characterise the process parameters (cream time, free-rise time, gel time, tack-free time, and foam rise), physico-mechanical properties (density, water absorption, compressive strength, and creep recovery), flammability properties (IT, FPR, AGT) and morphology of the COPUFs.

(iv) Relate the structure of the COPUFs to their properties.

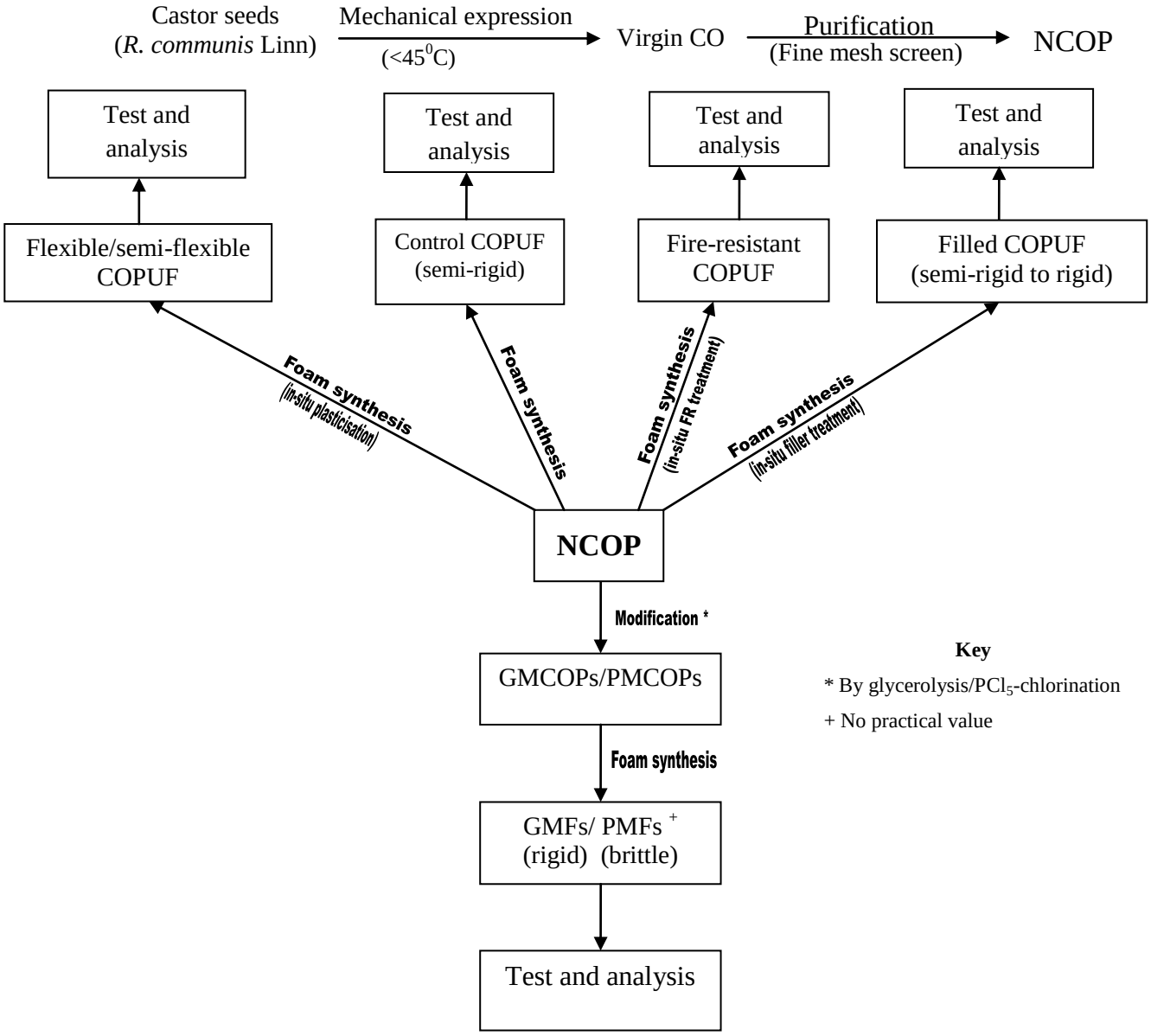


Fig. 1.8: Flow chart of CO utilisation potential in COPUF synthesis during the study.

1.16 Statement of Research Problem

Polyol and organic isocyanate are the major raw material ingredients in the production of polyurethane foams (PUFs). Petroleum-based polyols are not only environmentally unsafe, but are very expensive; and this is costing Nigeria a lot of foreign exchange, as foam-making industries in the country are still stitched in mass importation of petro-polyols. Bio-based polyols derived from vegetable oils are renewable and environment friendly, and could be used as replacement for the petro-polyols. However, these natural oil polyols (NOPs) are known to produce mainly rigid/

semi-rigid PUFs (Guo *et al*., 2000; Zlatanic *et al*., 2002). A major challenge, therefore, is to produce soft, flexible PUFs (from bio-based polyols) with physico-mechanical properties (density, water absorption, compressive strength etc) within prescribed standards for the conventional flexible PUF. Another challenge is how to optimally impart fire retardancy characteristics on the PUFs to enhance their ability to suppress or mitigate incident fires during use. This work has sought to address both challenges using 100% castor oil or its modified polyols as polyol component.

1.17 Justification/Significance of the Study

This study is premised on the need to continue to provide, through research, additional perspectives and insight into the possibility of replacing expensive and environmentally unsafe petroleum-based raw materials for the chemical industry, with renewable, biodegradable and non-toxic bioresources of plant origin, on a sustainable basis. Castor oil, a vastly available, cheap, non-edible vegetable oil that is locally sourced in Nigeria, could replace conventional polyols in the industrial production of PU foams (Ogunniyi, 2006; Ogunfeyitimi *et al*., 2012). If actualised, this has the potential of saving a lot of foreign exchange for the country. As highlighted earlier in this work, castor oil has numerous advantages over other vegetable oils, chief among which are its being hydroxylated , its high thermal stability and its hydrophobicity/hydrolytic stability as a result of a long (C_{18}) fatty acid chain structure.

Globally, there has been a growing research interest in this area. However, to date, there has been only limited research on castor oil-based PU foams in Nigeria. More research work is imperative therefore, to further explore this potential in the country.

1.18 Contributions to Knowledge

(i) The study utilised modified castor oil polyol to produce castor oil-based polyurethane foams.

(ii) The castor oil and modified castor oil were characterised by titrimetric, FTIR, GC-MS and some physico-chemical characteristics (parameters).

(iii) The structure-property relationships of castor oil-based polyurethane foams were established through process; physico-chemical, mechanical, morphological and flammability parameters.

(iv) Additives improved the density, compressive strength and fire retardancy characteristics of the polyurethane foams.

(v) The study demonstrated that the use of $CaCO_3$ filler and fire retardants enhanced the fire retardancy characteristics of the polyurethane foams.

1.19 Scope/Limitations of the Study

In order to fulfill the above stated objectives, the scope of study will cover the following :

(1) Extraction of castor oil from wild *Ricinus communis* Linn seeds.

(2) Chemical modification of purified castor oil by

(i) transesterification/alcoholysis using glycerol (glycerolysis);

(ii) sulphation using concentrated H_2SO_4;

(iii) chlorination using PCl_5 .

(3) Characterisation of the pure and modified castor oil in terms of specific gravity, viscosity, refractive index, as well as hydroxyl, saponification, acid and iodine numbers.

(4) FTIR and GC-MS analysis of the modified oils to establish modification of oil structure.

(5) Preparation of PU foams of different formulations from the neat and modified castor oil.

(6) Density and water absorption measurements of foams.

(7) Mechanical property testing, e.g. compressive strength, creep recovery etc of the produced PU foams using standard methods.

(8) Analysis of the cellular morphologies of the foams using SEM.

(9) Studying the effects of chemical modification on morphology and mechanical properties of the PU foams.

(10) Investigating how the use of reinforcing fillers in the PU matrix would affect morphology, mechanical properties and flammability characteristics of the PU foams.

(11) Studying the flammability of the PU foams generally, and the effect of incorporating fire retardants in the PU matrix.

Limitations/constraints encountered during the study included:

(i) Inability to access functional Cone Calorimeter and DSC instruments. The former would have been used for detailed study of the flame properties of the foams, while the latter could have been used to monitor the glass transition temperatures of filled, plasticised and crosslinked COPUFs.

(ii) Shortage of funds.

CHAPTER TWO

LITERATURE REVIEW

2.1 Chemical Modification of Vegetable Oils for PUF Synthesis

Vegetable oils consist mainly of triglycerides of saturated and unsaturated fatty acids, but may also contain small amounts of mono- and diglycerides, free fatty acids, sterols and tocopherols (Gunstone, 2002). In other words, vegetable oils are heterogeneous entities with overall compositions and properties varying from oil to oil.

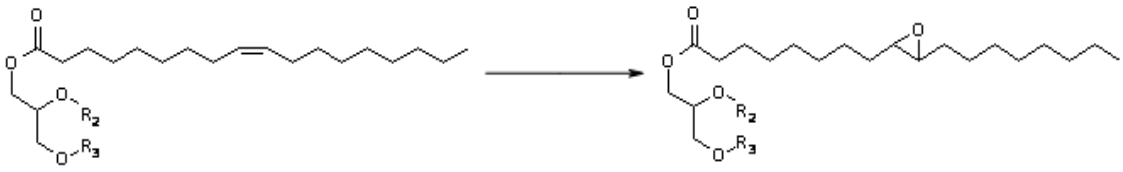
It is the presence of certain functional groups or reaction sites in vegetable oil triglycerides such as double bonds and ester linkages, and in few cases (e.g. castor oil triglyceride) hydroxyl groups, that make vegetable oils polymerisable. However, a number of researchers have reported that PUFs produced by direct polymerization of most of these vegetable oils were of poor compressive properties and low resilience (Ramirez *et al.*, 2008; Del Rio, 2011; Bleys, 2012). These shortcomings were attributed mainly to insufficient reactivity of both the double bonds and the often secondary hydroxyl groups in their triglyceride molecules. In addition, these oils, when used directly as polyols have much lower hydroxyl numbers (e.g. 160-168 mgKOH/g for castor oil) compared to petroleum-based polyols such as polyether and polyester polyols with hydroxyl numbers as high as 400-500 mgKOH/g (Narine *et al*., 2007).

Chemical modifications allow for the introduction of new and usually more reactive functional groups into the oil structure such as hydroxyls, epoxies, carboxyls, acrylates etc (Esen and Cayli, 2015) to yield modified vegetable oil polyols, thus enhancing the properties of vegetable oils as macromonomers. These modified vegetable oil polyols have found increasing patronage as polymerisable monomers in polymer synthesis

because of their environmentally friendly character and low cost, when compared to petro-polyols (Saremi *et al*., 2012). Studies by Firdaus (2010) have shown that soybean oil polyol (SBOP) can be produced through two-step synthesis involving epoxidation of the unsaturated sites with acetic acid and hydrogen peroxide, followed by epoxy ring opening with mono alcohol (methanol, butanol) and polyfunctional alcohol (ethylene glycol), at a temperature of 110 ± 0.5^{0}C for 1-2 hrs. The product was characterised in terms of viscosity, as well as oxirane and hydroxyl numbers. Petrovic (2008) obtained SBOPs by the epoxidation of soybean oil, followed by ring opening with methanol, HCl, HBr, and by hydrogenation. PUs obtained from these polyols showed relatively higher glass transition temperatures and improved mechanical properties. Halogenated polyols obtained via ring opening by HCl and HBr gave PUs that were less thermally stable than the ones without halogens, and had higher Tg ($70 - 80^{0}$C) than the latter. Influence of isocyanate in the final properties of PU for soy-polyol obtained by ring opening with methanol showed that the properties of the PU strongly depended on crosslink density and the structure of the isocyanate. Dworakowska *et al*.(2012) produced flexible PUFs from synthesised rapeseed oil polyols, which they obtained by first incomplete epoxidation of the vegetable oil, and subsequent complete oxirane ring opening under microwave irradiation.

Also, vegetable oils such as sunflower, corn and linseed oils have been epoxidised and reacted with boiling methanol in presence of a catalyst, to obtain polyols for PU synthesis.

(a)



(b)

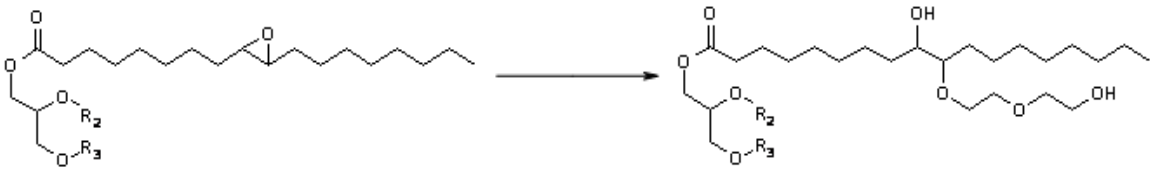


Fig.2.1: Synthesis of polyol from rapeseed oil – (a) epoxidation of oil by peracetic acid at 60-65^{0}C; (b) oxirane ring-opening and subsequent hydroxylation of epoxidised oil using diethylene glycol (DEG) (Dworakowska *et al*., 2010). R_2 and R_3 are the residues of fatty acids.

Sinadinovic-Fiser *et al*. (2012) studied the epoxidation of castor oil in benzene with peracetic acid generated *in situ* from acetic acid and hydrogen peroxide in the presence of an ion exchange resin as catalyst. They obtained highest relative epoxy yield of 78.32% at 323K after 8 hrs, when 0.5 mol of acetic acid and 1.5 mol of 30 wt% of aqueous hydrogen peroxide per mol of oil double bond were used in the presence of 15 wt% of Amberlite IR-120.

Another major procedure involves transesterifying/alcoholysing the vegetable oil using polyhydroxy compounds such as ethanolamine, glycerol, pentaerythritol etc in presence of an acid or base catalyst (e.g. NaOH, PdO, CaO, para-toluene sulphonic acid) to

generate the polyol (Petrovic *et al.*, 2009; Islam *et al.*, 2014) - see Scheme 1 in Chapter One. This reaction splits the triglycerides in the oil into mono- and diglyceride fractions, with each fraction bearing additional hydroxyl group (s) (Kimmel, 2004). However, partial transesterification of vegetable oils with glycerol yields mono- and diglycerides with free hydroxyl groups that can be used in other reactions (Sonntag, 1984). Lubguban *et al.* (2009) who carried out the direct hydroxylation of vegetable oils via transesterification/alcoholysis using glycerol/pentaerythritol in the presence of a catalyst noted that high temperature and long reaction time were needed to obtain the desired polyol. Tanaka *et al*. (2008) prepared PUFs using a palm oil-based polyol (obtained by the glycerolysis of palm oil) mixed with polyethylene glycol (PEG) or diethylene glycol (DEG) and reacted with an isocyanate compound. Thermal and mechanical analyses of the foams produced showed that the monoglyceride molecules formed during palm oil glycerolysis served as soft segments. Vashisht and Kaushal (2013) prepared castor oil polyol by alcoholysis of castor oil with diethanolamine at a temperature of 160^0C (for 5hrs) using different molar ratios, and characterized the polyol in terms of viscosity, as well as acid and hydroxyl values. The polyol was reacted with MDI to produce PU foam. Saetae and Pornpakakul (2008) performed the alcoholysis of castor and palm oils using glycerol at an elevated temperature of 240-250^0C, and in presence of PbO catalyst, to obtain the corresponding oil polyols. They observed, however, that in their reaction with diisocyanate, castor oil polyols gave more complex structure in the PU due to higher degree of crosslinking associated with the presence of hydroxyl groups in the castor oil alkyl chains. Similarly, Kumar and Kaur (2013) transesterified castor oil using glycerol at a temperature of 220 ± 10^0C for 3-4hrs, to obtain castor oil polyols of hydroxyl value 390-410 mgKOH/g, which were then reacted with MDI in MDI-polyol ratios of 1:1, 2:1 and 3:1 to yield rigid PUs with high

mechanical strength and high load bearing capacity. Brei *et al.* (2012) undertook the glycerolysis of rapeseed oil over several solid bases such as Mg-Al hydrotalcite and Al_2O_3 supported CaO-ZnO using bed flow reactor. They obtained a monoglyceride yield of 70% with 96% conversion at 513K. They observed that catalyst pore size was an important factor in the intensification of the glycerolysis process.

Many other procedures have also been applied for the chemical modification of vegetable oils to obtain polyols. Narine *et al.*(2007) prepared canola and soybean oil-based polyols by ozonolysis and hydrogenation in tetrahydrofuran (THF), with Raney Nickel as catalyst. Reaction of the double bonds in vegetable oils with maleic anhydride to attach maleates (Eren *et al*., 2003) and the addition of acrylonitrile by the Ritter reaction to acrylamide derivatives, which are then radically polymerized (Eren and Kusefoglu, 2005) have also been reported. Enzyme-catalysed glycerolysis of soybean oil has also been reported (Noureddini and Harmeier, 1998; Tayde *et al*., 2011), but this is at present a very costly procedure.

Another dimension to the modification of vegetable oils to obtain PUs, is the preparation of inter-penetrating polymer networks (IPN)-type PUs. The IPNs, which are essentially polymer blends, can be prepared by permanent entanglement between two or more distinctly crosslinked polymers (Islam *et al*., 2014). The IPNs possess excellent properties because of the interlocking of polymer chains in their structure (Sperling, 1981). Of the many kinds of IPNs that are known, sequential IPNs and simultaneous IPNs are the two most important types (Roland, 2013). Kong and Narine (2008) prepared sequential IPNs using canola-oil-based polyol with terminal primary functional groups and poly (methyl methacrylate). Eren *et al*. (2006) produced IPNs based on bromoacrylated castor oil polyurethane. In all these, the mechanical properties of the IPNs were found to be superior to those of the constituent polymers.

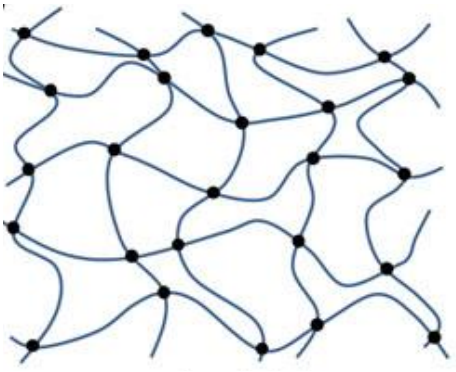


Fig. 2.2: Structure of sequential IPN for a conventional elastomer (Roland, 2013).

2.2 Polyurethane Additives

Additives are materials which are dispersed in a polymer substrate without their having much deleterious effect by way of altering or sacrificing the molecular structure and desirable properties of the base polymer (Murphy, 2001; Fox, 2008). The use of additives in polymer systems has been widely reported by researchers. According to Fox (2008), the discovery of natural polymers created a need for additives to modify polymer properties, so that the polymers would have improved characteristics that could allow for a wider variety of uses. In practice, polymer additives may be reactive (chemically bound into polymer backbone or grafted onto it) or non-reactive (only physically integrated) (Singh and Jain, 2008; Zweifel *et al*., 2009).

As stated earlier in this work, major components needed to synthesize PUs are diisocyanate, polyol, water, physical blowing agents, catalysts, surfactants and crosslinking agents. In addition to these basic raw material ingredients for PU synthesis, there are a great number of chemical compounds or additives that are incorporated to control or modify the processing of PUs and their final properties. Additives can alter physical properties of PUs such as density, water sorption and dimensional stability through improved void size distribution, porosity and whether the material's cellular

structure is open - or closed-cell. They also influence chemical properties like fire retardancy, thermal conductivity and adhesion (Patterson *et al*., 2014). Additives commonly used in PU systems include chain extenders, fillers, flame retardants, plasticisers, stabilisers, antioxidants, processing aids etc.

2.2.1 Chain extenders

Chain extenders are reactive low molecular weight bifunctional, hydroxyl and/or amine terminated compounds that are often used in flexible PU formulations, PU fibres, microcellular elastomers, casting elastomers, polyureas, adhesives and coatings to improve their properties by modifying their morphologies (SouthernChem, 2008). This is because during PU synthesis, hydroxyl groups from a hydroxyl terminated diol react with diisocyanate to form PU hard segments, while amine groups from an amine terminated diamine react with diisocyanate to form polyurea hard segments. These hard segments are covalently coupled to the polyol soft segments and because of strong hydrogen bonding in the former, they can easily aggregate in various sizes and phase-separate from the latter to yield a segmented, biphasic morphology (Petrovic and Ferguson, 1991; Edhi *et al*., 2012). The chain extenders form PUs that phase-separate well, exhibit elastomeric properties and are melt processable (Xu *et al*., 2008). Examples of chain extenders are hydroxylamines, glycols and diamines. Functionality is what distinguishes between chain extenders ($f=2$) and crosslinkers ($f\geq3$).

Corcuera *et al*. (2010) used two different chain extenders namely 1,4-butanediol (BD) and corn sugar based 1,3-propanediol (PD) to synthesise novel segmented PUs. Physicochemical, mechanical and morphological characterisation of the PUs revealed the effect of phase separation between the polymer's hard and soft segments. They observed that the PU's hard segment structures exhibited elastomeric to rigid behavior

with increase in hard segment content. They also found that the PUs synthesised using the bio-based chain extender (PD) showed a slightly lower crystallinity in the hard segment structure than that synthesised using BD. This also explains observed lower thermal stability of PD-based PUs compared to the BD-based. Yemul and Petrovic (2010) also prepared segmented PUs with 50 and 70% soft segment concentration (SSC) by reacting polyester polyol with MDI, and using BD as chain extender. They noted that determined thermal and mechanical properties of the polymers were suggestive of good micro-phase separation, with both soft and hard segments displaying a certain degree of crystallisation. Edhi *et al*. (2012) studied the effect of ethylene glycol (EG) chain extender on the structure of PU foam produced by reacting isocyanate with a polyol mixture consisting of polypropylene glycol and castor oil. The foams were characterised in terms of their bulk density, cell density and cell diameter. FTIR analysis of the foams showed that adding chain extender (EG) in making castor oil based PUFs coul improve foam structure by adding hard segment. Firdaus (2011) who investigated the effect of addition of EG chain extender to the final properties of PU derived from soybean oil obtained flexible and semi-rigid PUs with improved density and mechanical properties up to a certain (threshold) extender concentration.

2.2.2 Fillers

Fillers are particulate materials added to polymers mainly to reduce cost and improve polymer properties. In polymer systems, fillers can improve processing, abrasion resistance, density control, dimensional and thermal stability and optical effects (Rothon, 2002). Among notable fillers used to achieve improved properties in foams are inorganic materials such as calcium carbonate, dolomite, aluminium silica, titanium

dioxide and talc (Nunes *et al*., 2000), while common organic materials used include carbon black and natural fibres (Mothe and Araujo, 2000; Mothe *et al*., 2002). In polymer processing, the choice of filler is informed by shape, size and surface area of the filler particle, as well as the end-use requirements of the article to be processed.

The application of reinforcing fillers in PU systems is, in practice, more relevant with regard to flexible (rather than rigid) PUFs, and this is a widely reported subject in PUF literature. Many studies have shown that modification in the properties of flexible PUFs is achieved by effective dispersion of filler particles across the PUF matrix, along with polyurea hard segments. It is also well known that foams reinforced with fillers have smaller cells and higher cell density than foams without fillers (Zhu *et al*., 2011; Linul *et al*., 2013). According to Latinwo *et al*. (2010), the incorporation of fillers in flexible PUFs results in the formation of flexible PUF/filler composite materials. For such composites, three requirements are necessary to achieve good mechanical performance:

(1) Good compatibility between filler and PUF matrix;
(2) Good dispersion of filler across PUF matrix;
(3) Strong interfacial interaction and adhesion between filler and matrix.

Good filler dispersion depends on the particle size and dispersion quality of the filler, and on the efficiency of mixing during filler incorporation. Size of filler particles affects the surface area that is exposed to the matrix.

The effect of incorporating calcium carbonate filler in flexible PUF matrix has been reported by a number of researchers including Latinwo *et al*. (2010), Usman *et al*. (2012) and Agarry *et al*. (2015). Latinwo *et al*. (2010) observed that in flexible PUFs, calcium carbonate fills voids in the open cell porous structure of the polymer matrix to promote, among others, an increase in density and resistance to compression, with

attendant improvement in mechanical strength. This effect, Usman *et al*. (2012) noted, tends to reduce resilience, and contribute to an increase in permanent deformation of the polymer. However, wood flour was found to have an opposite effect on the mechanical properties of castor oil based rigid PUF such as compression modulus and yield strength. Both properties were found to decline when the filler was incorporated in a foam formulation involving alcoholyzed castor oil and isocyanate as reactants (Mosiewicki *et al*., 2009). This was explained on the effects of wood flour-isocyanate reactions on the foam's characteristics.

Addition of fibres to polymers to produce so-called fibre-reinforced polymers (FRPs) (Masuelli, 2013), presents huge prospects in polymer modification and application. According to Petrovic (2010), incorporation of fibres into a polymer matrix will produce elastomeric composites, exhibit combined behaviour of soft, elastic rubber matrix and firmly strong fibrous reinforcement. Composites obtained using natural fibres have low cost, and often show improvements in mechanical properties such as tensile strength, tear strength and hardness over the unfilled polymers (Narine and Kong, 2005). Chang (2014), who studied the effect of incorporation of wood fibre in soybean-based PUFs, found that the added fibre generally enhanced the compression performance of the PUFs, especially when the fibre was treated with alkali. Chang (2014) further reported that the developed soy-based PUFs were found suitable for use as the core in structural insulating panels (SIPs). Effects of various nanosized organoclays on the thermomechanical and morphological properties of PUFs have also been investigated. Results from an investigation carried out by Chang and An (2002) showed that most clay layers were dispersed homogeneously into the polymer matrix, and that addition of only small amount of organoclay was enough to improve the thermal stabilities and mechanical properties of foams. Also, Javni *et al*. (2002) in their

study found that nano-silica used as filler in flexible PUF increased the hardness and compression strength, but decreased the rebound resilience of the foam. In their study on the effects of nanoparticle addition on the thermo-physical and mechanical properties of PUFs, Lorusso *et al*. (2015) found that acetic- and oleic-modified titania nanocrystals, TiO_2 ,dispersed into the PUF matrix yielded improved mechanical characteristics compared to the neat foam. This was presumably due to the different shape, size and distribution of the nanoparticles which favoured the formation of nucleation centres.

2.2.3 Flame retardants (FRs)

The purpose of incorporating a flame retardant additive into a polymer substrate is to aid in inhibiting, resisting, or suppressing polymer combustion process, thereby reducing polymer flammability. The FRs are capable of achieving this because they can act physically (by means of cooling and thinning) or chemically (by radical quenching in the vapour phase, or by formation of a protective carbon layer in the solid phase) to interfere at particular stages of the polymer combustion process (Kirk-Othmer, 2001; Dufton, 2003; Weil and Levchik, 2009; Laoutid *et al.*, 2009). In practice, the incorporation of FRs may be additive (FR physically integrated) or reactive (FR chemically bound into polymer backbone or grafted onto it). High halogen-containing polymers such as PVC, poly (tetrafluoro ethylene) (PTFE), and high performance plastics such as poly (ether ether ketone) (PEEK), poly (phenylene sulphide) (PPS) are inherently flame resistant. But polymers that include polyolefins, polyacetals, polyamides and polyesters are very flammable, and maintain a burning process automatically, once started. For such polymers, FR addition is highly beneficial. For instance, additives such as zinc borate in combination with antimony oxide can produce low smoke formulations in many polymers (Genovese and Shanks, 2007). Generally, an

ideal FR polymer system should have high resistance to ignition and flame propagation, a low rate of combustion, a low rate and amount of smoke generation, no change in flammability during use, performance of base material should be close to the original, and that there should be no difference in appearance between them (Pearce,1986).

Foamed organic polymers are inherently flammable on account of their high hydrocarbon content, as well as their predominantly cellular structure. In PUFs, flexible or open cell foams are of lower density and more porous than rigid foams and therefore, more flammable (Sivertsen, 2007). A number of researchers have reported that the oxygen index (OI) of conventional PUF is in the range of 16-18 (Cullis and Hirschler, 1981; Benrashid and Nelson, 1994). Consequently, highly porous lightweight combustible foams tend to have a fast flame spread and high thermal emissions (Weil *et al*., 1996). Thus, PUFs in the absence of FRs are extremely combustible. From literature, FRs usually incorporated into PUFs to reduce their flammability include phosphorus-containing compounds, halogen-containing compounds, nitrogen-containing additives, silicone-containing products, aluminium and magnesium hydroxides etc (Pearce, 1986; Papazoglou, 1994; Weil and Levchik, 2004; Jurs, 2004; Singh and Jain, 2008; Wang *et al*., 2012).

2.2.3.1 Mechanisms of flame retardant action

The basic mechanisms of flame retardancy vary depending on the specific FR and the polymer substrate. In general, FRs act by either preventing ignition or preventing the spread of a fire. Kirk-Othmer (2001) cited in Leonard (2005) gave a detailed summary of five specific mechanisms by which flame retardancy may occur: physical dilution, chemical interaction, inert gas dilution, thermal quenching and protective coating.

(i) Physical dilution – FR increases the heat capacity of product, thereby reducing the fuel content to a level below the lower limit of flammability.

(ii) Chemical interaction (by gas phase radical quenching) - this is the general flame-retarding mechanism by which halogenated FRs operate. FR first dissociates into radical species that compete with chain propagating and branching steps in the combustion process.

$$\mathbf{RX \rightarrow R^* + X^*} \qquad \mathbf{(11)}$$

High energy H* and HO* radicals formed by chain branching in the fire are removed by the halogen-containing FR thus:

$$\mathbf{X^* + H^* \rightarrow HX} \qquad \mathbf{(12)}$$

$$\mathbf{HX + H^* \rightarrow H_2 + X^*} \qquad \mathbf{(13)}$$

$$\mathbf{2HX + O^* \rightarrow H_2O + 2\,X^*} \qquad \mathbf{(14)}$$

The halogen radical (X*) has much lower energy than H* or HO* and thus has much lower potential to propagate the radical oxidation reactions of combustion.

Furthermore, the addition of metallic compounds such as zinc and antimony oxides is said to enhance the efficiency of organohalogen retardants in a synergistic manner (Pearce, 1986; Jurs, 2004; Laoutid *et al.*, 2009).

(iii) Inert gas dilution –the large volumes of non-combustible gases that are produced by FRs during combustion are said to dilute the oxygen supply to the flame i.e. they dilute the fuel concentration below the flammability limit.

(iv) Thermal quenching – endothermic breakdown of FR means a cooling effect on the polymer substrate, and attendant (thermal) quenching of polymer combustion process. Materials that act in this manner include metal hydroxides (e.g. aluminium and magnesium hydroxides) and carbonates (e.g. calcium carbonate).

(v) Protective coatings – protective liquid or char barrier formed by some FRs that acts as an insulating layer to impede or reduce heat transfer from the flame to the combusting product. Phosphorus compounds which decompose on heating to form stable crosslinked structures of solid material and the so-called "intumescent" systems (Papazoglou, 1994; Weil and Levchik, 2009) operate by this mechanism.

2.2.4 Plasticisers

Plasticisers are usually inert organic compounds with low molecular weights, high boiling points and low vapour pressures that are used as polymer additives (Wojciechowska, 2012). They may be high-boiling organic liquids or low-melting organic solids added to tough or hard resins to impart flexibility, extensibility and/or processability and to reduce brittleness of the product. This is achieved by lowering the glass transition temperature below room temperature, thus achieving a change in properties from those of a hard, brittle, glass-like solid to those of a soft, flexible, tough material. Plasticisers also reduce the elastic modulus and the melt viscosity of the polymer but do not alter the chemical nature of the macromolecules. Plasticisers have been used as polymer additives since 1800s (Vieira *et al*., 2011), but interestingly, up to about 90% of all plasticisers are used in plasticised or flexible poly (vinyl chloride) (PVC) products (Zweifel *et al*., 2009; PAGM, 2015).

Polymer plasticisation is attributed to the ability of the plasticiser molecule to reduce the intermolecular attractive forces between the polymer chains, resulting in a softened and flexible polymeric matrix (Benaniba and Masserdier-Nageotte, 2010). Plasticis ers work by increasing the free volume available to the polymer chains and thus allowing for greater internal chain rotation and unwinding. By embedding themselves between the polymer chains, plasticisers are able to push or space the chains further apart (Fox, 2008).

The main role of a plasticiser is to improve mechanical properties of polymers by increasing flexibility, decreasing tensile strength and lowering the second order transition temperature (Rahman and Brazel, 2004). The basic requirements that must be met by a plasticiser are compatibility, performance and efficiency. Another important factor is plasticiser permanence, which is related to its resistance to migration. The permanence of a plasticiser is dependent on size or molecular weight of the plasticiser molecule (Han, 2005; Gil *et al*., 2006). In other words, the higher the plasticiser molecular weight, the more permanent the plasticiser is. Plasticisers should also be aroma free or non-toxic, otherwise there is possibility of their migration into foods where the polymer article is used for food packaging applications (Wilson, 1995). Other requirements are thermal and photothermal stability (Rahman and Brazel, 2004). According to Han (2005), the efficiency of a plasticiser is the amount or quantity of it required to provide desired mechanical properties in the base polymer.

2.2.4.1 Classification of plasticisers

There are two major classes of plasticisers: internal and external. In external plasticisation, plasticity is provided through physical mixing. Thus, external plasticisers are not chemically bound to the polymer and can evaporate, migrate or exude from polymer products by liquid extraction (Rahman and Brazel, 2004). Examples are

plasticisers used as processing aids (Vieira *et al*., 2011), which may be primary or secondary external plasticisers, based on their compatibility levels with the base polymer. Internal plasticisation on the other hand involves the plasticisation of a polymer by incorporation of a comonomer or reaction with the polymer, providing flexible chain units (Wojciechowska, 2012). Internal plasticisers are therefore groups (flexible segments) constituting a part of a basic polymer chain, which may be incorporated regularly or irregularly between inflexible monomers (hard segments) or grafted as side chains, thus reducing intermolecular forces (Ehrenstein, 2001; Elias, 2003; Wypych, 2004).

2.2.4.2 Mechanisms of plasticisation

Several theories have been put forward to explain the concept of polymer plasticisation. Among them are:

I. Lubricity theory - developed by Kilpatrick, Clark and Houwink (Wojciechowska, 2012) regards plasticiser as acting as a lubricant, reducing intermolecular friction between polymer molecules responsible for rigidity of the polymer. On heating, the plasticiser molecules slip between polymer chains and weaken the polymer-polymer interactions (van der waals' forces) shielding polymer chains from each other. This prevents the reformation of a rigid network, resulting in more flexible, softer and distensible polymer matrix.

II. Gel theory - developed by Aiken and others (Wojciechowska, 2012) holds that polymers are formed by an internal three-dimensional network of weak secondary bonding forces (van der Waals' forces, hydrogen bonding) sustained by loose attachments between the polymer molecules along their chains. These bonding forces, are easily overcome by external strain applied to the material, allowing the plasticised polymer to be bent, stretched, or compressed. Plasticiser molecules attach along the

polymer chains, reducing the number of the polymer-polymer attachments and hindering the forces holding polymer chains together. The plasticiser by its presence separates the polymer chains and increases the space between polymer molecules, thus reducing the rigidity of the gel structure. Moreover, plasticiser molecules that are not attached to polymer tend to aggregate allowing the polymer molecules to move more freely, thus enhancing the gel flexibility.

III. Free volume theory - holds that the presence of a plasticiser lowers the glass transition temperature (Tg) of the polymer. Free volume is a measure of internal space available within a polymer matrix. There are three main sources of free volume in polymer: motion of polymer end groups, motion of polymer side groups, and internal polymer motions. When the free volume increases, more space or free volume is provided for molecular or polymer chain movement. A polymer in the glassy state has an internal structure with molecules packed closely and small free volume. This makes the material rigid and hard. When the polymer is heated to above the glass transition temperature,the thermal energy and molecular vibrations create additional free volume which allows greater internal chain rotation and an increase in the segment mobility. This makes the system more flexible and rubbery. When small molecules such as plasticisers are added, the free volume available to polymer chain segments increases and therefore the glass transition temperature lowers.

Recent advances in plasticiser theory and application have also led to:

IV. Mechanistic theory of plasticisation (Wojciechowska, 2012), which considers that plasticiser molecules are not bound permanently to the polymer, but rather there is a dynamic exchange process whereby, a constant association and disassociation of polymer-polymer, polymer-plasticiser and

plasticiser-plasticiser molecules form. Some plasticisers form stronger associations with polymer than others. At low plasticiser levels, the plasticiser-polymer interactions are the dominant interactions, what explains "antiplasticisation". At high plasticiser loadings plasticiser-plasticiser associations predominate.

Plasticisers have been employed in many urethane applications including adhesives, coatings, elestomors and foams. Examples of plasticisers are phthalate esters (e.g. dioctyl phthalate – DOP), phosphate esters (e.g. butylated triphenylphosphates – BTPPs), fatty acid esters, hydrocarbons and hydrocarbon derivatives.

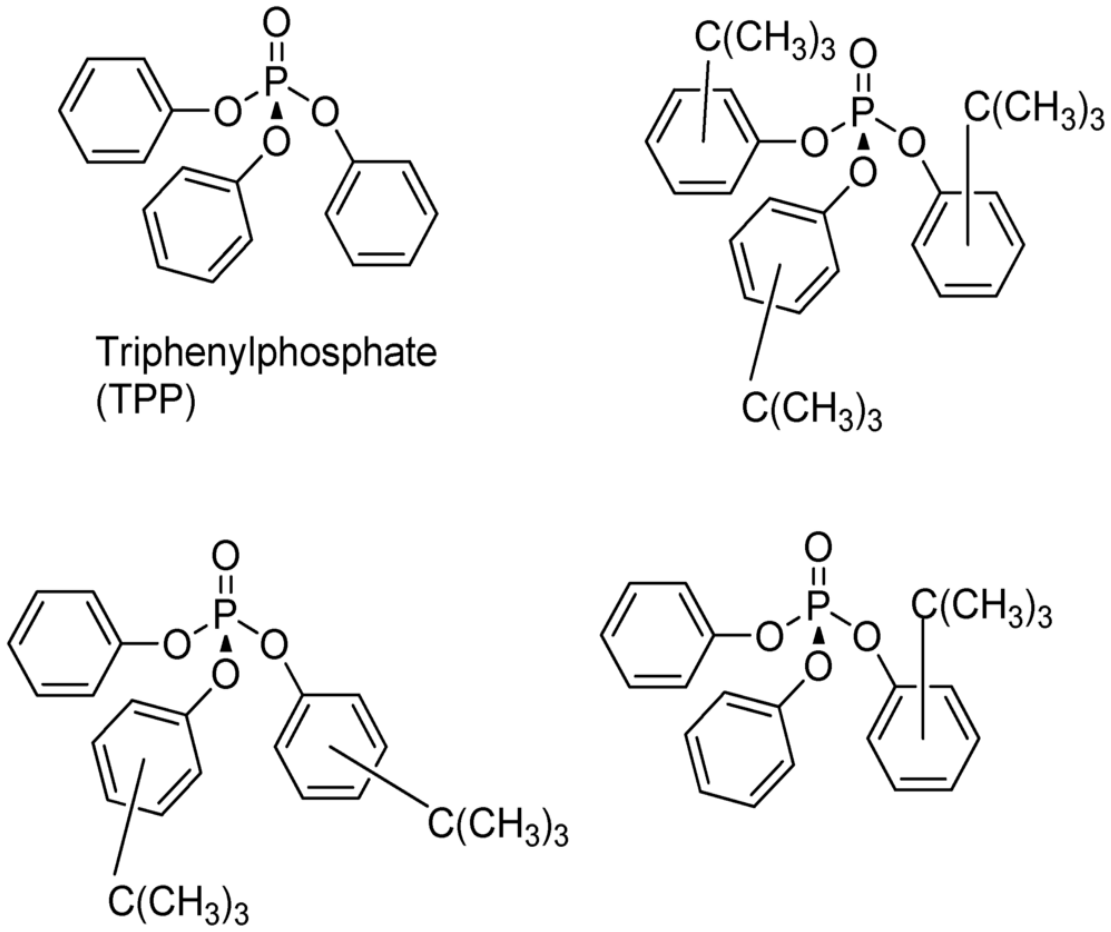


Fig.**2.3**: Structures of the four components of commercial BTPP additives (Johnson and Hils, 2013)

However, with regard to phosphate esters, there are concerns about the toxicity of certain isomers of aromatic esters like tricresyl phosphates. These concerns have led to the use of more highly substituted materials such as butylated triphenyl phosphates (BTPPs) as replacement (Johnson and Hils, 2013). Similarly, there have been worldwide growing concerns about the potential toxicity of phthalate esters to humans and the environment (MSP, 2011). Studies conducted to evaluate the potential toxicity of phthalate plasticisers on human health have implicated these plasticisers with regard to hormonal disorders, reproductive toxicity, carcinogenicity and allergic symptoms in children, among others (Imai *et al*., 2006; Babu and Wu, 2010; Cao, 2010; Wittassek *et al*., 2011). Consequently, these plasticisers are gradually being replaced by alternative plasticisers such as non-toxic alkyl esters of adipic and citric acids, or bio-based plasticisers like triglyceride vegetable oils (Vieira *et al*., 2011), in addition to restrictions on their use in children's toys, cosmetic products and the like, within the European Union (Lindstrom and Hakkarainen, 2006; Wittassek *et al*., 2011).

2.3 Characterisation of PUF Properties

2.3.1 Physicochemical properties

The physico-chemical properties of a polymer are its measurable physical and chemical properties with which it interacts with other systems, and that collectively determine its characteristic nature or behaviour. The physical properties include molecular weight, viscosity, hardness, volatility, porosity, water sorption, dimensional stability, glass transition, etc, while the chemical properties include chemical resistance, flammability, hydrolytic, thermal and electrical properties etc. Various standard methods or analytical techniques available in the literature are used to characterise polymers in terms of these properties (Hunt and James, 2012). Thermo-gravimetric or dynamic mechanical thermal

analysis (Badri, 2012; Trovati *et al*., 2010) of PUFs, for instance, can reveal a lot about the thermal stability of these polymers. With differential scanning calorimetry (DSC), one could monitor among others, the glass transition, melting and crystallization behaviour of PUFs. X-ray diffraction (XRD) can analyse the extent of crystallinity in a PU system as a function of extender concentration or isocyanate (NCO)/polyol (OH) ratio (Rehman, 2010) etc. A well-established method for examining and characterising functionalities formed in cured PUFs is Fourier transform infra-red (FTIR) spectroscopy (McDaniel *et al*., 1999; Asefnejad *et al*., 2011).

2.3.1.1 FTIR

According to Badri (2012), PUF analysed by FTIR spectroscopy usually shows the absence of free hydroxyl groups, and this indicates a complete conversion of these groups to the urethane moiety (NH-C(O)-O). Asefnejad *et al*. (2011) have assigned among others absorption bands at 3323 cm^{-1} and 1734 cm^{-1} in PU FTIR spectra to NH and C=O stretching vibrations respectively.

Modern fibre technology upgraded FTIR technique (McDaniel *et al*., 1999) has enabled *in-situ* FTIR measurements, and made it possible to monitor isocyanate reactions during foam formation. During rigid PUF synthesis, the technique is capable of tracking isocyanate urea (free, loosely associated and bidentate), urethane (free and hydrogen bonded) and isocyanate concentrations throughout the reaction (Table 2.1).

Table 2.1: PU chemistry frequencies in FTIR spectrum (McDaniel *et al*., 1999)

Frequency (cm^{-1})	Functionality
1640	Bidentate hydrogen bonded urea
1650-1690	Loosely hydrogen bonded urea
1705	Loosely hydrogen bonded urethane
1710	Trimer (isocyanurate)
1717	Free urea
1735	Free urethane
2270	Isocyanate

Also, Dounis and Wilkes (1997) had used FTIR data to monitor monodentate and bidentate urea presence in slabstock and moulded PUFs. Similarly, Mortley *et al*. (2007) used FTIR to establish the presence (or absence) and amount of carbonyl (C=O), -NH and -N=C=O functionalities in non-irradiated and radiation modified, thermally cured CO-based PUs. They observed changing areas of carbonyl and –NH absorbance peaks, and disappearance of the isocyanate peak in the FTIR spectra as irradiation progressed, indicating increased hydrogen bonding and intermolecular crosslinking in the radiation modified PU system.

2.3.2 Mechanical properties

2.3.2.1 Basic mechanical properties of polymers

(a) Test methods

Mechanical testing of polymeric materials is carried out in order to characterise the materials in terms of their different responses to applied stresses. These tests are also used to assess the aging or chemical resistance of materials, but are of limited use in predicting product performance. Mechanical properties could be seen as those properties that determine the response of the material to the applied stresses or strain

during service. These properties are affected by temperature, time or aging, molecular structure and product formulation recipes, among others.

(b) Tensile strength (ASTM D 638)

Changes in the tensile properties of a material are an indication of the degradation of the material. Tensile properties are the most important single indicators of material strength. The force necessary to pull the specimen apart is determined, along with how much the material stretches before breaking (Hunt and James, 2012).

(c) Stress-strain properties in tension

The generalised stress-strain curve serves to define several useful quantities, including modulus or stiffness (the slope of the curve), yield stress, and strain or elongation at break. Measured elongation or strain produced at various values of applied stress (or load) is plotted as stress – strain curve, and the nominal stress (σ) is given by the expression

$$\sigma = \frac{F}{A} \qquad \textbf{(15)}$$

Where F = applied force or load (N)

A = original cross sectional area (m^2)

The tensile strain (□) is elongation per unit length

$$□ = \frac{l - l_o}{l_o} \qquad \textbf{(16)}$$

Where l = extended length

l_0 = original length

Therefore,

$$\% \text{ strain or elongation at break} = \frac{l - l_o}{l_o} \times 100 \qquad \textbf{(17)}$$

Tensile strength $= \frac{Tensile\ Stress}{Tensile\ Strain}$ **(N/m^2)** **(18)**

(d) Elastic modulus

Elastic modulus (young's modulus) is the ratio of the applied stress to strain (Hunt and James, 2012). It is produced in the region where strain is proportional to stress i.e. in the initial stress - strain curve. This quality permits absorbing rapid impact and shock. Thus the total area under a stress – strain curve is indicative of overall toughness. A material of very high tensile strength and little elongation would tend to be brittle in service.

(e) Flexural properties of plastics (ASTM D 790)

The stiffness or rigidity of materials when subjected to bending or flex is of great and increasing importance, especially with their use in engineering and structural applications. Excessive stiffening may occur at low temperature whilst creep or softening may occur at elevated temperatures. For a rectangular cross-section, flexural stress (Qf) is evaluated as

$$\mathbf{Qf} = \frac{3}{2}\left(\frac{Fl}{bh^2}\right) \quad \textbf{(19)}$$

And modulus of elasticity in flexure (Eb) as

$$\mathbf{E_b} = \frac{l^3}{4bh^3}\left(\frac{dF}{dD}\right) \quad \textbf{(20)}$$

Where l is the distance between supports; b is the width of the test piece; F is the applied force; h is the thickness of the test piece; dF is the change in force in the linear portion of the load – deflection curve and dD is the change in deflection corresponding to dF (Hunt and James, 2012).

(f) Hardness (ASTM D 785)

It is a concept of resistance to penetration, scratching, marring. Hardness is measured by either static penetration of the specimen with a standard indenter at a known force, or dynamic rebound of a standard indenter of known mass dropped from a standard height, or scratching with a standard pointed tool under known force. Hardness is a combination of three absolute properties that are expressed in units of stress, strain and elastic modulus (Ghosh, 2007).

(g) Compressive strength (ASTM D 695)

Urethane elastomers have greater load bearing capacity than other elastomers. Their compression-deflection relationships depend upon load surface conditions. These materials have high load carrying capacity in shear (Ghosh, 2007). Compressive strength is the maximum compressive load (N) a material can withstand prior to failure, divided by its cross-sectional area (m^2). This quantity may be useful in specifications for distinguishing between grades of a material, and also for assessing along with other property data, the overall strength of different kinds of materials.

2.3.2.2 Mechanical properties of solid PUFs

Foam is a three-dimensional cellular solid containing pore space and a skeletal frame (Chang, 2014). Cellular structure of foam dictates its mechanical response. A cellular material is one which is made up of an interconnected network of solid struts or plates which form edges and faces of cells (Gibson and Ashby, 1997).

(a) Nature of cell structure and orientation

Solid foams comprise cells, with solid material defining their edges and membrane walls in some cases. The cell structure may be closed-cell (with membrane cell walls) or open-cell (without). Furthermore, the structure of closed-cell foams is such that there is always liquid or gas entrapped inside their cells, while fluids flow relatively freely in open-cell foams. Hence the mechanical properties of closed-cell foams are influenced by the properties of the fluid (density, viscosity, compressibility, pressure etc) entrapped inside their cells.

During PUF production, synthetic methods and procedures may also have a bearing on foam cell structure and orientation. For instance, in the production of PUF by the hand-pour (free rise) method in an open mould, foam would expand and rise in the direction of the open end, producing foam cells that are elongated in the foam rise direction. This can give rise to anisotropy in the mechanical properties of foam, with such properties being stronger in the foam rise direction (Tsai and Wu, 1971; Huber and Gibson, 1988). Another example involves the technology of PUF manufacture, whereby moulded and slabstock foams were found to display quite different morphological characteristics. Dounis and Wilkes (1995) reported that slabstock foams were geometrically anisotropic in cell structure while moulded foams were not, probably because in the production of the latter, operation involved the pressurisation of reactants from all directions into the mould. Again, moulded foams had a significantly greater number of closed cells, and their cell struts were thicker than those of slabstock foams.

Consequently, solid foams have certain unique properties different from those of non-cellular solids namely, relatively low stiffness, low thermal conductivity, high compressibility and density adjustability (Ridha, 2007).

These properties are as a result of the different mechanical behaviour of solid foam under compression/tension, compared to that of non-cellular solids.

(b) Compression

Ridha (2007) described typical stress-strain curves obtained for solid foams made from three different kinds of solid materials - (a) elastomeric foam; (b) elastic-plastic foam and (c) elastic-brittle foam under compression/tension (Figs 2.4 and 2.5). He explained that extended stress-strain plateau shown by all three foams is quite different from that of common solid materials such as metals, which normally do not have an extended stress-strain plateau under compression. Long stress-strain plateau is suggestive of high compressibility of PUF.

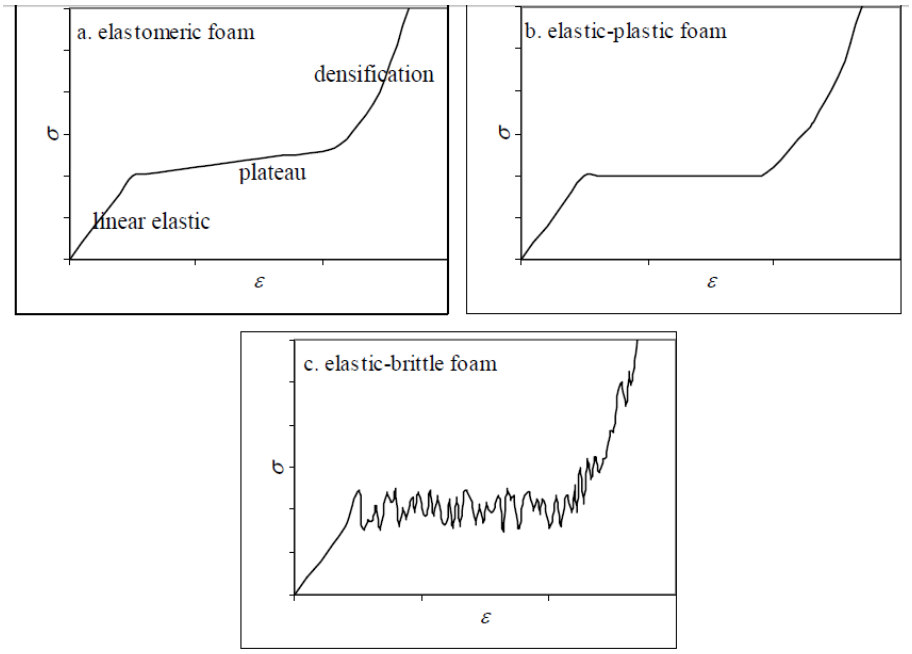


Fig. 2.4: Stress-strain relationships for foams under compression (Ridha, 2007).

(c) Tension

At low strains, all the foams exhibit linear elasticity similar to their compressive behavior (Gibson and Ashby, 1997), but at higher strains, different deformation mechanisms occur in the three types of foam, causing differences in their stress-strain curves.

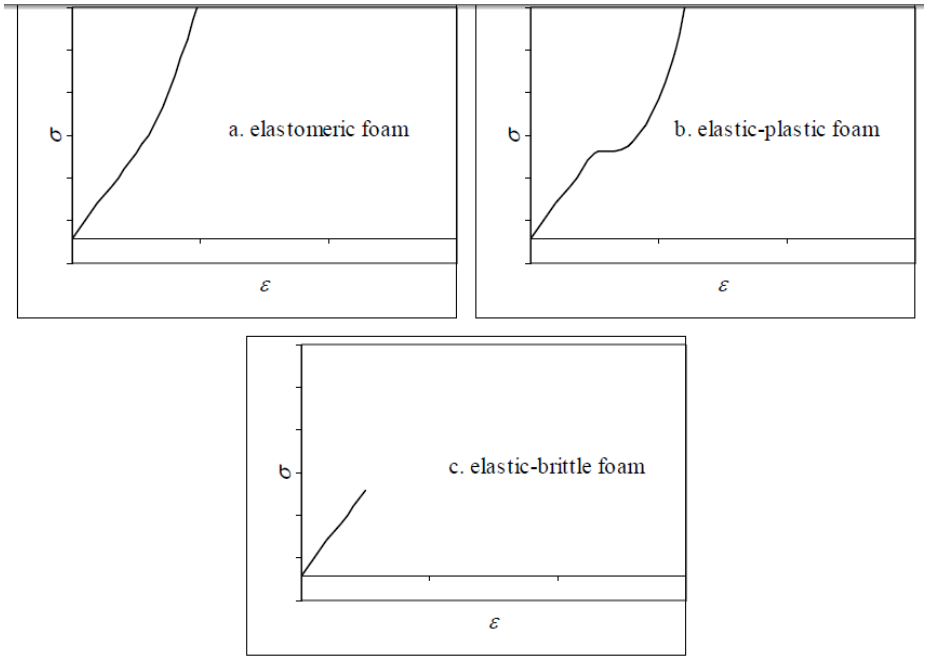


Fig. 2.5: Stress-strain curves for foams under tension (Gibson and Ashby, 1997).

However, stress-strain curves for the brittle foams do not show any non-linearity, as brittle fracture occurs immediately at the end of the linear elasticity.

2.3.2.3 Factors influencing mechanical properties of solid foams

Mechanical properties of solid foams are influenced by a number of factors namely:

(i) Cell structure;

(ii) Mechanical properties of the solid material defining the cell edges (struts) and walls (membranes); and

(iii) Properties of fluids inside the cells.

Cell structure is very important because the way and manner the cell struts and walls deform under load determines the overall mechanical behaviour of the foam. When solid foams are loaded by compression/tension, the struts at the cell edges deform, and they undergo bending and tension/compression. According to Gibson and Ashby (1997), their compliance in bending is much higher than that in tension/compression; and hence bending is the primary deformation mechanism. However, compressing foam beyond its elastic limit damages the cellular structure. On the other hand, compressing brittle foam causes collapse and buckling of cellwalls, whereas tension results in sudden failure dominated by defects in the structure (Gibson and Ashby, 1997). Foam properties like stiffness, strength and viscoelasticity depend largely on the mechanical properties of the solid material in the cell edges and walls, e.g. the stiffer and stronger the cell strut and wall material, the stiffer and stronger the solid foam. Closed-cell foams have fluid entrapped inside their cells and hence their mechanical properties are influenced by the properties of the fluid (density, viscosity, compressibility etc) contained. The factors explained above underscore the need to have a well characterised morphology for solid PUFs, in order to properly understand their response to mechanical stresses.

Mechanical properties of PUFs such as elastic moduli and strength in tension and compression are also known to strongly depend on density (Saint-Michel *et al*., 2006; Song *et al*., 2009). Linul *et al*. (2013) studied the effect of density, loading rate, material orientation and temperature on dynamic compression behavior of rigid PUFs. Their results showed that young's modulus, yield stress and plateau stress values increased with increasing density. Goods (1997) who investigated the tensile, compressive and impact properties of PU encapsulant foam as a function of density, found that over the range of densities examined, both the modulus and elastic collapse

stress of the foam exhibited power-law dependencies with respect to density. He explained that the density dependence of both the modulus and the elastic collapse stress of cellular foam can be understood in terms of the mechanical properties of the polymer material from which the cell struts and/or the cell walls are made, and the deformation mechanics of the cellular structure itself.

2.3.3 Morphological properties

Polymer morphology represents the sum total of polymer structure at the micro- and macroscopic levels. PUFs are cellular structured materials that are usually produced in one of two different forms: flexible and rigid. The main parameters that characterise cellular structure in PUFs are cell number density, nature and shape of cells (open or closed), strut (wall) thicknesses and cell diameter (Voiconi *et al*., 2014). Cell number density is defined as the number of cells per unit volume of foam. In flexible PUFs with large, open (porous) cells, Sharma *et al*. (2014) observe that the microscopic foam morphological units are pneumatically connected to each other by a segmented polymeric phase consisting of an "open cell" structure. Open-cell foam has less inherent resistance under external force due to ruptured cell wall and a lower R-value because of the interconnected pores. Rigid PUFs on the other hand, are made of interconnected networks of solid struts and cell walls incorporating voids with entrapped gas (Voiconi *et al*., 2014). High rigidity and high R-value of closed-cell foam are attributed to the support of cell walls and insulation of gas enclosed in foam cells respectively (Chang, 2014).

In segmented PU elastomers with phase-separated biphasic (hard and soft segment) structure, their morphology depends on the structure and relative amounts of these hard and soft phases, and their ordering (Xu *et al*., 2008). In such segmented structures, the

hard domains play the role of physical crosslinks and act as high modulus filler, whereas the soft phase provides extensibility (Hepburn, 1991; Petrovic and Ferguson, 1991; Oertel, 1993). However, in composite PUFs in which additives have been incorporated into the PUF matrix, PUF morphology and foam characteristics are definitely altered. For instance, foams reinforced with fillers are known to have smaller average cell size, greater cell number density and narrower cell size distribution than foams without fillers (Zhu *et al*., 2011; Linul *et al*., 2013; Lorusso *et al*., 2015). Consequently, such foams exhibit more stiffness and greater mechanical strength (Latinwo *et al*., 2010; Agarry *et al*., 2015).

Optical microscopy (OM) and scanning electron microscopy (SEM) are among widely used techniques for probing the morphologies of PUFs (Dounis and Wilkes, 1997; Herrington and Hock, 1998; Kaushiva and Wilkes, 2000). These techniques can examine cell structure, including cell size and distribution, and cell orientation (Rhodes, 1994; Chian and Gan, 1998). More significantly, however, is 3D analysis of foam structure and geometry involving the use of micro-computer tomography (CT), a powerful tool for the analysis of PUFs (Montminy *et al*., 2004; Moesen *et al*., 2015).

The major advantage of this technique is its ability to provide unambiguous 3D parameters for the following:

(1) Relations between structure and physical (e.g. mechanical, thermal, acoustic) properties.

(2) Direct simulation of physical properties based on micro-CT models.

(3) More realistic computer-generated models of foam structures that allow parametric simulation of their physical properties.

Ridha (2007) employed micro-CT scanning and OM to examine the internal structure of rigid PU and its behaviour under compressive and tensile loads. Micro-CT images of

cells in the foam indicated that the cells exhibited a good degree of resemblance with an elongated tetrakaidecahedron. Further, images of the cell struts showed that their cross-sections are similar to that of a plateau border, while microscopic examination of rigid PUF samples under tensile and compressive loading showed that cell struts were both bent and axially deformed, with bending being the main deformation mechanism. Tan *et al*. (2011) used SEM to characterise the morphology of rigid PUFs synthesised by substituting a polypropylene-based polyol with soybean oil-based polyol (SBOP). They found that all the soy-based foams maintained a regular cell structure and had even smaller average cell size than the control foams. Edhi *et al*. (2012) have also used SEM to probe the morphology of a polypropylene glycol/castor oil PUF system treated with ethylene glycol (EG), and to determine cell diameter and cell number density of the PUF. Similarly, Chang (2014) used SEM and X-ray CT to characterise the morphology of wood fibre-reinforced soybean-based PUF.

Atomic force microscopy (AFM) is another powerful tool for the characterisation of polymer morphology (Kaushiva and Wilkes, 2000). Among many other researchers, Lan and Haugstad (2011) employed AFM to characterise different types of PUFs that included flexible foam, two different elastomeric foams and a rigid foam nanocomposite, while keeping the foam cells intact. They further used this method to investigate the distribution of nanoparticles in closed-cell PUFs. Advantages of AFM include its ability to permit the study of polymer features even in the nanometer range, and does not require the use of staining techniques. Other useful techniques employed for the same purpose include transmission electron microscopy (TEM), dynamic mechanical spectroscopy (DMS), small angle x-ray scattering (SAXS), wide angle x-ray scattering (WAXS) etc.(Armistead and Wilkes, 1988; Herrington and Turner, 1992; Priester and Turner, 1994).

2.4 Structure-Property Relationships in PUFs

Polyurethane foams are cellular structured polymers formed by the polyaddition reaction between isocyanates and polyols/amines in the presence of catalysts and other additives. Properties of PUFs are determined by cellular structure and morphology of the PU polymer (Lan and Haugstad, 2011). Change in structure affects the physical, thermal and mechanical properties of foam. However, in order to appreciate structure-property relationships in PU foams, it is necessary to consider the major chemical and physical transformations involved in their synthesis. During PU foam synthesis, two types of reactions take place simultaneously namely, blow or foaming reaction and gelation or polymerisation reaction; the water-isocyanate (blow) reaction starting earlier and faster compared to the polyol-isocyanate reaction (Bailey Jr. and Critchfield, 1981; Macosko and Artavia, 1994). Controlling the relative rates of these reactions is critical, in order to obtain a foam with a stable cellular structure and good physical properties (Aneja, 2002). The blow reaction produces carbon dioxide and an amine. This reaction not only helps in foam expansion, but also leads to the generation of oligomeric urea hard segments (UHSs). The gelation reaction (which produces urethane linkages) then covalently bonds these UHSs to soft polyol segments. With biurets and allophanates present in the PU matrix, additional physical crosslinks may be formed. When the concentration of the hard segments exceeds a system dependent solubility limit, the hard segments phase-separate to form so called ‘urea microdomains’, which represent a more ordered (micro-phase separated) state (Woods, 1982; Herrington and Hock, 1998). These microdomains are not quite crystalline, but have been suggested to possess ordering of a paracrystalline nature (Herrington and Hock, 1998). Also, bidentate hydrogen bonding takes place in the hard segment domains between polyurea carbonyl groups and two hydrogen atoms from adjacent polyurea groups, and these

strongly influence the cohesive strength of the urea hard domains (Yilgor *et al.*, 2000; Kaushiva *et al.*, 2000). At higher hard segment content (often promoted by higher water content in the formulation), urea microdomains are known to aggregate and form larger urea-rich structures called 'urea balls' or 'urea aggregates' (Aneja, 2002). The urea balls have been shown to be regions which are richer in urea compared to the general surrounding polyol matrix which also contains dispersed urea microdomains.

The physical properties of PU foams such as load-bearing capacity, compression stress relaxation, creep etc, are a function of both the cellular structure and the phase separated morphology of the polymer, comprising the struts in the foam (Herrington and Hock, 1998). These two factors are intimately related because both are influenced by the forces exerted during the expansion and stabilisation of the foam (Aneja, 2002). Solid-state morphology will depend on the structures and relative amounts of the hard and soft phases, and their ordering. However, PU foam literature suggests that it is quite difficult to separate the effects of cellular structure and the solid-state polymer morphology on foam properties. Again, it is also difficult, if not impractical, to know the exact size, shape and location of each cell in a cellular structured material. Therefore, mean cell diameters and average cell volumes have been used to characterise cell size, since a distribution in a cell size is always noted (Gibson and Ashby, 1997). Apart from cell size, shape and location, degree of cell openness is another important parameter in relation to the properties of cellular structured materials. Kaushiva and Wilkes (2000) have used air flow measurements to characterise the extent of cell openness in cellular plastics. By this notion, flexible foam is considered as having an open-celled structure, and very few closed cells; a rigid one having a closed-cell structure, with very few open cells. In addition to closed-cell structure, rigid PU foams

also have high concentration of hard segments. In such systems, chain extenders are often applied to reduce foam rigidity, and enhance processing of the foam (Lees, 2013).

The effect of fillers on PUF cellular morphology and physical properties like density and compressive strength is also very important. This is because filler incorporation alters foam cellular structure. Zhu *et al*. (2011) who investigated structure-property correlations on water-blown rigid soy-based PUFs filled with microfibers and nanoclays found that the cellular structure, mechanical properties, as well as the thermal decomposition behaviour of the PUFs were substantially altered or modified. With regard to PUF morphology, average cell size decreased, cell size distribution narrowed and number fractions of small cells increased. However, mechanical properties were found to increase with addition of the two fillers, while thermal degradation characteristics improved with microfibre addition only.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Castor oil (CO) was sourced locally by mechanical extraction from the seeds of wild *Ricinus communis* Linn or castor plant at ambient temperature. Modified castor oil polyols (MCOPs) i.e. glycerol modified castor oil polyols (GMCOPs) and PCl_5 - modified castor oil polyols (PMCOPs) of varying modifier concentrations (10-60%) and varying hydroxyl values (Table 3.1) were produced in our laboratory. Foam-making chemicals made up of an isocyanate (80%: 20% mixture of 2, 4 - and 2, 6 - isomers of toluene diisocyanate - TDI), a surfactant (silicone oil), an amine catalyst (dimethylaminoethanol - DMAE), a gelation catalyst (stannous octoate), a physical blowing agent (methylene chloride) and calcium carbonate ($CaCO_3$) filler were all kindly supplied by Vitafoam Nig. Plc, Jos. Distilled water was used as chemical blowing agent. Two straight chain chlorinated paraffins namely 2, 4, 5, 8, 10, 11, 14-heptachlorotetradecane (HCTD) (formula $C_{14}H_{23}Cl_7$) and 2, 5, 6, 7, 8, 11, 15-heptachloroheptadecane (HCHD) (formula $C_{17}H_{29}Cl_7$), products of Dover Chemical Corporation USA, were purchased from a local supplier and used as plasticisers/flame retardants(FRs).

Glycerol (99.5%), lead (II) oxide, petroleum ether (40-60^{0}C, bp), diethyl ether, iodine and potassium iodide crystals, Na_2SO_4, NaOH and KOH were all May and Baker products, while PCl_5, conc. H_2SO_4 (98%), conc. HCl (36.5%), glacial acetic acid, acetic anhydride, pyridine, absolute ethanol and chloroform were from BDH Chemicals Ltd, Poole, England. All reagents were of analytical grade and were used without further purification.

3.2 Equipment/machines used

(i) Locally fabricated machine extractor (cold-press), NARICT, Zaria

(ii) Glass electrode pH meter (HANNA-209-209R), Hanna Instruments Inc., USA

(iii) Refractometer (DIGITAL REFM960.4d.p)

(iv) Shimadzu 8400S FTIR spectrophotometer, Japan

(v) GC-MS QP2010 plus, Shimadzu, Japan

(vi) Instron Universal Testing Machine - TecQuipment Ltd, Nottingham, UK

(vii) TecQuipment SM 1006 Creep Machine, Nottingham, UK

(viii) Phenom (Pro) scanning electron microscope, Dillenburgstraat 9E, 5652 AM, Eindhoven, The Netherlands

3.3 Methods

3.3.1 Seed collection and preparation

Seeds were obtained from castor plants (*Ricinus communis* Linn) growing wild on wet marginal lands around Lambun Sarki, K/Marusa, Katsina. Harvested ripe castor fruits were manually cleaned and sun-dried for 4-5 days, until fruit capsules split open to discharge encased seeds. This was followed by seed pod removal and tray-winnowing to separate shells from beans (cotyledons). Castor beans (100g) were further dried at 80^0C to constant weight for 9hrs in a hot air oven. The beans were then ground to a paste using mortar and pestle, prior to extraction.

3.3.2 Determination of moisture content of seeds

Percentage moisture content of seeds was based on the % of total weight loss from the original sample weight after drying to constant weight. Moisture content of seeds therefore determined in accordance with AOAC (1990) method as

$$\%\text{moisture (seed)} = \frac{W_o - W_1}{W_o} \times 100 \quad (21)$$

Where W_0= weight of sample before oven-drying; W_1= weight of sample after oven-drying.

3.3.3 Extraction and purification of oil from castor bean

Castor bean paste (8.42 kg) was wrapped in clean cloth and mechanically cold-pressed (below 45^0C) using a manual (locally fabricated) machine extractor from the National Research Institute for Chemical Technology (NARICT), Zaria, to obtain clear, viscous, pale-yellow virgin oil.

Percentage oil yield was evaluated using the expression (Muzenda *et al*., 2012):

$$\%\ \text{yield} = \frac{y_1 - y_2}{y_1} \times 100 \quad (22)$$

Where y_1 and y_2 are the weights of castor beans before and after extraction respectively.

After settling for about 1 hr, good quality cold-pressed oil was further purified by filtration through sintered glass (fine mesh screen) in a Buchner funnel. This was to eliminate any dust, gum or other particulates present. The purified oil was kept in tightly stoppered dark bottles and stored in a refrigerator at 4^0C.

3.3.4 Characterisation of oil from castor bean

(a) Physical analyses

(i) pH measurement

pH of 2.30g dispersion of the oil in 15cm^3 hot water was determined (after cooling to 30^0C in a water bath) with the aid of a glass electrode pH meter (HANNA-209-209R).

(ii) Determination of refractive index (RI)

Refractive index was measured at 30^0C using a refractometer, DIGITAL REFM960.4d.p. Drops of oil sample were placed on the glass slide of the refractometer kept at a uniform temperature of about 30^0C by water circulating round the glass slide. After making necessary adjustments through the eyepiece of the refractometer (Akpan *et al*., 2006; Kyari, 2008) and at no parallax, the refractive index of the sample was read off on the refractometer scale. For each oil sample, the average of three such readings was recorded as the refractive index.

(iii) Determination of specific gravity (SG)

Clean, dry specific gravity bottle was weighed empty (W_0) on a digital top-loading balance. Bottle was then filled with castor oil and weighed again (W_1). Oil was then discharged from the bottle, and the latter cleaned and dried. Bottle was now filled with distilled water and weighed (W_2). Specific gravity of castor oil was evaluated at 30^0C as

$$\mathbf{SG} = \frac{W_1 - W_o}{W_2 - W_o} \qquad \mathbf{(23)}$$

(iv) Determination of relative viscosity (RV)

Relative viscosity of oil (in chloroform) was determined at 30^0C from viscometric measurements using an Ubbelohde dilution type viscometer with an efflux time of about 120 seconds for the solvent. Portion (10 cm^3) of solvent (chloroform) was taken into the viscometer and its efflux time (t_0) determined repeatedly until reproducible. Thereafter, viscometer was emptied and dried. Castor oil (1 cm^3) was then poured into it and diluted with 10 cm^3 of the solvent oil. Efflux time of the diluted oil (t) was also determined repeatedly until reproducible. Relative viscosity of castor oil was evaluated using the expression

$\eta_{rel} = \eta/\eta_0 = t/t_0$ **(24)**

Where η = viscosity of the diluted castor oil; η_0 = viscosity of the solvent (chloroform).

(b) Chemical analyses

(i) Determination of acid number (AN)

Acid number was evaluated as the number of mg of KOH required to neutralize the free fatty acids (FFAs) present in 1g of oil sample. Method used by Akpan *et al*. (2006) was followed. Exactly 10g of oil sample was shaken with 50 cm^3 of a 1:1 mixture of absolute ethanol and diethyl ether until the oil was completely dissolved. Two drops of phenolphthalein indicator were added to the solution and titrated with 0.1M KOH solution to a pink end point. Acid number of oil was evaluated as

$$\mathbf{AN} = \frac{56.1 \times V \times C}{W} \quad \textbf{(25)}$$

Where V= volume of KOH used; C= molar concentration of KOH solution; W= weight of the oil sample and 56.1 is the relative molar mass of KOH.

(ii) Determination of hydroxyl number (HN)

Hydroxyl number was evaluated as the number of mg of KOH required to neutralize the acetic acid capable of combining by acetylation with 1g of oil sample. Standard procedures described by the International Union for Pure and Applied Chemistry (IUPAC) (1979) were followed. Acetylating agent for the determination was first prepared by taking 25g (equivalent of 23.15 cm^3) of acetic anhydride into a 100 cm^3 volumetric flask. Portion (76.85) cm^3 of pyridine was added to make up to the 100 cm^3 mark. Acetylating agent was then stored in a glass stoppered amber bottle prior to use.

Exactly 5g of oil sample was weighed into a 250 cm^3 conical flask and 5 cm^3 of the earlier prepared acetylating agent added. Mixture was heated in a steam bath for 1 hr. It

was then cooled substantially, and 1 cm^3 distilled water added to obtain a clear solution. Flask was placed again on the steam bath for a further 10 minutes. After cooling, 5 cm^3 of absolute ethanol was added to the solution, followed by two drops of phenolphthalein indicator. The mixture was then titrated with freshly prepared 0.5M ethanolic KOH solution. A blank was also titrated under same conditions by measuring an equal amount of the acetylating agent into a second 250 cm^3 conical flask.

From the titration results, hydroxyl number of oil was evaluated using the expression

$$\mathbf{HN} = \frac{\mathbf{56.1}\,(V_o - V_1)C}{W} + \mathbf{AN} \qquad \mathbf{(26)}$$

Where C= molar concentration of the ethanolic KOH solution; V_0= titre value for the blank; V_1= titre value for oil; W= weight of oil sample and AN is the acid number of oil.

(iii) Determination of saponification number (SN)

This is the number of mg of KOH required to saponify 1g of the oil sample. Indicator Method as specified by ISO 3657 (2002) was used. Exactly 2g of oil sample was weighed into a conical flask, and 25 cm^3 ethanolic KOH added. Solution was refluxed for 2 hrs, during which contents were shaken by swirling the conical flask from time to time. Few drops of phenolphthalein indicator were then added to the warm solution and titrated with 0.5M HCl to end point, until the pink colour of the indicator just disappeared. Same procedure was followed for the blank determination. From the titration results, saponification number of the oil was evaluated as

$$\mathbf{SN} = \frac{\mathbf{56.1}\,(V_1 - V_2)C}{W} \qquad \mathbf{(27)}$$

Where V_1= volume (cm^3) of HCl used for the blank test; V_2= volume (cm^3) of HCl used for the oil sample; C= molar concentration of HCl solution used and W is the weight (g) of test portion.

(iv) Determination of peroxide number (PN)

American Oil Chemists Society (AOCS) official method Cd 8-53 (2003) was followed. Portion (5g) of oil sample was weighed into a conical flask and 30 cm^3 of solvent mixture of glacial acetic acid and chloroform in the ratio 3:2 was added to the oil sample. Half cm^3 of saturated KI solution was added to the mixture and allowed to stand for 1 minute. Thereafter, 30 cm^3 of distilled water was added and titrated with 0.02M sodium thiosulphate ($Na_2S_2O_3$) solution using starch indicator, until the yellow colour was discharged. A blank titration (without oil) was also carried out under same conditions. Peroxide number of oil was evaluated as

$$\mathbf{PN} = \frac{\mathbf{10}\,(V_2 - V_3)}{W} \qquad \mathbf{(28)}$$

Where V_2= volume of $Na_2S_2O_3$ solution for oil determination; V_3= volume of $Na_2S_2O_3$ solution for blank determination and W= weight (g) of oil sample.

(v) Determination of iodine number (IN)

This is the number of grams of iodine absorbed per 100g of oil sample.

Hanus method (ISO 3961:1996) was used. Hanus reagent containing iodine monobromide was prepared as described by the method. Exactly 0.3g of oil was weighed into a flask with glass stopper. Portion (10 cm^3) of chloroform was added to dissolve the oil. Exactly 24 cm^3 of Hanus reagent was then added in a fume chamber. Flask was stoppered and swirled vigorously to mix the contents. Mixture was stored in the dark for 21/2 hrs. Thereafter, 15 cm^3 of 10% KI solution and 50 cm^3 of distilled water were added respectively and stirred. The content was titrated with 0.1M $Na_2S_2O_3$ solution until the yellow colour almost disappeared. Three drops of 1% starch indicator were added and the titration continued by dropwise addition of $Na_2S_2O_3$ solution until

blue coloration turned colourless. A blank titration (without oil) was also carried out using same procedure. Iodine number of oil was evaluated as

$$\mathbf{IN} = \frac{12.69\,(V_3 - V_4)C}{W} \qquad \mathbf{(29)}$$

Where V_3= titre for blank; V_4= titre for oil; C= molar concentration of the $Na_2S_2O_3$ solution and W= weight of the oil sample.

All physico-chemical determinations were performed in triplicate, and an average evaluated in each case.

(c) FTIR spectroscopic analysis

FTIR was used to characterise structural functionalities in the oil. FTIR spectrum of oil (in KBr pellets) was recorded with a Shimadzu 8400S FTIR spectrophotometer over the range 4500-350 cm^{-1} using 10 scans at a resolution of 4 cm^{-1}.

(d) GC-MS analysis

(i) Fatty acid profile

The oil was also characterised in terms of its fatty acid profile. Fatty acid composition was determined after converting the fatty acids in the oil to fatty acid methyl esters (FAMEs), as the acids are not volatile enough for the GC-MS process owing to hydrogen bonding.

The FAMEs were prepared according to modified ISO method (BS EN ISO 5508, 1995) as follows:

Exactly 0.2g of the oil sample was dissolved in 6 cm^3 of 2% (w/v) methanolic NaOH and mixture refluxed for 10 minutes at 100^0C in a tightly sealed Pyrex tube. After cooling to room temperature, 10 cm^3 of n-hexane was added, followed by 10 cm^3 of distilled and deionised water and mixed gently. Mixture was then allowed to settle until

the upper n-hexane layer became clear. The distinct upper layer of methyl esters in n-hexane was separated carefully using a separating funnel and used for the gas chromatography-mass spectrometry (GC-MS) analysis. Exactly 2 µL of the n-hexane aliquots was injected into the chromatographic column, and components were separated on a GC-MS QP2010 plus Shimadzu (Japan) instrument, comprising an AOC-20i liquid autosampler and a GC equipped with fused silica capillary column (30 x 0.25mm ID x 1 µm df) coated with 5% phenyl- , 95% dimethyl siloxane polymer. This is interfaced to a mass spectrometer at an interface temperature of 250^0C.

Initial oven temperature was 70^0C (hold time 0 min), but this was increased at the rate of 10^0C/min. to 280^0C (hold time 5min.). Inlet temperature was 250^0C, with a split ratio of 20.0. Ion-source temperature was 200^0C. Helium was the carrier gas with flow rate of 1.8ml/min.

Peak identification was done by comparing peak retention times with reference standards for the individual FAMEs.

3.3.5 Chemical modification of castor oil

(a) Sulphation

Method used by Akpan *et al*. (2006) was followed. Portion (20g) of oil was warmed at 30^0C. Exactly 15.5 cm^3 of concentrated sulphuric acid (98%) was then added and the reaction was allowed to completion with constant stirring. Thereafter, the product (sulphated castor oil or Turkey-red oil) was washed with hot distilled water and left to stand for 2 hrs in a separating funnel, after which water was then removed. The sulphuric acid ester formed was finally neutralised with 10 cm^3 of 0.1M NaOH.

(b) PCl_5 chlorination (by substitution)

Portion (32g) of castor oil was dissolved in petroleum ether (40-60^{0}C, bp) in a 500 cm^3 distilling flask. Exactly 10 wt% equivalent of PCl_5 was calculated, measured and added, and the mixture refluxed for 1 ½ hrs. The reaction was monitored periodically after every 20 minutes by taking a small portion of the reaction mixture and determining its hydroxyl value. This procedure was repeated using 20, 30, 40 50 and 60 wt% PCl_5 in the mixture. After each treatment, resultant polyol was water-washed, dried over anhydrous Na_2SO_4 and the solvent evaporated under vacuum.

(c) Alcoholysis (glycerolysis) of castor oil

Castor oil containing 10wt% glycerol was introduced into a round bottom flask equipped with thermometer, stirrer and reflux condenser along with lead (II) oxide (PbO) catalyst (0.05%). Mixture was refluxed at 240-250^{0}C for 2 ½hrs. The reaction was monitored after every 30 minutes by taking a small portion of the reaction mixture and determining its hydroxyl value. This procedure was repeated using 20, 30, 40, 50 and 60 wt% glycerol in the mixture. At the end of 2 ½ hrs and after allowing mixture to cool and settle down, excess (unreacted) glycerol in the bottom layer was removed using separating funnel and resultant polyol in each case was dried at 80^{0}C under vacuum.

Table 3.1: Polyols used in COPUF formulation:

Polyol	Hydroxyl number (mg KOH/g oil)
NCOP	164
GMCOP	168-320
PMCOP	50-161

NCOP = Neat castor oil polyol
GMCOP = Glycerol - modified castor oil polyol.
PMCOP = PCl_5 - modified castor oil polyol

Table 3.2: Basic COPUF formulation I (NCO/OH of 1/2)

Component	Actual weight (g)	Pph polyol
Neat/modified CO polyol	50.00	100.00
TDI (index = 107)	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	4.5

* Without filler, plasticiser or FR

Table 3.3: Basic COPUF formulation II (NCO/OH of 1/1)

Component	Actual weight (g)	Pph polyol
Neat/modified Co polyol	50.00	100.00
TDI (index = 110)	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

*Without filler, plasticiser or FR

3.3.6 Foam-making procedure

One-shot technique of foam synthesis was used. Foams were produced in locally fabricated card board moulds of dimension 18 x 15 x 9 cm^3 at room temperature, by the free-rise method. Foam-making ingredients were accurately weighed on a digital top-loading balance or measured out using syringes and micro-pipettes as per formulation (Tables 3.2 and 3.3). Polyol based A component made up of castor oil polyol (neat/modified), DMAE, silicone oil, stannous octoate, methylene chloride and distilled water were premixed for 20 seconds in a plastic mug with the aid of a high speed (1000 rev/min) mechanical stirrer. Where required in formulation, accurately measured quantity of fine grade $CaCO_3$, liquid plasticiser/FR was also added (*in-situ*) as part of

the polyol (A) component, with continuous stirring. TDI, measured out separately in another container, constituted the B component.

Components A and B were then rapidly added together, with continuous vigorous stirring, until the reaction mixture creamed. High speed continuous stirring was maintained, to ensure complete dispersion of reagents, so that homogenous foams with good cell structure could be produced. The time taken (seconds) to form creamy-like bubbles that just began to rise above the level of the reaction mixture (cream time) was measured using a stopwatch. The contents were then quickly poured into the open mould in a fume cupboard and the stopwatch set on again. Meanwhile, all containers were thoroughly cleaned with methylene chloride. The resulting foam was allowed to rise freely until rising stopped (free rise time noted). Thereafter (in sequence), the time required for the foaming mixture to form semi-solid matter or gel was noted as the gel time (seconds). The time when the outer surface of the solidifying foam lost its stickiness was taken as the tack-free time. Solid foam was then kept in a fume cupboard for 24 hours to cure completely, before demoulding. Foam rise (cm) for each foam sample was measured post-cure.

3.3.7 Foam testing

(a) Visual observation

Foams were observed for colour, texture, feel, and for signs of shrinkage.

(b) Density determination

Test pieces of same dimension (3 x 3 x 3cm^3) were cut from foam and accurately weighed on a digital top-loading balance. Density (kg/m^3) of foam was calculated as mass per unit volume. Density of each PU foam sample was evaluated at room temperature (30-35^{0}C) as the average of the mass/volume measurement results of 5

specimens from the sample, as per ASTM D3574-11/D1622-08 procedures for flexible and rigid foams respectively.

(c) Water absorption

Water absorption test was performed according to ASTM D570-98/D2842-12 procedures for flexible and rigid foams respectively. Water absorption of foam was measured by taking the initial weight of foam sample and final weight after dipping sample in distilled water in a measuring cylinder at room temperature for 24 hours. Excess water on foam surface was completely mopped up with tissue paper before reweighing. Water absorption of foam was evaluated using the expression:

$$\%\ \boldsymbol{water\ absorption} = \frac{\boldsymbol{weight\ of\ wet\ foam - weight\ of\ initial\ foam}}{\boldsymbol{weight\ of\ initial\ foam}}\ \boldsymbol{x\ 100} \qquad \textbf{(30)}$$

(d) Determination of mechanical properties

(i) Compressive strength

Compressive strength (i.e. the ability of a specimen to resist compression under an applied force /compressive load) of the CO-based PU foams in this study was measured on a computer-coupled Instron Universal Testing Machine - TecQuipment Ltd, Nottingham, UK - (model SM 1000) available in the LNG Multiuser laboratory at the Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria. Measurements were in accordance with ASTM D1621-10 procedure. Instrument load capacity was 100 KN (10 tons). Crosshead speed was 3.0 mm/min.

PU foam samples for compressive strength test were punched out from the bulk foam in cylinders of 30 mm diameter and 25 mm length, i.e. a length - to - diameter ratio of 0.83.

Test specimen was placed between two compressive 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, and to which specimen data had been fed. For each sample, three test-pieces or 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 (ASTM D1621-10).

i.e. $$\boldsymbol{Compressive\ strength} = \frac{\boldsymbol{maximum\ compressive\ load\ (N)}}{\boldsymbol{Minimum\ cross-sectional\ area\ (m^2)}} \quad \textbf{(31)}$$

(ii) Creep recovery

Creep recovery test was performed on a TecQuipment (TQ) SM 1006 Creep Machine with a cell load of 250N and equipped with an SM 1006CK thermocouple transmitter. The test was carried out as per ASTM D2990-09 procedure. Specimen shape (as described in the manufacturer's manual) of dimension 63.5mm x 4.8mm x 1.8mm was cut from the bulk foam sample. Specimen was fitted and gripped between steel support clips in the machine and subjected to a tensile force of 20N at a speed of 60mm/min at ambient temperature, using the method of constant rate of extension (Dalen *et al.*, 2014). The maximum extension (mm) of the specimen, recorded as the peak of an extension-time chart was noted. On removal of the applied load after 5 seconds, the amount of relaxation (mm) per specimen was also noted.

Creep recovery was evaluated as the difference between the total extension (mm) on application of load and the relaxation (mm) on removal of load after 5 seconds (ASTM D 2990-09). Percentage creep recovery was then calculated using the formula

$$\%\ \boldsymbol{creep\ recovery} = \frac{\boldsymbol{creep\ recovery\ or\ resilience}}{\boldsymbol{extension\ on\ application\ of\ load}} \times \mathbf{100} \quad \textbf{(32)}$$

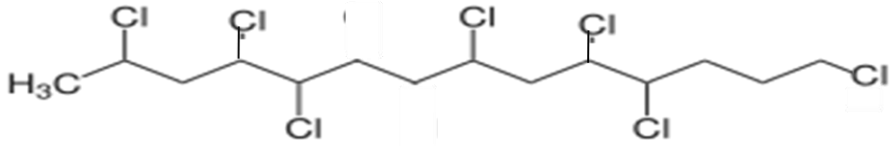
3.3.8 Flammability studies

Both FR-treated and un-treated PU foam samples were subjected to flammability testing. Tests employed included ignition time (IT), flame propagation rate (FPR) and after-glow time (AGT). Samples of dimension 15 x 3 x 0.15cm^3 were used (Ishidi *et al*., 2011). Time measurement was carried out using a stopwatch.

(a) FR treatment

Accurately weighed quantities of HCTD and HCHD FRs/plasticizers (Fig.3.1) in concentrations of 0.4, 0.8, 1.2, 1.6, 2.0 and 2.4 parts per hundred (pph) polyol were separately added *in-situ* into the polyol component of foam formulation. Blends of these FRs/plasticisers in weight ratios of 0/2.4, 0.4/2.0, 0.8/1.6, 1.2/1.2, 1.6/0.8, 2.0/0.4 and 2.4/0 were also separately added in formulation in selected samples. Treated samples were then subjected to flammability and other test procedures.

(a)



(b)

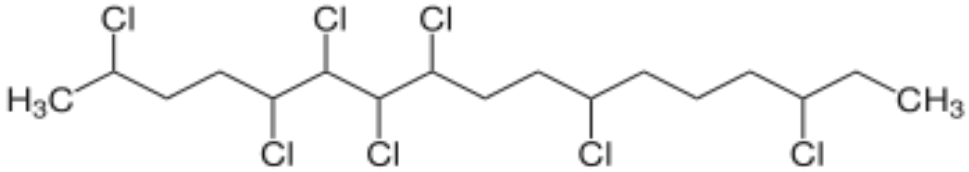


Fig. 3.1: Structures of FRs used in PU foam formulation: (a) HCTD; (b) HCHD

(b) Ignition time (seconds)

Each treated as well as untreated sample was clamped vertically to a retort stand at a distance of 5cm to a lighted gas burner in a draught-free room. The time taken for the sample to catch fire was recorded as the ignition time (Arinze *et al.*, 2015).

(c) Flame propagation rate (cm/s)

Sample was clamped vertically in a draught-free room and ignited at the base by means of a gas lighter. The time (T) taken (seconds) for the flame to traverse from base (Lo) to a marked distance (L_1) on sample before flame-out (Ishidi *et al*., 2011) was recorded. FPR was evaluated as:

$$\boldsymbol{FPR = \frac{L_1 - L_0}{T}\ (cm/s)} \qquad \textbf{(33)}$$

i.e. a measure of the speed with which fire spreads within the material.

(d) After-glow time (seconds)

AGT for each sample was obtained by recording the time interval between the extinguishing of flame or flame-out and the last visually observable glow on sample (Garba and Eboatu, 1990).

(e)Add-on (%)

For the FR-treated samples, add-on was evaluated as the difference in weight (of foams of same dimension) between FR-containing and non-FR containing foam, divided by the weight of the non-FR containing foam, multiplied by 100 (Eboatu *et al.*, 1995).

$$\boldsymbol{i.e.\ Add-on = \frac{W_1 - W_0}{W_0} \times 100} \qquad \textbf{(34)}$$

Where W_0 = weight of non-FR containing foam.

W_1= weight of FR-containing foam.

3.3.9 Scanning electron microscopic (SEM) analysis

Cell morphology for the COPUFs was observed under a Phenom (Pro) scanning electron microscope, Dillenburgstraat 9E, 5652 AM, Eindhoven, The Netherlands. Slices of 1mm thickness were cut from foam sample in x-direction. Dimensions of the foam pores were detected from SEM images obtained. The diameters and wall

thicknesses of all the pores visible in the images of the sections were measured and the arithmetic mean calculated in each case.

CHAPTER FOUR

RESULTS

4.1 Physico-chemical Properties of Castor Oil and Modified Castor Oil Polyols

The physico-chemical properties determined for the castor seed oil in this study are presented in Table 4.1, while figures 4.1 and 4.2 are the FTIR spectrum and GC-MS chromatogram for the seed oil respectively.

Table 4.1: Physico-chemical properties of purified CO from wild *R. communis* Linn

Property	Value	ASTM* Standard (2012)
pH	6.16	-
Specific gravity (30^0C)	0.959	0.957 - 0.961
Refractive index (30^0C)	1.472	1.476 - 1.478
Relative viscosity (30^0C)	1.86	-
Acid number (mg KOH/g oil)	2.07	2 (max.)
Hydroxyl number (mg KOH/g oil)	163.64	160 -168
Saponification number (mg KOH/g oil)	175.31	176 -184
Iodine number (Hanus) (gI_2/100g oil)	84.18	83 - 88
Peroxide number (cm^3/g oil)	38.00	-
% oil yield (cold press)	39.43	-

* American Society for Testing and Materials.

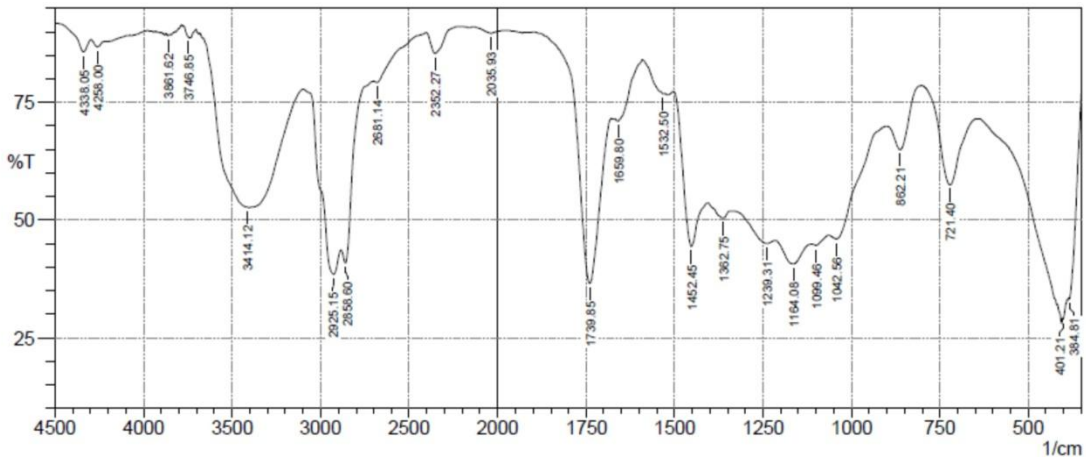


Fig. 4.1: FTIR spectrum for purified CO from wild *R. communis* Linn

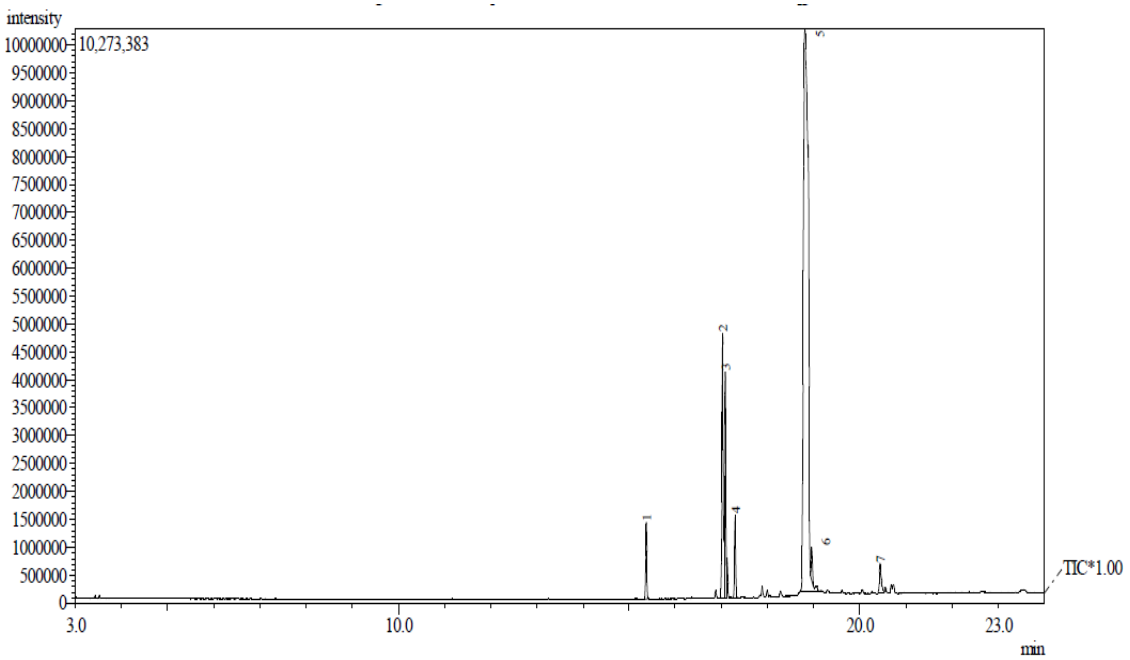


Fig. 4.2: GC-MS chromatogram for purified CO from wild *R. communis* Linn

4.1.1 Fatty-Acid Composition of the Castor Oil

The detailed fatty-acid profile for the castor seed oil is given in Table 4.2, while table 4.3 presents the saturated fatty-acid (SFA), monounsaturated fatty acid (MUFA) and polyunsaturated fatty acid (PUFA) weight% concentrations for the seed oil.

Table 4.2: Fatty acid composition of CO from wild *Ricinus communis* Linn by GC-MS

Fatty Acid	Percentage
Palmitic (C16:0)	2.59
Linoleic (C18:2)	10.32
Oleic (C18:1)	7.55
Stearic (C18:0)	2.81
Ricinoleic (C18:1)	74.10
Eicosadienoic (C20:2)	0.93
Erucic (C22:1)	1.70

Table 4.3: SFA, MUFA and PUFA contents (wt%) for the castor seed oil.

Parameter	Value
SFA total	5.40
MUFA total	83.35
PUFA total	11.25
UFA total (MUFA + PUFA)	94.60

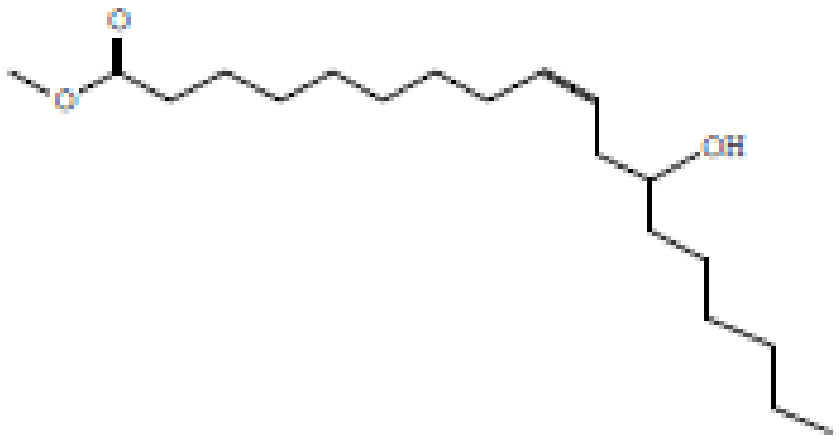


Fig. 4.3: Structure of methyl ricinoleate by GC-MS

4.1.2 Physico-chemical Properties of the Modified Castor Oil Polyols

Table 4.4 – 4.6 describe the physico-chemical properties determined for the chemically modified castor oil polyols namely, the glycerol modified castor oil polyols (GMCOPs), the PCl_5 modified castor oil polyols (PMCOPs) and the sulphated castor oil (SLCO).

Table 4.4: Physico-chemical properties of glycerol-modified castor oil polyols (GMCOPs)

	Wt % PCl_5						
Property	0	10	20	30	40	50	60
Specific gravity (30^0C)	0.959	0.962	0.974	0.994	1.020	1.072	1.094
pH	6.16	6.28	6.34	6.42	6.55	6.66	6.72
Refractive index(30^0C)	1.472	1.475	1.480	1.495	1.510	1.526	1.540
Relative viscosity	1.86	1.86	1.85	1.82	1.76	1.68	1.58
Acid number (mg KOH/g oil)	2.07	2.05	2.01	1.96	1.91	1.88	1.86
Hydroxyl number (mg KOH/g oil)	163.64	168.20	190.12	210.50	242.30	285.00	320.20
Saponification number (mg KOH/g oil)	175.31	168.05	152.20	140.40	120.00	100.90	94.00
Iodine number (Hanus) (gI_2/100g oil)	84.18	84.18	84.30	84.44	84.59	84.76	84.94
Peroxide number (cm^3/g oil)	38.00	38.20	38.70	39.60	40.20	40.90	41.40

Table 4.5: Physico-chemical properties of PCl_5-modified castor oil polyols (PMCOPs)

	Wt % PCl_5						
Property	0	10	20	30	40	50	60
Specific gravity (30^0C)	0.959	0.950	0.940	0.934	0.925	0.900	0.868
pH	6.16	6.04	5.90	5.85	5.70	5.60	5.50
Refractive index(30^0C)	1.472	1.470	1.465	1.460	1.455	1.488	1.442
Relative viscosity	1.86	1.82	1.74	1.62	1.55	1.44	1.21
Acid number (mg KOH/g oil)	2.07	2.82	2.68	2.98	3.40	3.80	4.02
Hydroxyl number (mg KOH/g oil)	163.64	161.00	150.52	126.88	110.10	80.00	50.20
Saponification number (mg KOH/g oil)	175.31	177.80	182.50	184.60	186.20	188.10	190.20
Iodine number (Hanus) (gI_2/100g oil)	84.18	84.18	84.18	84.00	83.80	83.48	83.30
Peroxide number (cm^3/g oil)	38.00	37.50	37.30	37.00	36.20	35.90	35.40

Table 4.6: Physico-chemical properties of sulphated castor oil (SLCO) or Turkey-red oil

Property	Value for 60wt% modifier
Specific gravity (30^0C)	0.856
pH	3.20
Refractive index (30^0C)	1.428
Relative viscosity	1.18
Acid number (mg KOH/g oil)	5.00
Hydroxyl number (mg KOH/g oil)	10.00
Saponification number (mg KOH/g oil)	220.10
Iodine number (Hanus) (gI_2/100g oil)	98.60
Peroxide number (cm^3/g oil)	32.00

(a) Variation of hydroxyl number (HN) and Relative Viscosity (RV) in the modified castor oil polyols (MCOPs)

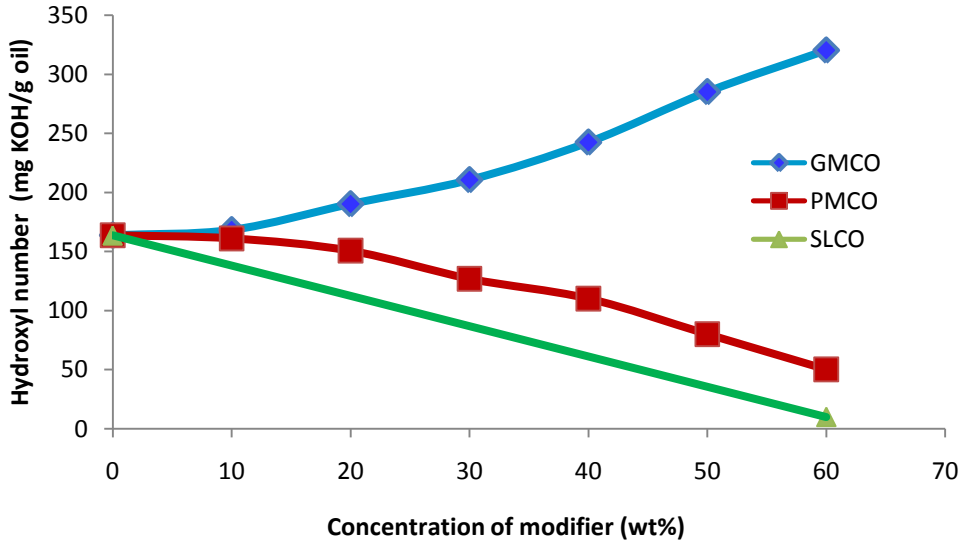


Fig. 4.4: Changes in hydroxyl number of CO with modifier concentration

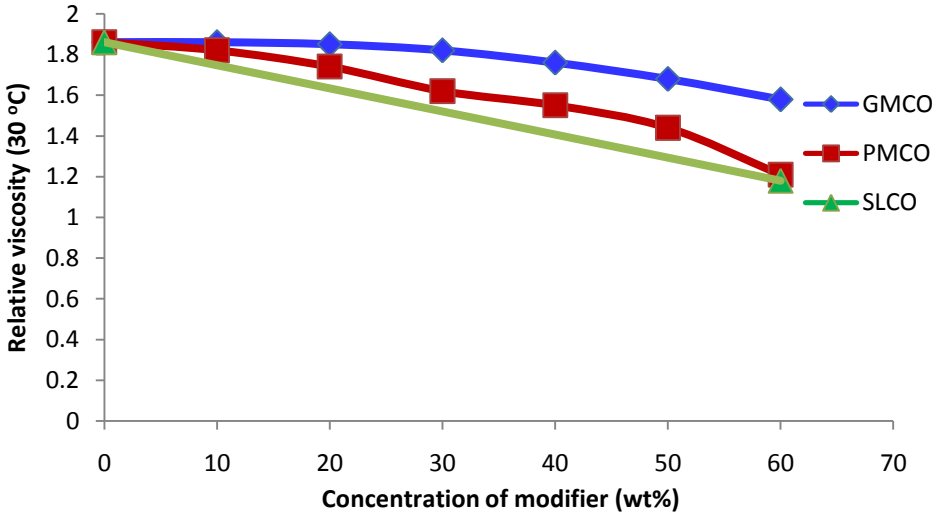


Fig. 4.5: Changes in viscosity of CO with modifier concentration

(b) Variation of iodine number (IN) in MCOPs

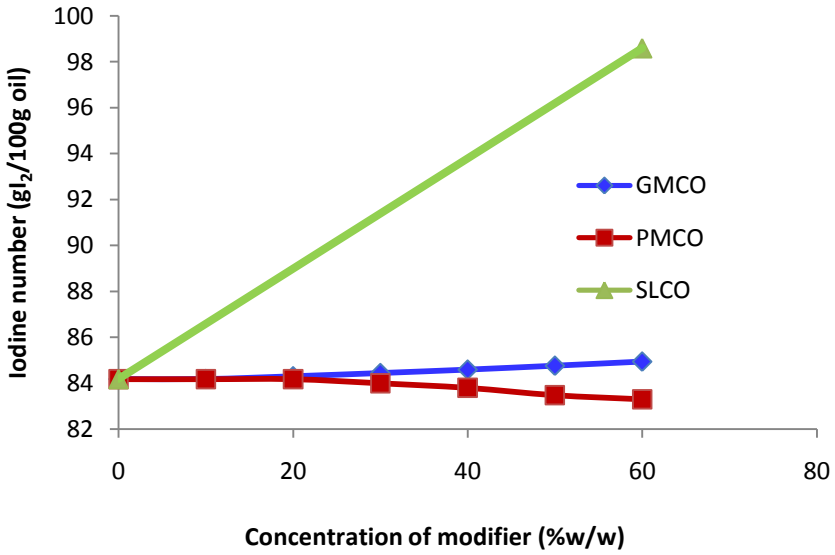


Fig. 4.6: Changes in iodine number of CO with modifier concentration

(c) Variation of hydroxyl number (HN) with reaction time during polyol synthesis

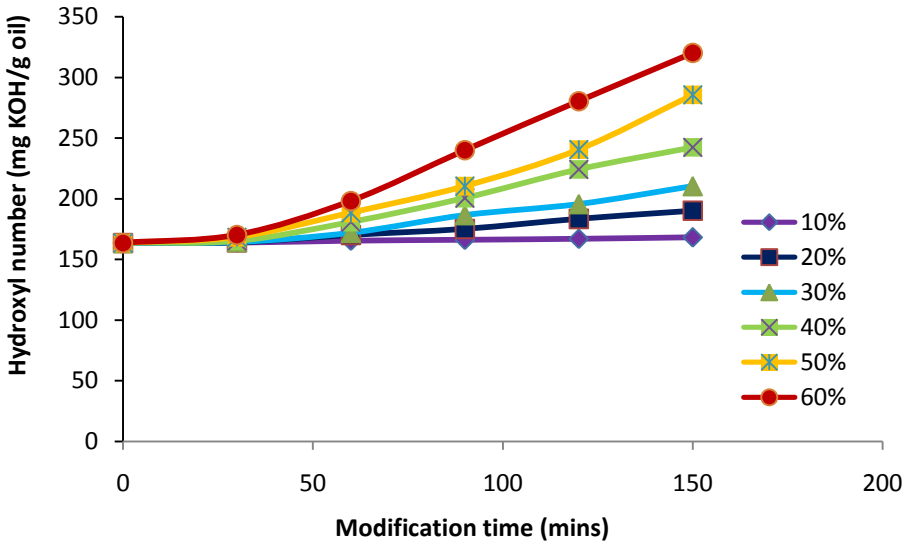


Fig. 4.7: Changes in hydroxyl number of CO with modification time in GMCOPs

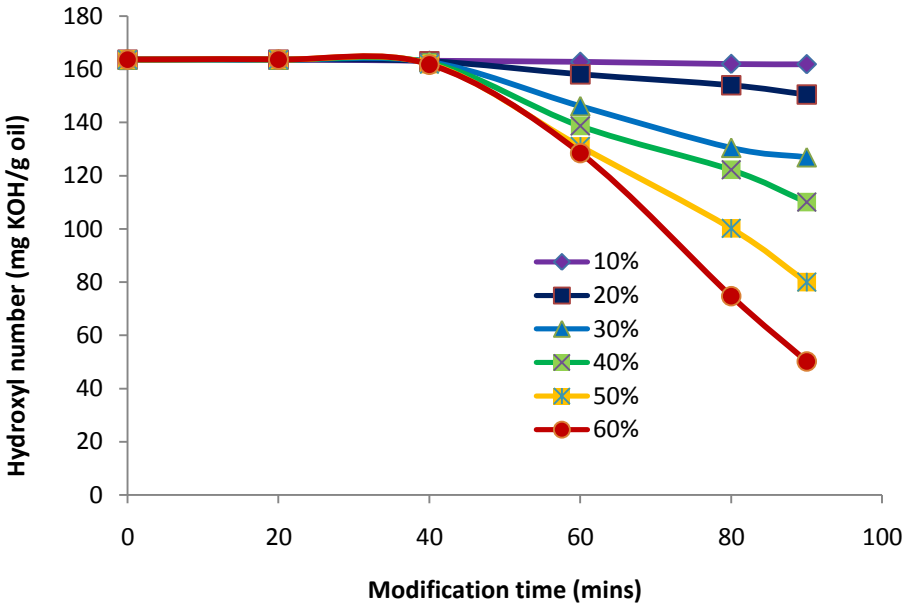
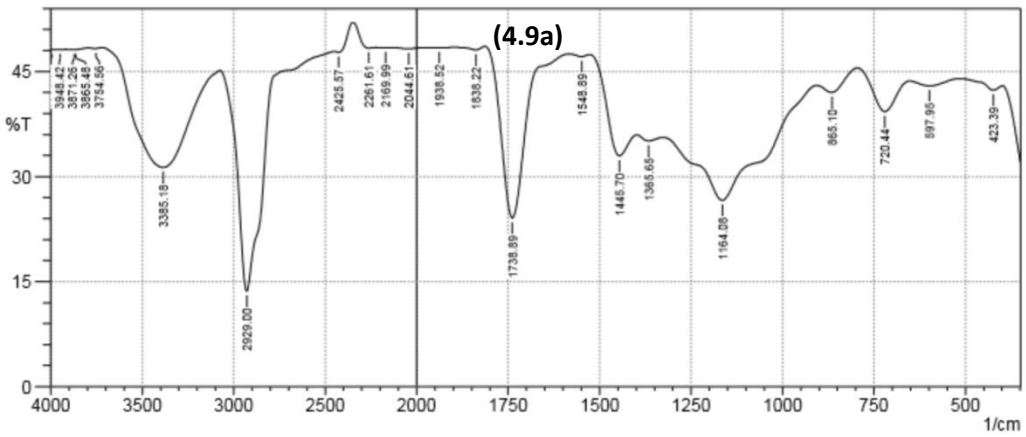


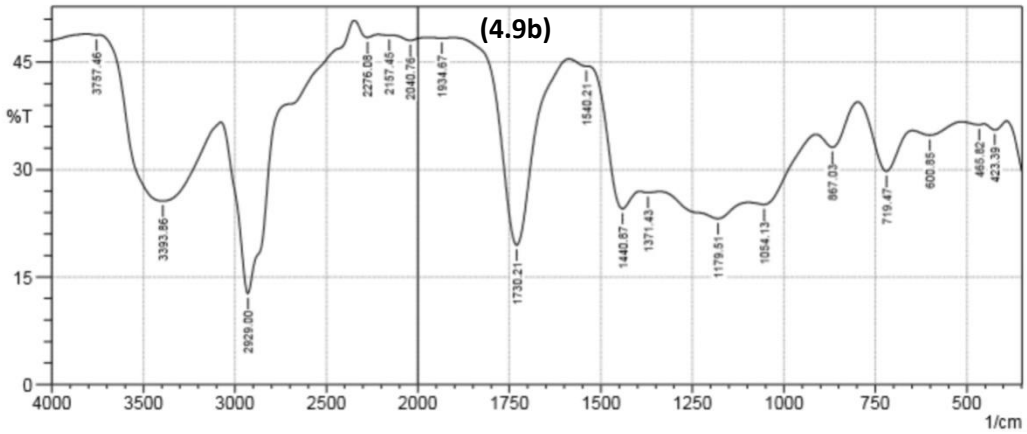
Fig. 4.8: Changes in hydroxyl number of CO with modification time in PMCOPs

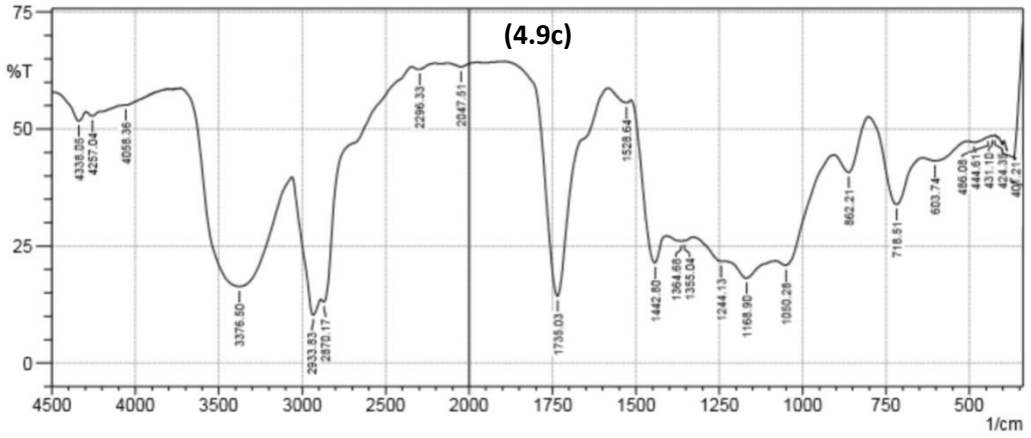
(d) Results of FTIR and GC-MS analyses of the modified castor oil polyols (MCOPs)

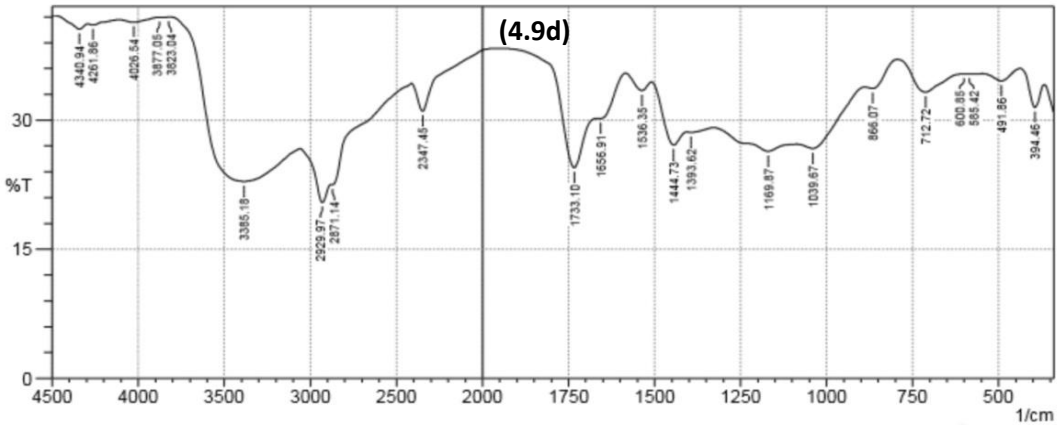
i) FTIR spectra

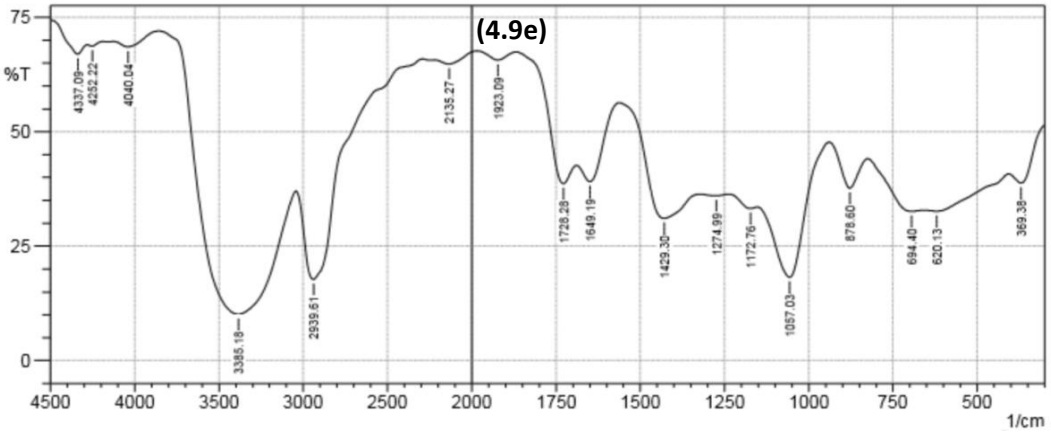
GMCOPs






(4.9c)
%T
1/cm
4338.05
4257.04
4058.36
3376.50
2933.83
2870.17
2296.33
2047.51
1738.03
1528.64
1442.80
1364.65
1355.04
1244.13
1168.90
1050.28
862.21
718.51
603.74
486.08
444.61
431.10


(4.9d)
%T
1/cm
4340.94
4261.86
4026.54
3877.09
3823.04
3385.18
2929.97
2877.14
2347.48
1733.10
1656.91
1536.35
1444.73
1393.62
1169.87
1039.67
866.07
712.72
600.85
585.42
491.86
394.46


(4.9e)
%T
1/cm
4337.09
4252.22
4040.04
3385.18
2939.61
2135.27
1923.09
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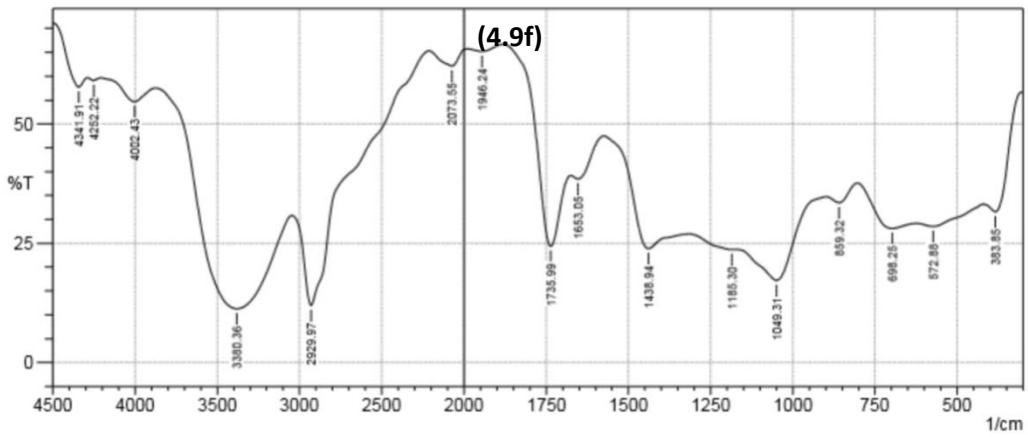
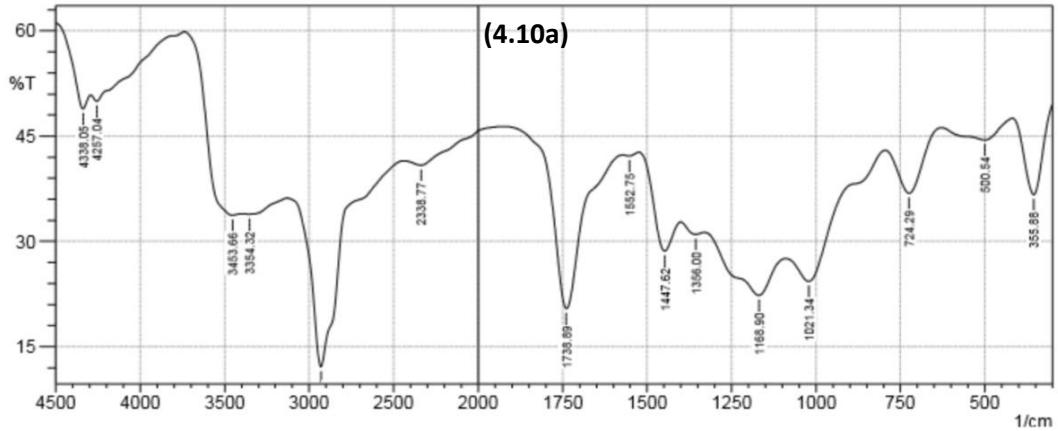
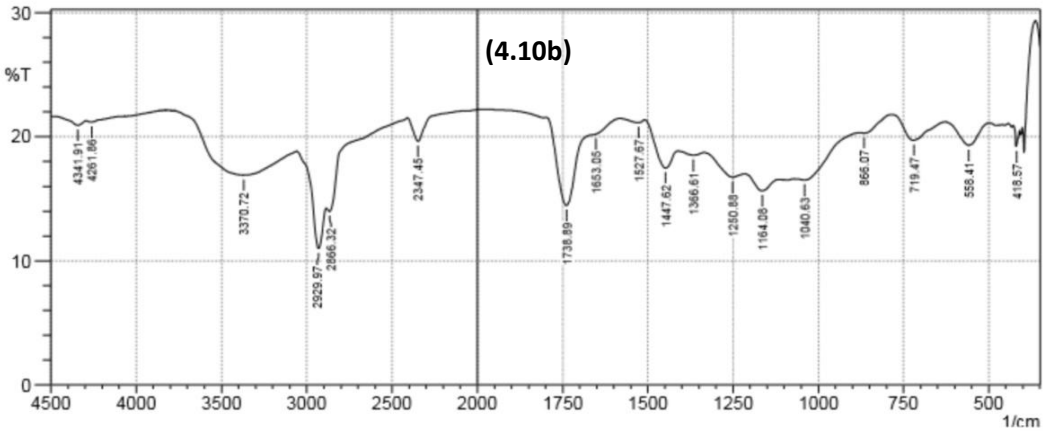
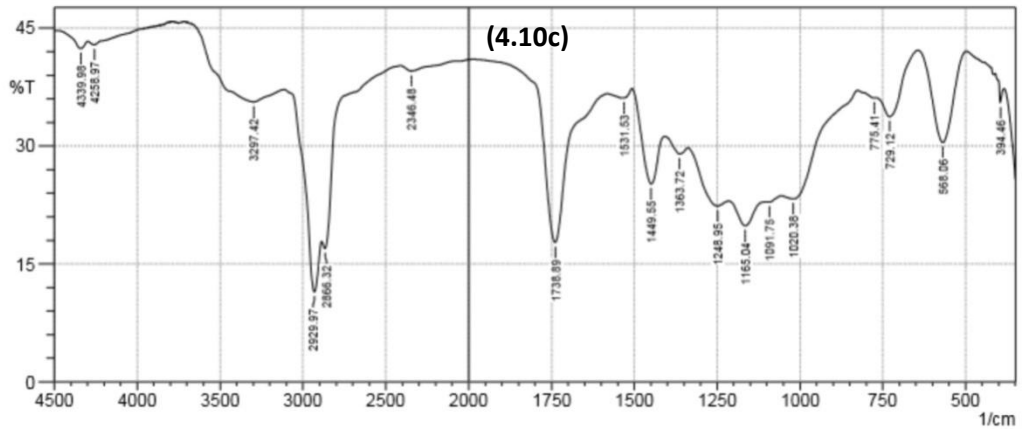


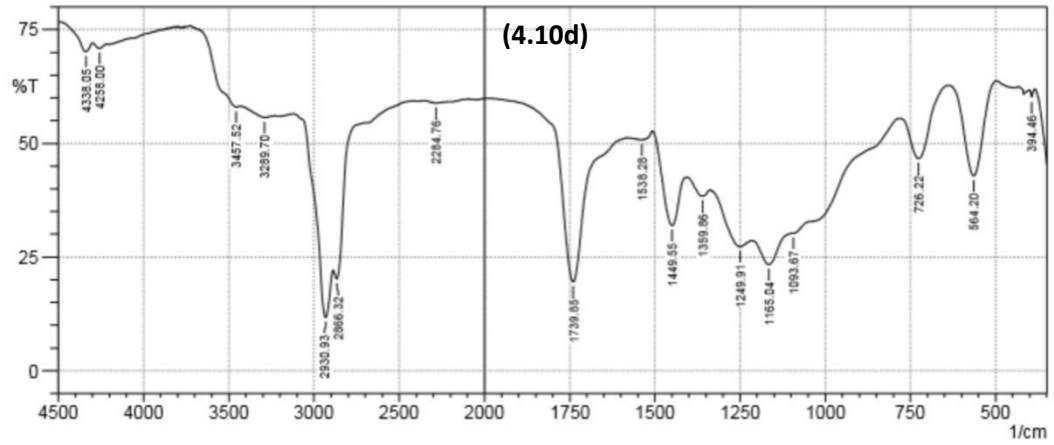
Fig. 4.9: FTIR spectra for GMCOPs - (a) 10% glycerol; (b) 20% glycerol; (c) 30% glycerol; (d) 40% glycerol; (e) 50% glycerol; (f) 60% glycerol.

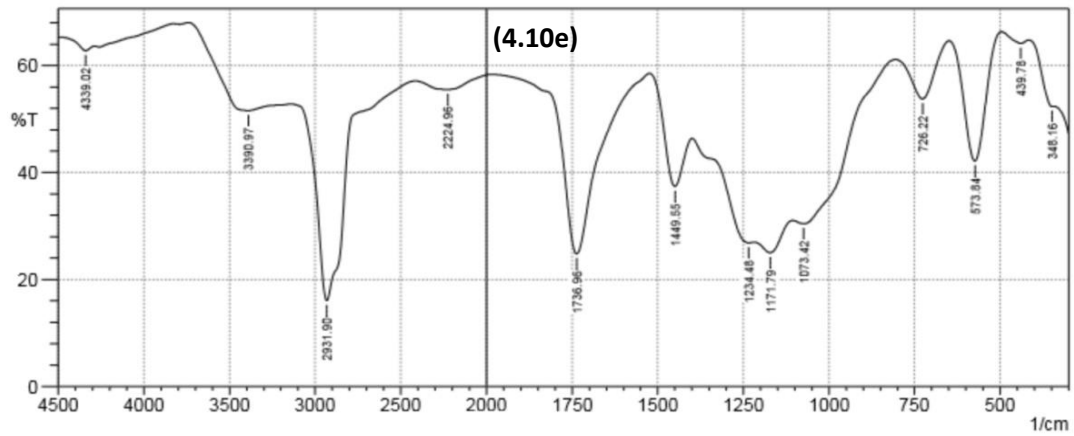
PMCOPs






(4.10c)
%T
45
30
15
0
4339.98
4258.97
3297.42
2929.97
2866.32
2346.48
1738.89
1531.53
1449.55
1363.72
1248.95
1165.04
1091.75
1020.38
775.41
729.12
568.06
394.46
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm


(4.10d)
%T
75
50
25
0
4338.05
4258.00
3457.52
3289.70
2930.93
2866.32
2284.76
1739.85
1538.26
1449.55
1359.66
1249.91
1165.04
1093.67
726.22
664.20
394.46
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm


(4.10e)
%T
60
40
20
0
4339.02
3390.97
2931.90
2224.96
1736.96
1449.55
1234.48
1171.79
1073.42
726.22
673.84
439.78
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3500
3000
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2000
1750
1500
1250
1000
750
500
1/cm

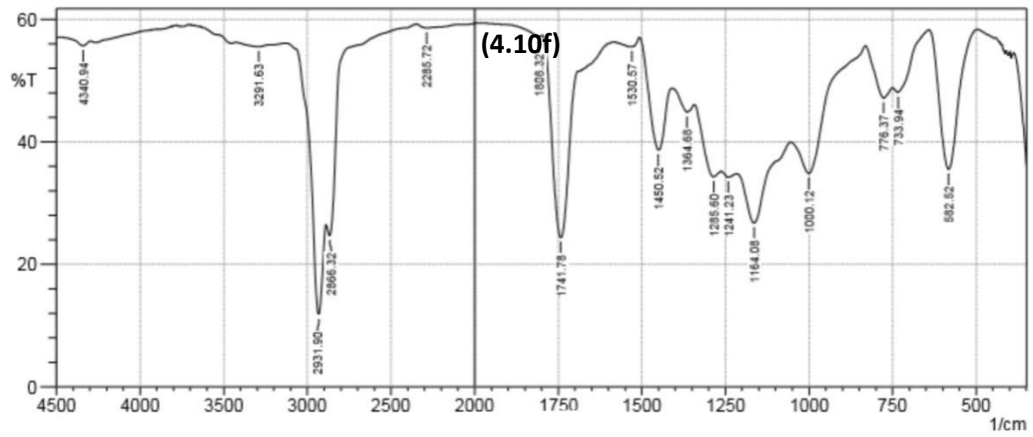


Fig. 4.10: FTIR spectra for PMCOPs – (a) 10%PCl_5; (b) 20%PCl_5; (c) 30%PCl_5; (d) 40%PCl_5; (e) 50%PCl_5; (f) 60%PCl_5;

SLCO (Turkey-red oil)

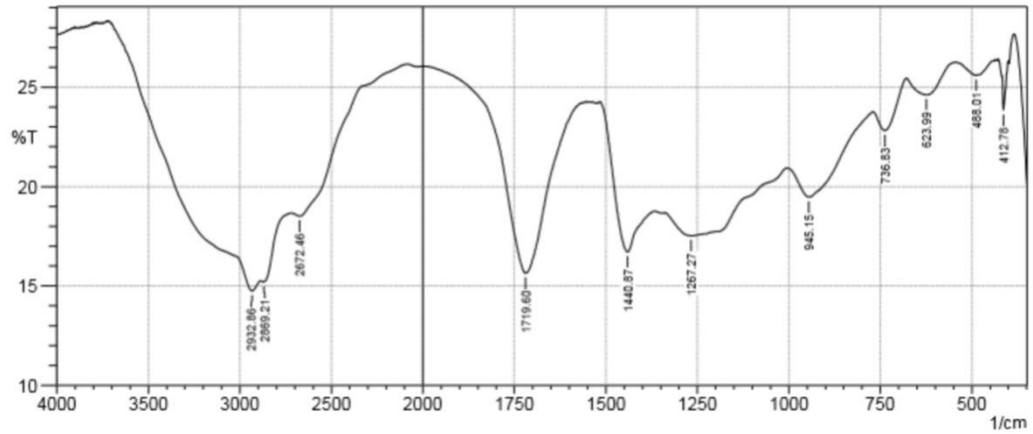
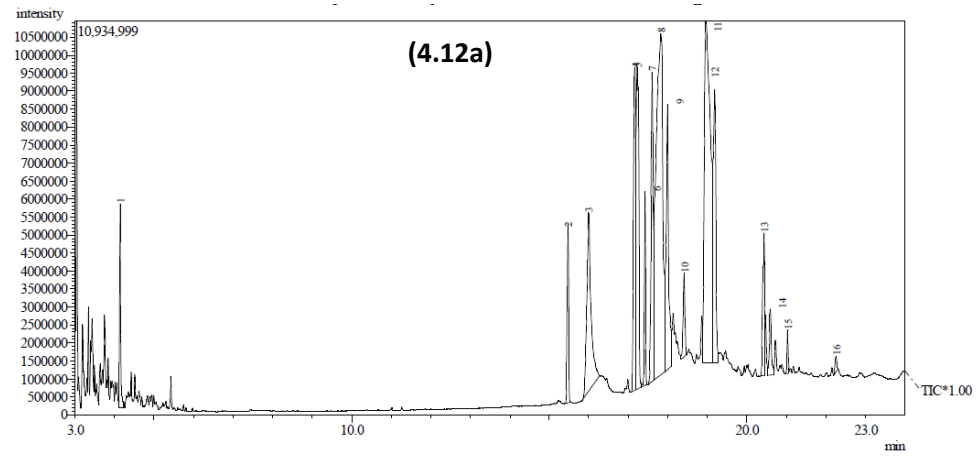


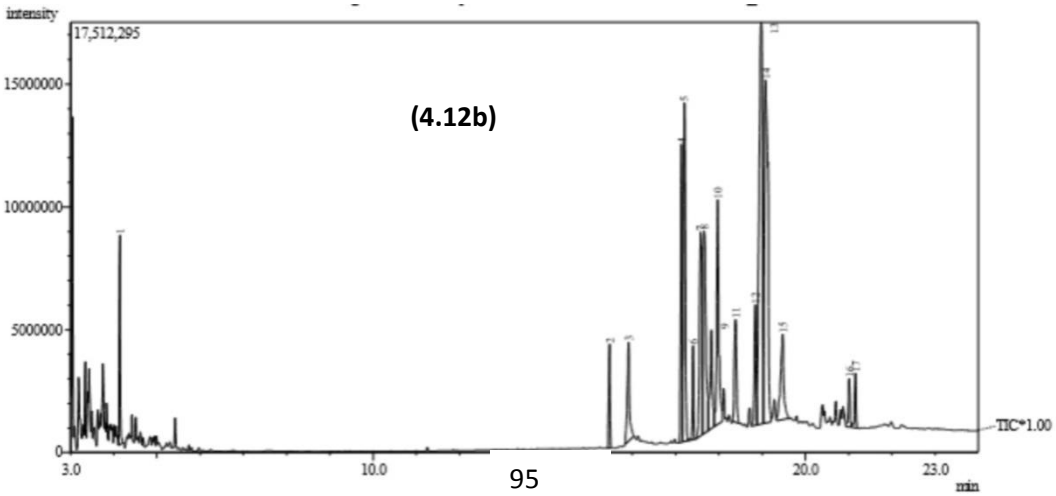
Fig. 4.11: FTIR spectrum for sulphated castor oil or Turkey- red oil.

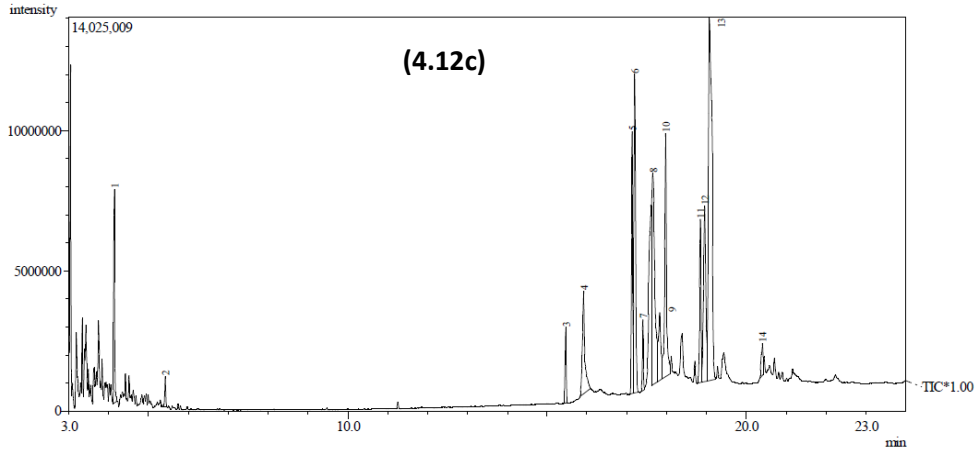
Table 4.7: Major functional groups of interest in CO and MCOP FTIR spectra

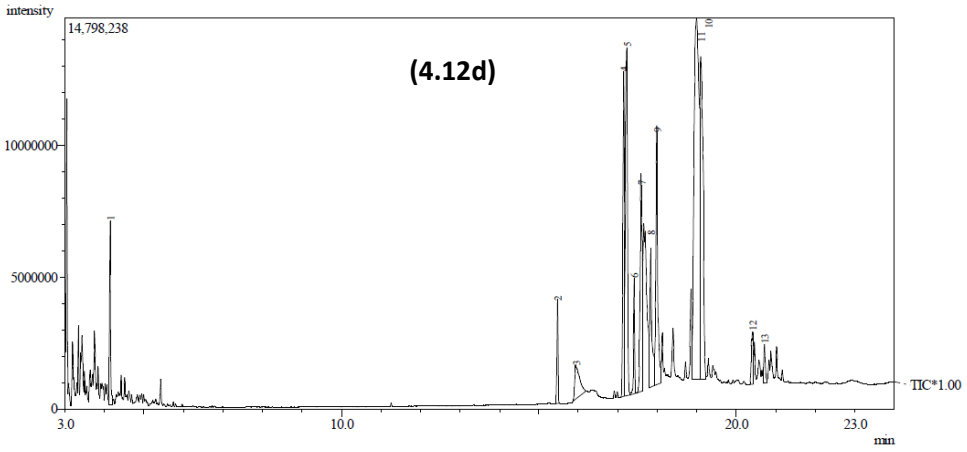
Functional group	Absorption (cm^{-1})	Assignment
-OH	3421-3289	O-H stretching
>C=O	1741-1719	C=O stretching (ester linkage)
C=C	1659-1649	C=C stretching
=C-H	1179-1164	=C-H bending (rocking)
=C-H	1054-945	=C-H bending (twisting)
XHC=CHX	736-712	Out-of-plane vibration of cis-disubstituted olefins
-C-OH	1099-1091	C-OH in-plane bending
-CHCL	582-500	C-Cl stretching
-C-H	2939-2858	C-H stretching
C-O-C	418-400	C-O bending (rocking)

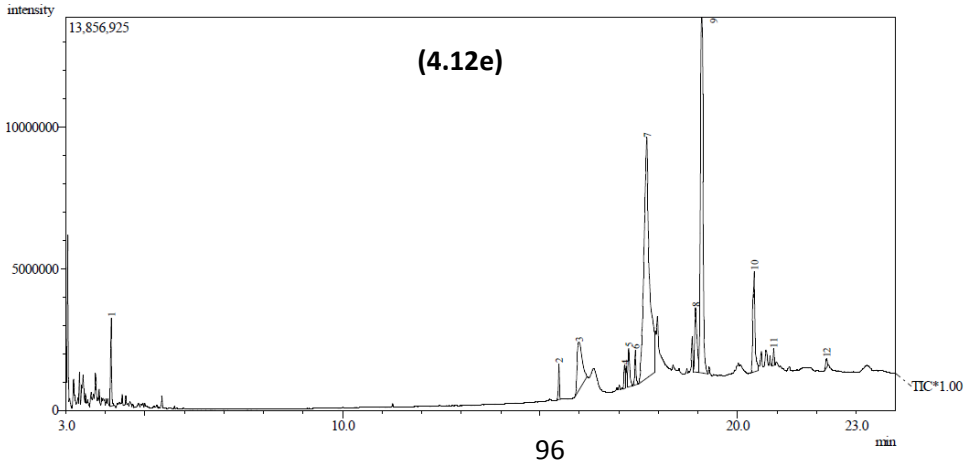
ii) GC-MS Chromatograms (PMCOPs)






intensity
14,025,009
(4.12c)
10000000
5000000
0
3.0
10.0
20.0
23.0
min
TIC*1.00


intensity
14,798,238
(4.12d)
10000000
5000000
0
3.0
10.0
20.0
23.0
min
TIC*1.00


intensity
13,856,925
(4.12e)
10000000
5000000
0
3.0
10.0
20.0
23.0
min
TIC*1.00

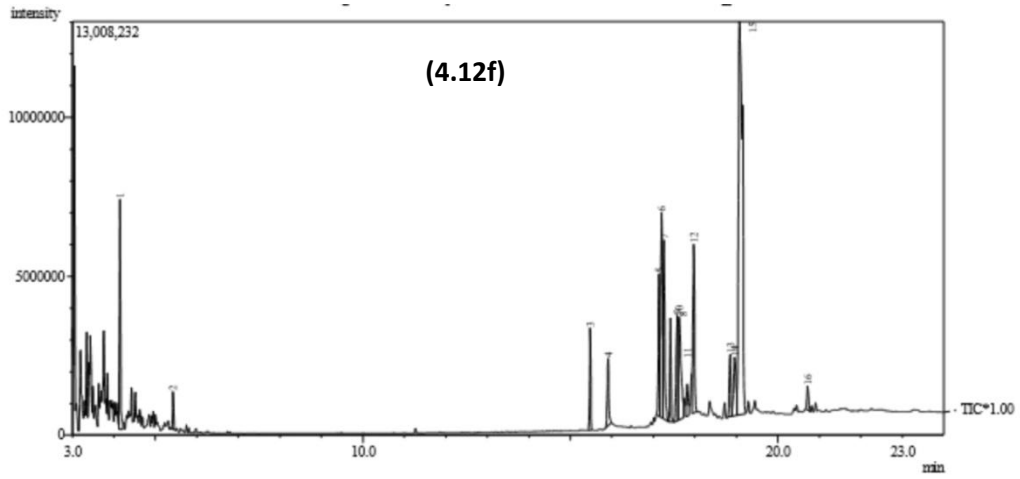


Fig. 4.12: GCMS chromatograms for PMCOPs – (a) 10% PCl_5; (b) 20%PCl_5; (c) 30% PCl_5; (d) 40% PCl_5; (e) 50% PCl_5; (f) 60% PCl_5.



Fig. 4.13: GC-MS suggested structure for 9,12-octadecadienoyl chloride

4.2 Physical Properties of Castor oil-based Polyurethane forms (COPUFs)

Table 4.8: Observed general features for different COPUFs containing NCO/OH ratio of 1/2 in formulation

PU foam	Colour	Texture	Post-cure state
Neat foam	Pale yellow	Soft to spongy	No shrinkage
GMF	White	Rigid	No shrinkage
PMF□	Light-to-dark brown	Coarse, hard	Brittle
CFF^{+}	White	Soft to semi-rigid	No shrinkage
HCTD/HCHD treated (1)	Pale yellow	Soft	No shrinkage
HCTD/HCHD treated (2)	White	Semi-rigid	No shrinkage

□ At 10 & 20% (w/w) modifier concentrations only

$^{+}$ At ≤ 20% (w/w) filler content

(1) Base polyol = NCOP

(2) Base polyol = GMCOP

GMF = Glycerol modified foam

PMF = PCl_5 modified foam

CFF = $CaCO_3$ filled foam

Table 4.9: Characteristics of GMFs (NCO/OH of 1/2) at room temperature (30-35^{0}C)

	Modifier concentration (wt%) in GMCOP						
Parameter	0*	10	20	30	40	50	60
Cream time(s)	45	40	39.5	39	38	38	37
Free rise time (s)	180	178	180	172	165	150	148
Foam rise (cm)	8	8.2	8.5	9.3	9.38	9.40	9.42
Gel time (s)	220	210	190	180	180	173	169
Tack-free time (s)	240	235	232	230	225	220	210
Density (kg/m^3)	23.60	24.5	26.8	30.4	34	39.2	45.8
Water absorption (wt%)	2.20	1.90	1.70	1.22	1.15	0.94	0.81

Table 4.10: Characteristics of GMFs (NCO/0H of 1/1) at room temperature (30-35^{0}C)

	Modifier concentration (wt%) in GMCOP						
Parameter	0*	10	20	30	40	50	60
Cream time(s)	40	38	34	30	26	20	19
Free rise time (s)	167	174	168	162	157	140	136
Foam rise (cm)	9	9.1	9.3	9.4	9.6	9.9	10.2
Gel time (s)	210	205	184	175	170	166	162
Tack-free time (s)	250	245	242	240	236	230	225
Density (kg/m^3)	24.3	25.8	26.9	33.5	36.7	44.2	50.5
Water absorption (wt%)	2.0	1.8	1.6	1.2	1.02	0.82	0.73

Table 4.11: Characteristics of PMFs (NCO/OH of 1/2) at room temperature (30-35^{0}C)

	Modifier concentration (wt%) in PMCOP						
Parameter	0*	10	20	30	40	50	60
Cream time(s)	45	50	80	-	-	-	-
Free rise time (s)	180	200	260	-	-	-	-
Foam rise (cm)	8	4	2	-	-	-	-
Gel time (s)	220	280	320	-	-	-	-
Tack-free time (s)	240	300	340	-	-	-	-
Density (kg/m^3)	23.6	22.0	10	-	-	-	-
Water absorption (wt%)	2.2	2.2	2.1	-	-	-	-

Table 4.12: Characteristics of PMFs (NCO/OH 1/1) produced at room temperature (30-35^{0}C)

Parameter	Modifier concentration (wt%) in PMCOP						
	0*	10	20	30	40	50	60
Cream time(s)	40	48	75	-	-	-	-
Free rise time (s)	167	185	250	-	-	-	-
Foam rise (cm)	9	5	2.5	-	-	-	-
Gel time (s)	210	260	300	-	-	-	-
Tack-free time (s)	250	300	350	-	-	-	-
Density (kg/m^3)	24.3	23.1	10.2	-	-	-	-
Water absorption (wt%)	2.0	2.04	2.3	-	-	-	-

* Parameter values in respect of zero modifier concentration are for the neat COPUF

(-) No foam produced

4.2.1 Density and water absorption of COPUFs

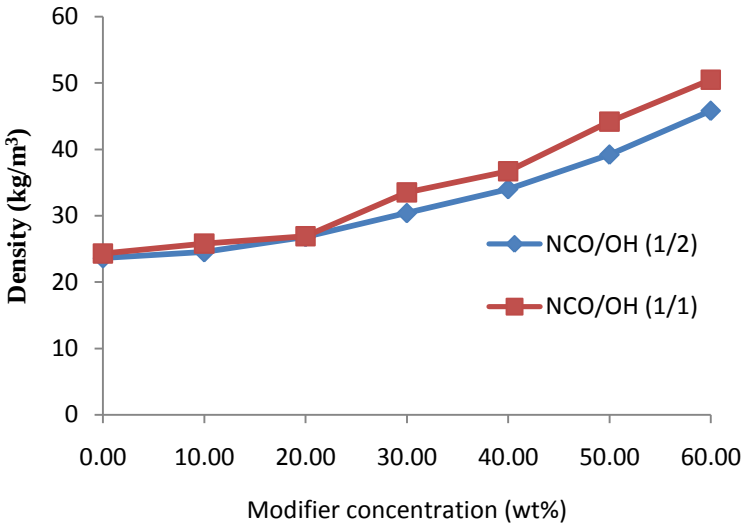


Fig. 4.14: Density versus concentration of CO modifier in GMFs

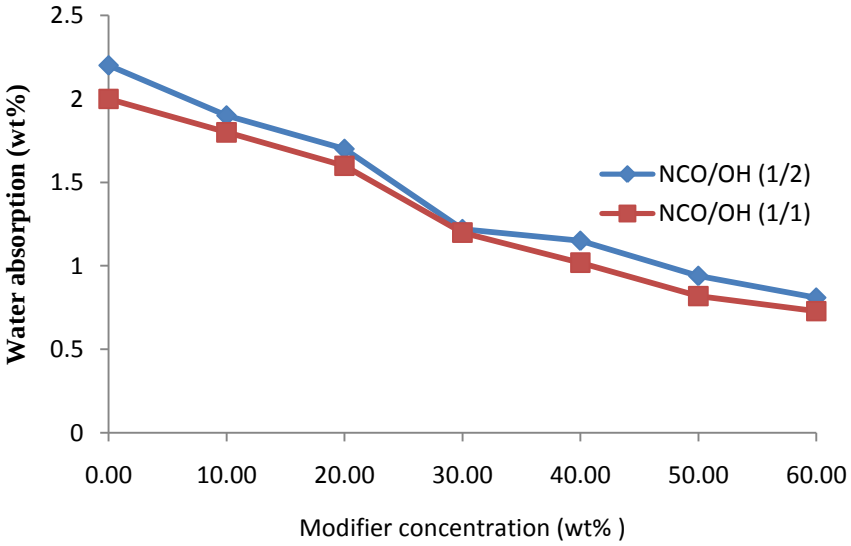


Fig. 4.15: Water absorption versus concentration of CO modifier in GMFs

4.2.2 Effect of filler incorporation on the physico-chemical properties of COPUFs

Table 4.13: Characteristics of CFFs (NCO/OH of 1/2) containing varying concentrations of $CaCO_3$ filler.

	wt% filler										
Parameter	0	2	4	6	8	10	12	14	16	18	20
Cream time(s)	45	42	38	39	36	30	23	20	18	18	18
Free rise time (s)	180	175	167	166	164	160	157	155	150	140	138
Foam rise (cm)	8	8.2	8.2	8.6	8.7	8.9	9	9.1	9.8	10	10.1
Gel time (s)	220	212	205	195	190	182	178	173	170	163	160
Tack-free time(s)	240	232	226	218	210	203	198	190	185	180	175
Density (kg/m^3)	23.6	23.6	23.65	23.72	23.8	23.9	24.02	24.1	24.25	24.32	24.50
Water absorption (wt%)	2.2	2.2	2.18	2.17	2.15	2.14	2.12	2.09	2.06	2.02	1.98

Table 4.14: Characteristics of CFFs (NCO/OH of 1/1) containing varying concentrations of $CaCO_3$ filler

Parameter	wt% filler										
	0	2	4	6	8	10	12	14	16	18	20
Cream time(s)	40	38	30	26	22	20	18	16	15	15	14
Free rise time (s)	167	154	148	143	140	137	134	130	124	122	120
Foam rise (cm)	9	9.4	9.8	10.3	10.8	11.2	11.6	12	12.2	12.8	13.2
Gel time (s)	210	208	197	190	180	170	161	153	140	132	120
Tack-free time(s)	250	240	230	220	212	208	200	194	190	184	180
Density (kg/m^3)	24.3	24.35	24.4	24.46	24.52	24.6	24.68	24.75	24.83	24.92	25.10
Water absorption (wt%)	2.0	1.99	1.99	1.98	1.95	1.92	1.9	1.86	1.82	1.67	1.65

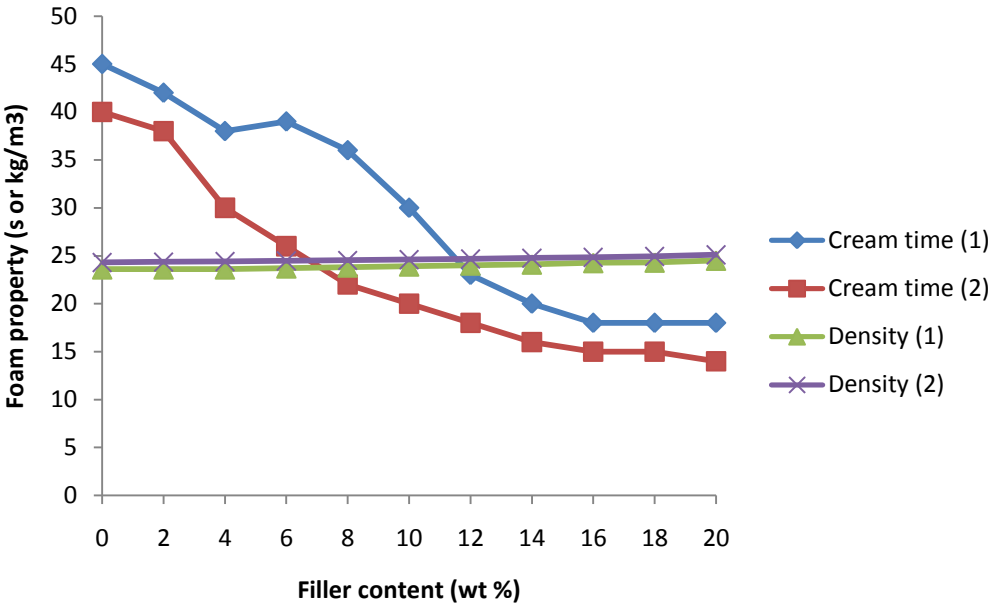


Fig. 4.16: Variation of cream time and foam density with filler content in COPUF.

(1) NCO/OH (1/2)

(2) NCO/OH (1/1)

4.2.3 Comparison of water absorption of GMFs, PMFs and CFFs of 20wt% modifier concentration and of different NCO/OH ratios.

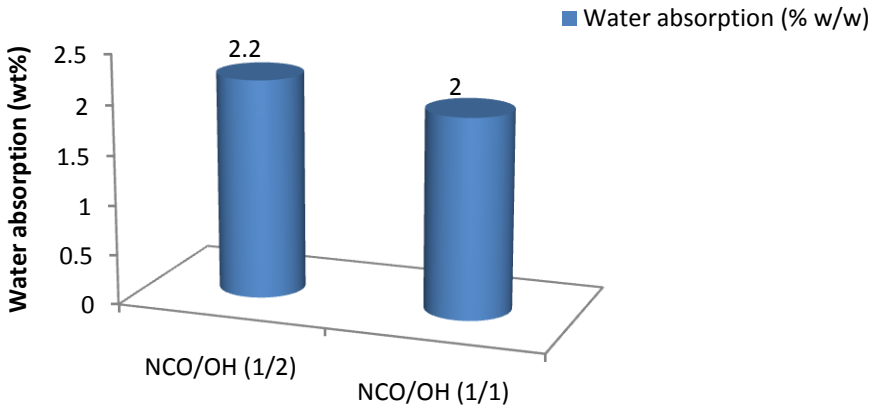


Fig. 4.17: Water absorption of neat COPUF

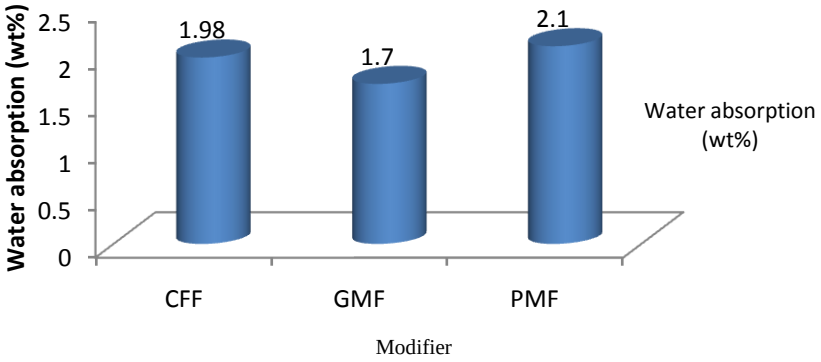


Fig. 4.18: Water absorption of PU foams containing 20wt% modifier (NCO/OH of 1/2)

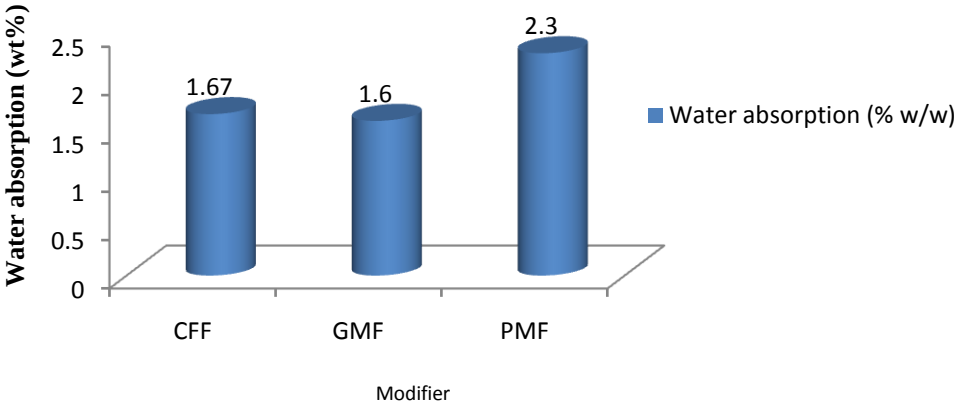


Fig. 4.19: Water absorption of PU foams containing 20wt% modifier (NCO/OH of 1/1)

4.2.4 Effect of plasticisation on the physical properties of COPUFs

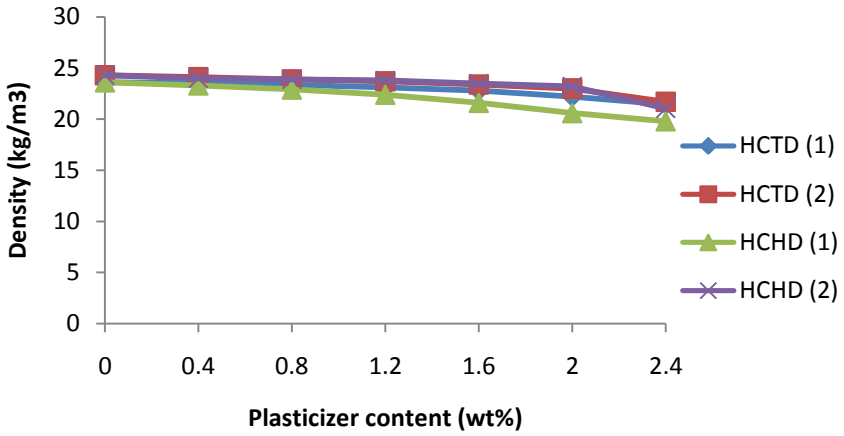


Fig. 4.20: Density *versus* plasticiser (HCTD/HCHD) content in COPUF

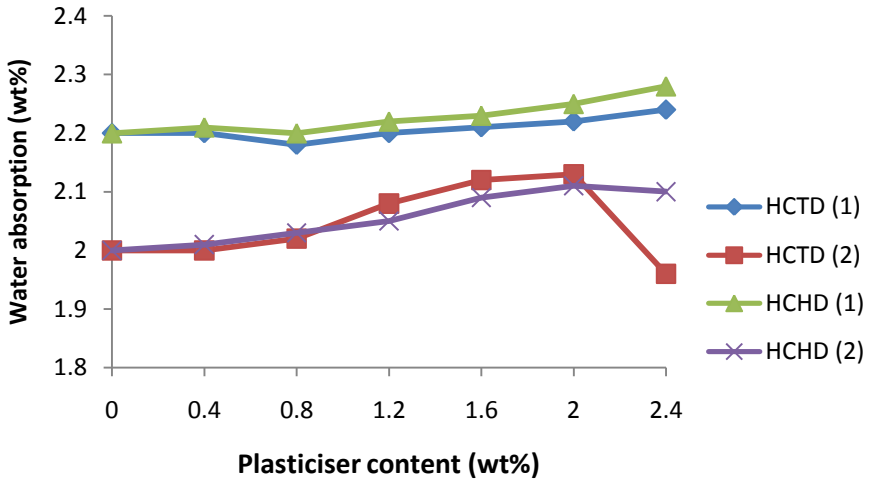


Fig. 4.21: Water absorption *versus* plasticiser (HCTD/HCHD) content in COPUF

4.3 Mechanical Properties of COPUFs

4.3.1 Compressive Strength

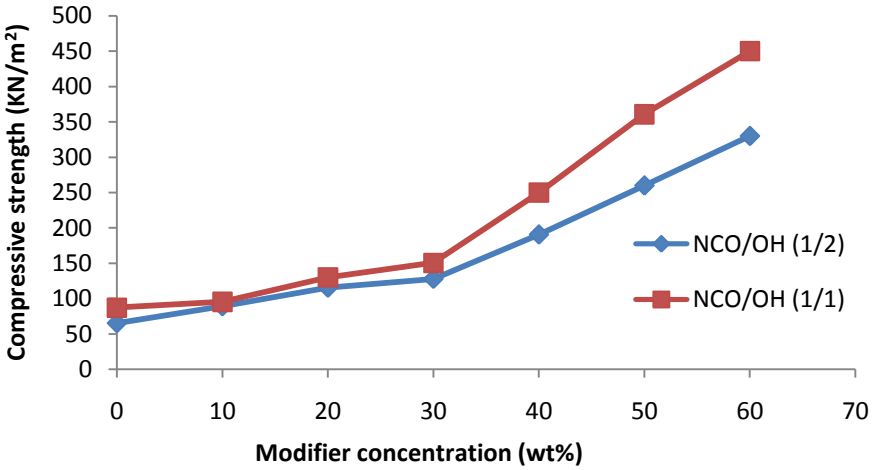


Fig.4.22: Compressive strength *versus* modifier concentration in GMFs

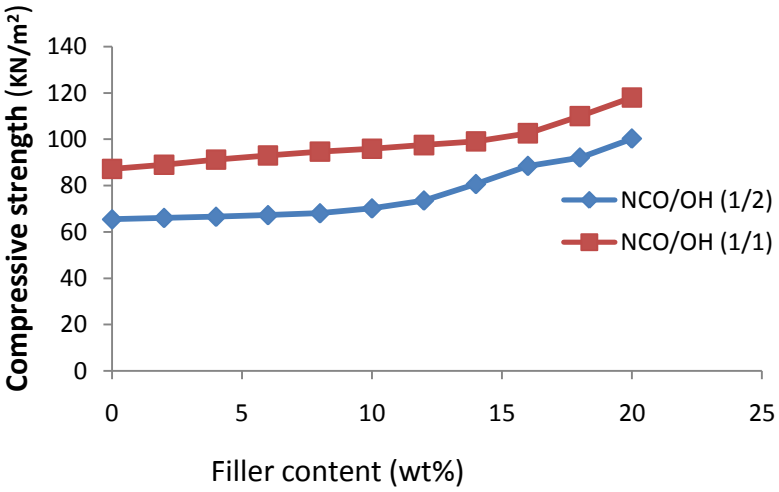


Fig.4.23: Compressive strength *versus* filler concentration for CFFs

(a) Effect of plasticiser concentration on the compressive strength of COPUFs

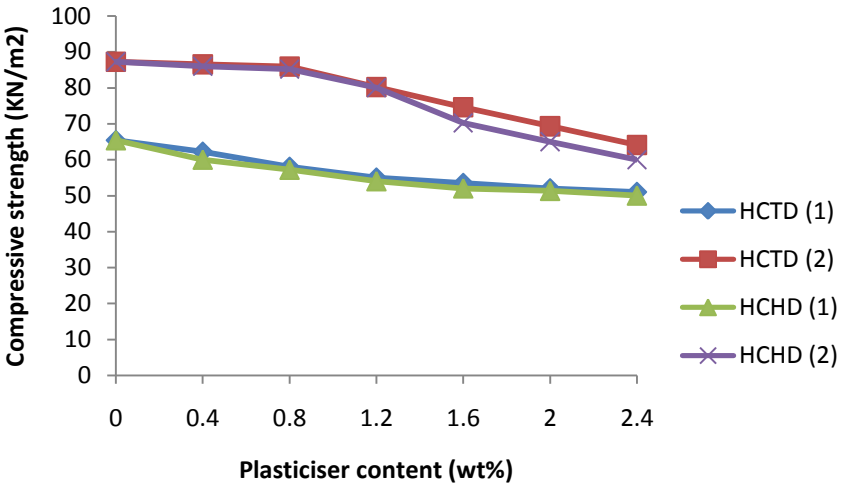


Fig. 4.24: Compressive strength *versus* plasticiser content for HCTD/HCHD plasticised COPUFs

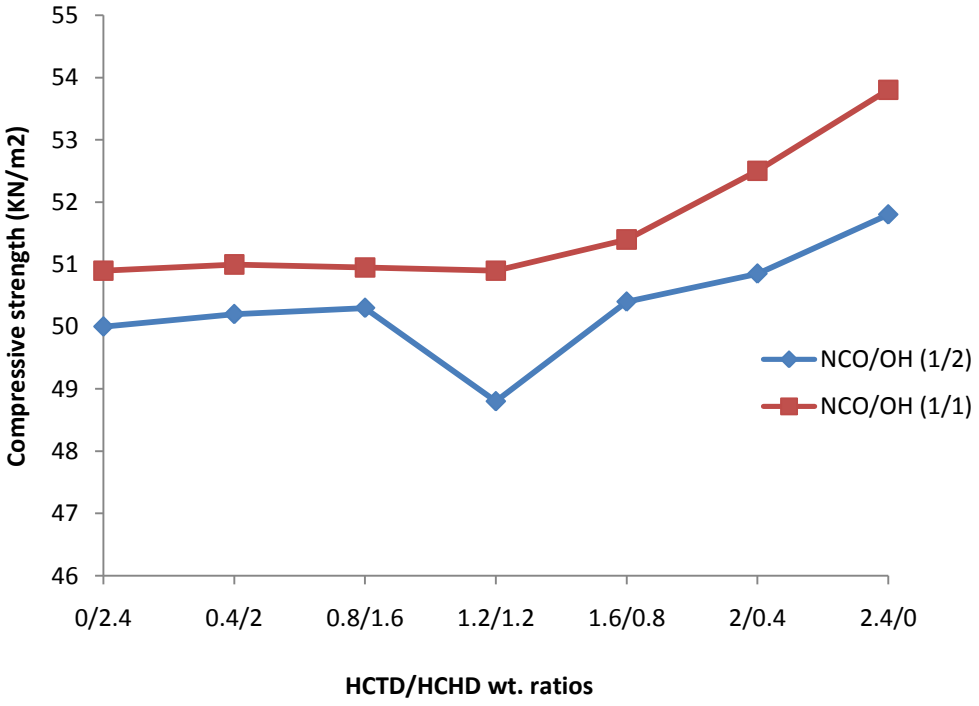


Fig. 4.25: Compressive strength *versus* HCTD/HCHD wt. ratios for COPUFs plasticised by blends of HCTD/HCHD

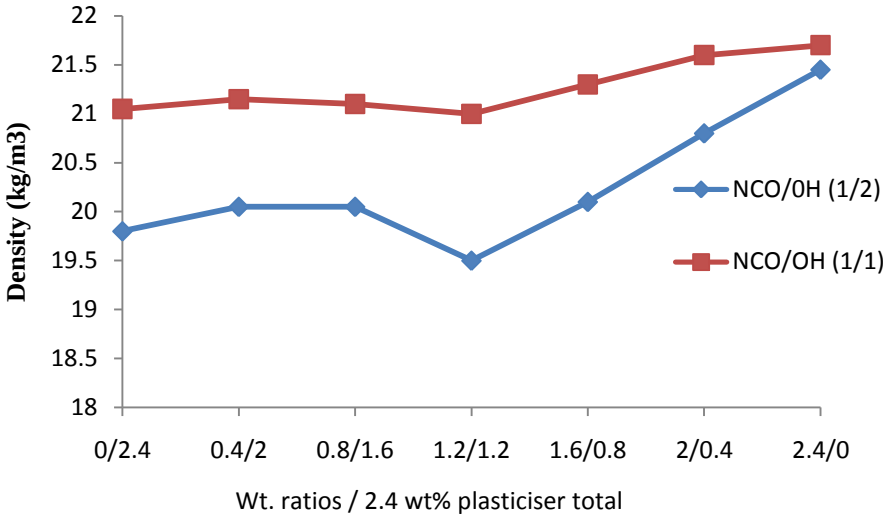


Fig. 4.26: Density *versus* plasticiser wt. ratios (HCTD/HCHD) in COPUF

4.3.2 Creep recovery

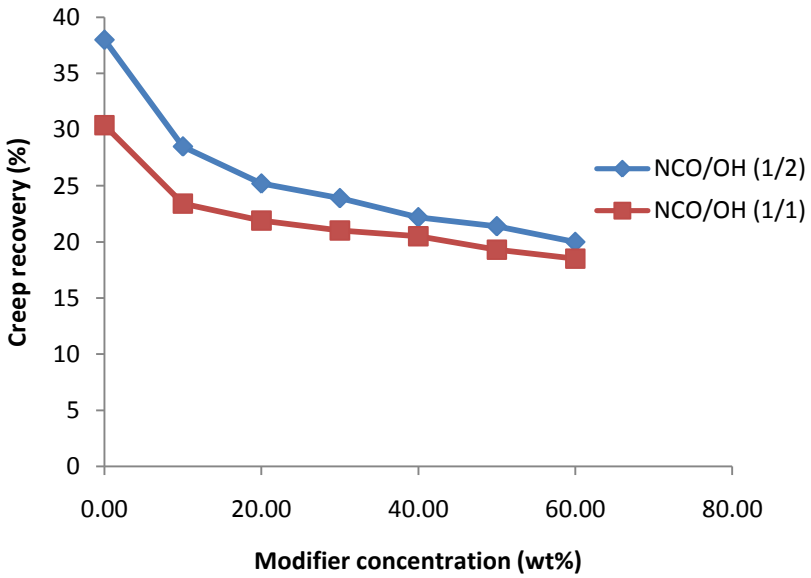


Fig. 4.27: Creep recovery *versus* modifier concentration in GMFs

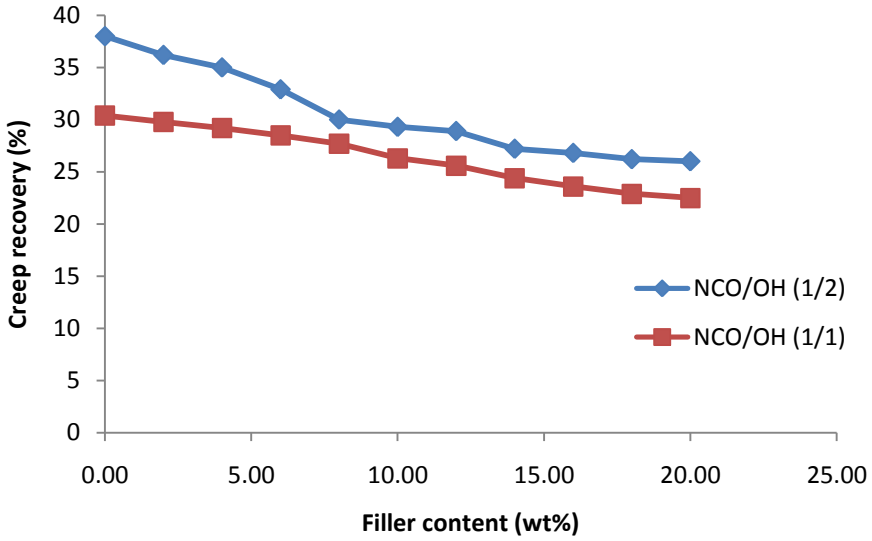


Fig. 4.28: Creep recovery *versus* filler concentration in CFFs

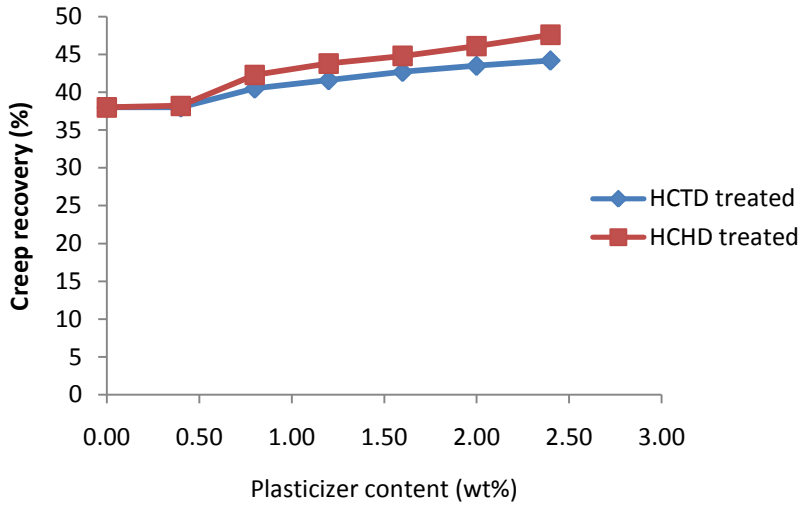


Fig. 4.29: Creep recovery *versus* plasticiser (HCTD/HCHD) concentration for COPUFs

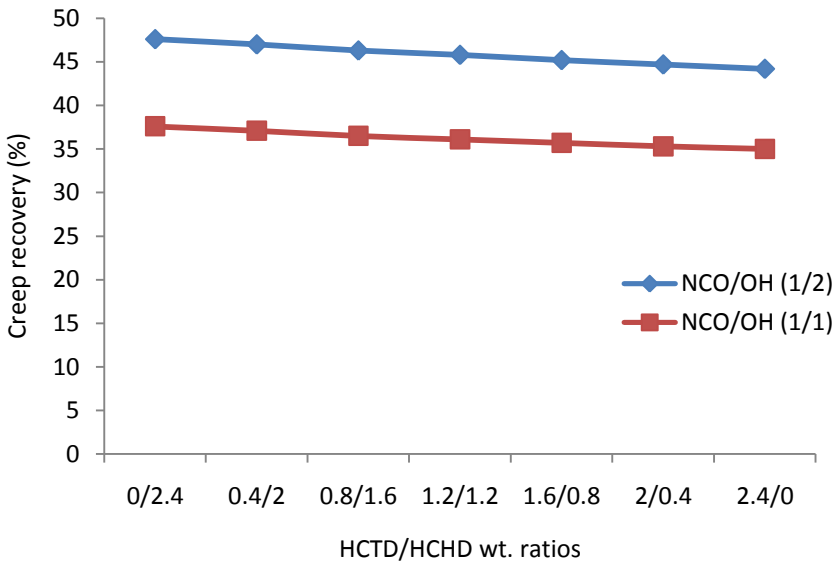


Fig. 4.30: Creep recovery *versus* HCTD/HCHD wt. ratios for COPUFs plasticised with blends of HCTD/HCHD

4.3.3 Effect of density on mechanical properties of COPUFs

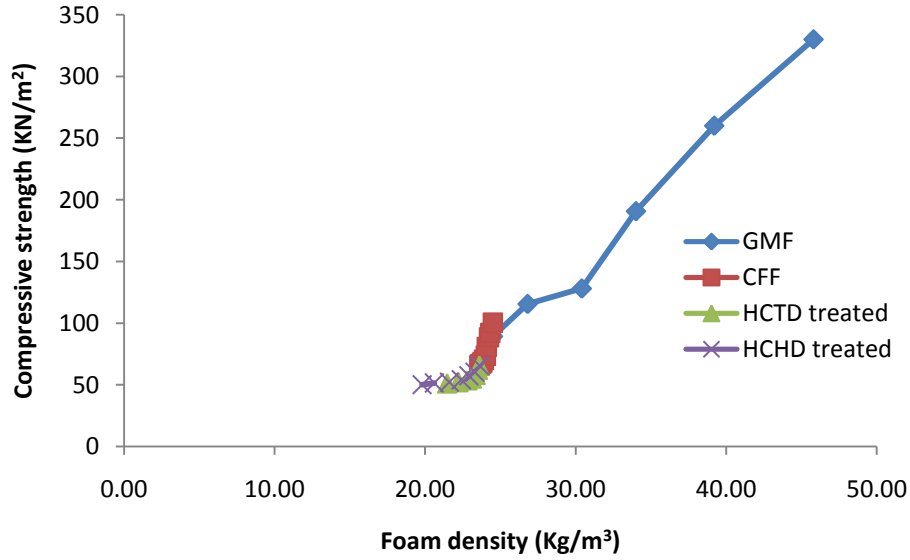


Fig. 4.31: Compressive strength *versus* density for GMFs, CFFs and HCTD/HCHD plasticised COPUFs (NCO/OH of 1/2)

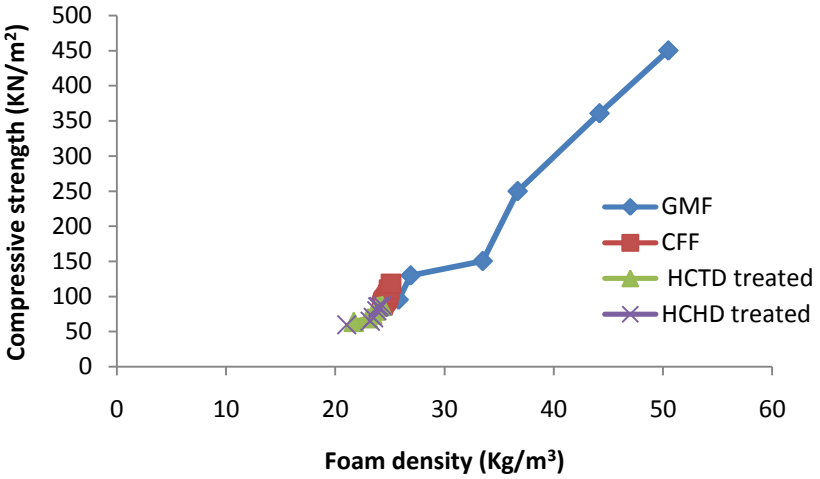


Fig. 4.32: Compressive strength *versus* density for GMFs, CFFs and HCTD/HCHD plasticised COPUFs (NCO/OH of 1/1)

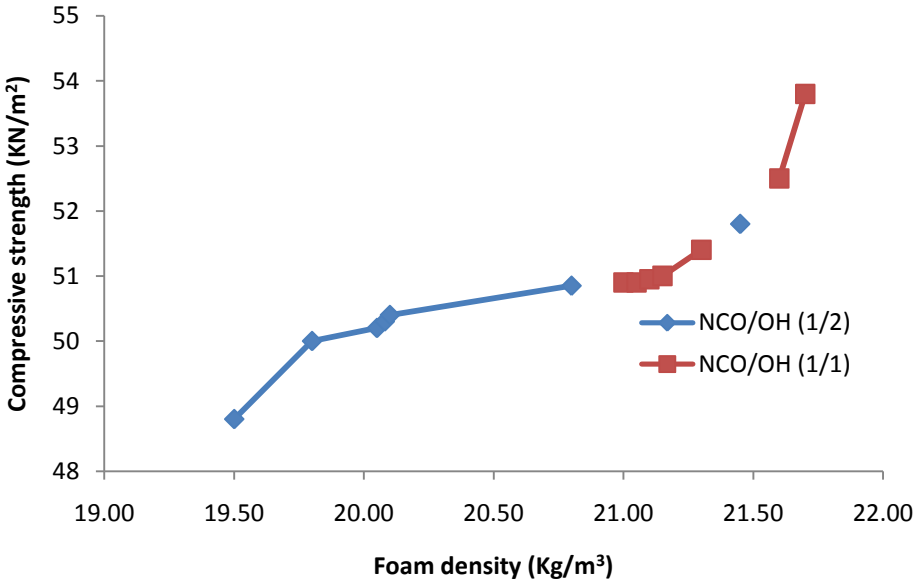


Fig. 4.33: Compressive strength *versus* density for COPUFs plasticised with blends of HCTD/HCHD

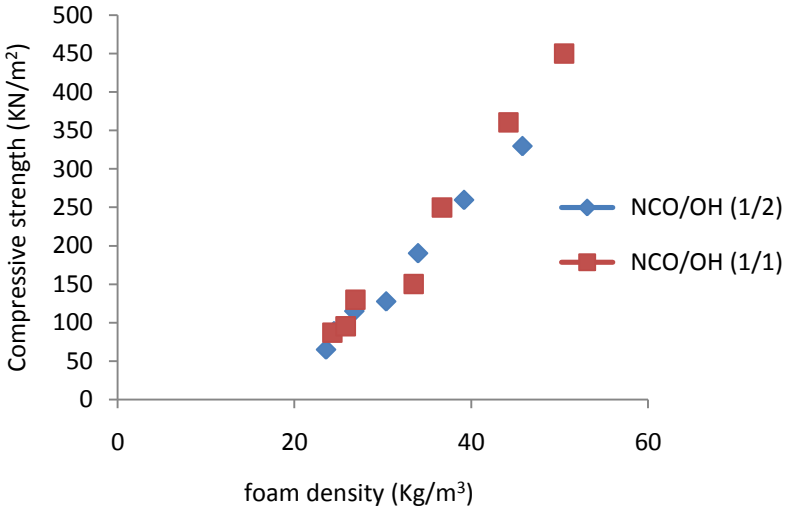


Fig. 4.34: Compressive strength *versus* foam density for GMFs

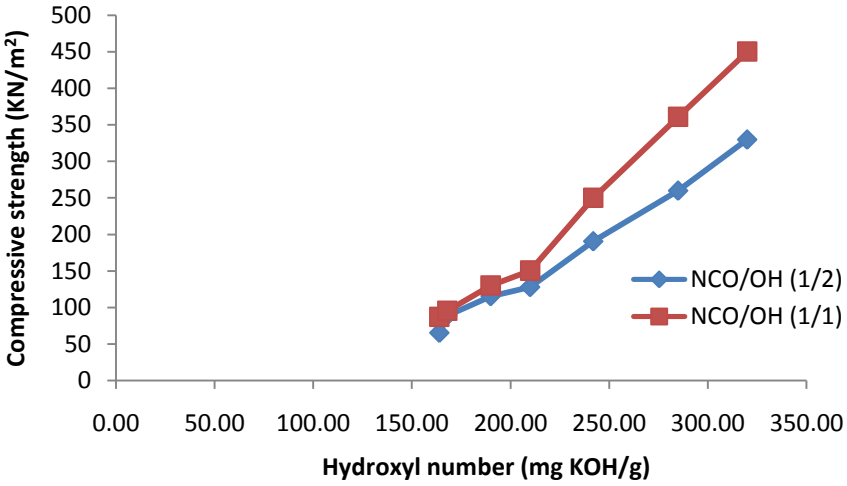


Fig. 4.35: Compressive strength of GMF *versus* hydroxyl number of GMCOP

4.4 Comparison of Physico-mechanical Properties of COPUFs with Standard Values for the Conventional Polyurethane Foam (PUF)

Table 4.15: Values of physico-mechanical properties of flexible COPUFs obtained in this study *versus* international standards for the conventional PUF.

Property	Observed	Standard
Core density (kg/m^3)	19.50-21.45	12.81 -40.05 (ASTM D3574-11)
Water absorption (wt%)	2.24-2.26	<3 (ASTM D570-98)
Compressive strength (KN/m^2)	48.80-51	>172 (ASTM D1621-10)
Creep recovery (%)	44.20- 47.60	-

Table 4.16: Values of Physico-mechanical properties of rigid COPUFs obtained in this study *versus* international standards for the conventional PUF.

Property	Observed	Standard
Core density (kg/m^3)	25.80	34-37 (ASTM D1622-08)
Water absorption (wt%)	0.73-1.80	0.80 (ASTM D2842 -12)
Compressive strength (KN/m^2)	95.50-450.20	≥195 (ASTM D1621-10)
Creep recovery (%)	18.50-23.40	-

4.5 Flame Properties of COPUFs

Table 4.17: Flame properties of COPUFs (NCO/OH of 1/2) treated separately with HCTD and HCHD FR additives

	HCTD				HCHD			
FR content (wt %)	Add-on (%)	IT (s)	FPR (cm/s)	AGT (s)	Add-on(%)	IT (s)	FPR (cm/s)	AGT (s)
0	0	10.0	0.29	15.0	0	10.0	0.29	15.0
0.4	9.5	11.5	0.225	12.25	2.0	10.05	0.228	12.75
0.8	20.5	14.0	0.195	9.5	3.5	11.5	0.20	10.75
1.2	28.05	18.0	0.165	8.0	5.0	14.0	0.17	9.25
1.6	36.5	22.25	0.145	6.75	10.5	16.7	0.15	8.0
2.0	44.5	26.7	0.14	5.5	16.0	19.7	0.145	7.0
2.4	50.0	31.0	0.082	4.5	22.0	23.0	0.12	6.0

Table 4.18: Flame properties of COPUFs (NCO/OH of 1/1) treated separately with HCTD and HCHD FR additives.

FR content (wt %)	HCTD				HCHD			
	Add-on (%)	IT (s)	FPR (cm/s)	AGT (s)	Add-on (%)	IT (s)	FPR (cm/s)	AGT (s)
0	0	11.5	0.24	13	0	11.5	0.24	13
0.4	6.0	13.75	0.216	9.33	3.5	13	0.22	10.4
0.8	20.0	17.0	0.19	7.25	7.5	15	0.20	8.5
1.2	33.0	20.0	0.168	5.85	13.5	18	0.17	7.0
1.6	41.5	24.0	0.145	4.85	23.5	20.5	0.15	5.7
2.0	42.5	27.5	0.122	4	34	23.5	0.124	5.18
2.4	43.0	31.0	0.094	3.33	43	27	0.097	4.25

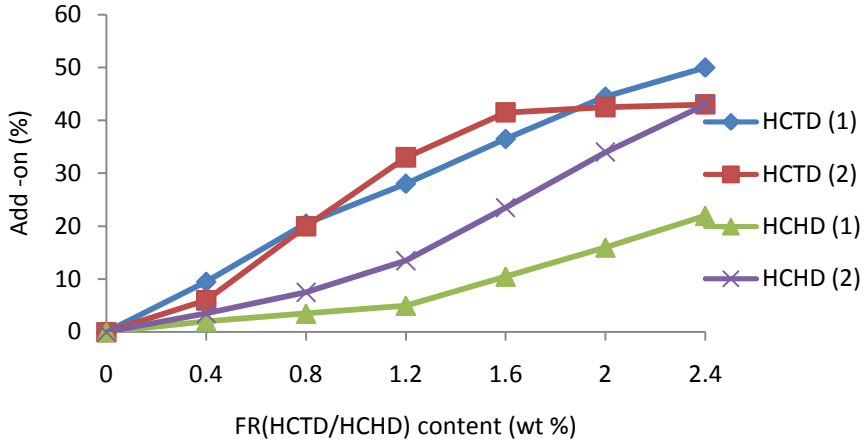


Fig. 4.36: Add-on *versus* flame retardant concentration for COPUFs

4.5.1 Effect of foam density/modifier concentration on flame properties of GMFs

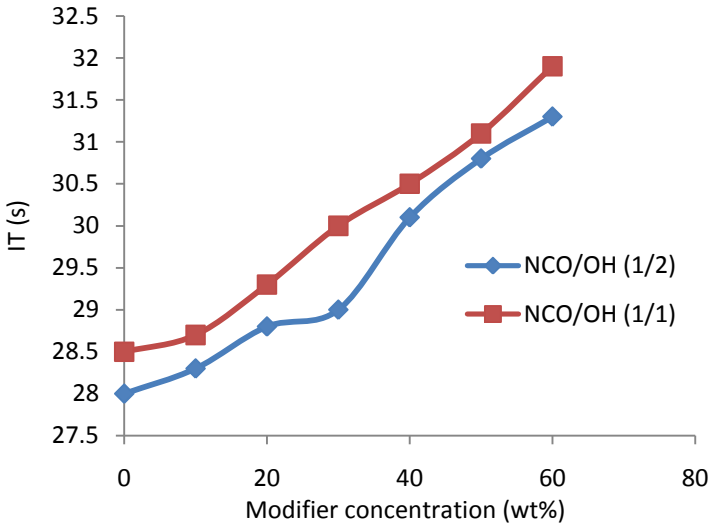


Fig. 4.37: Ignition time *versus* modifier concentration in GMFs

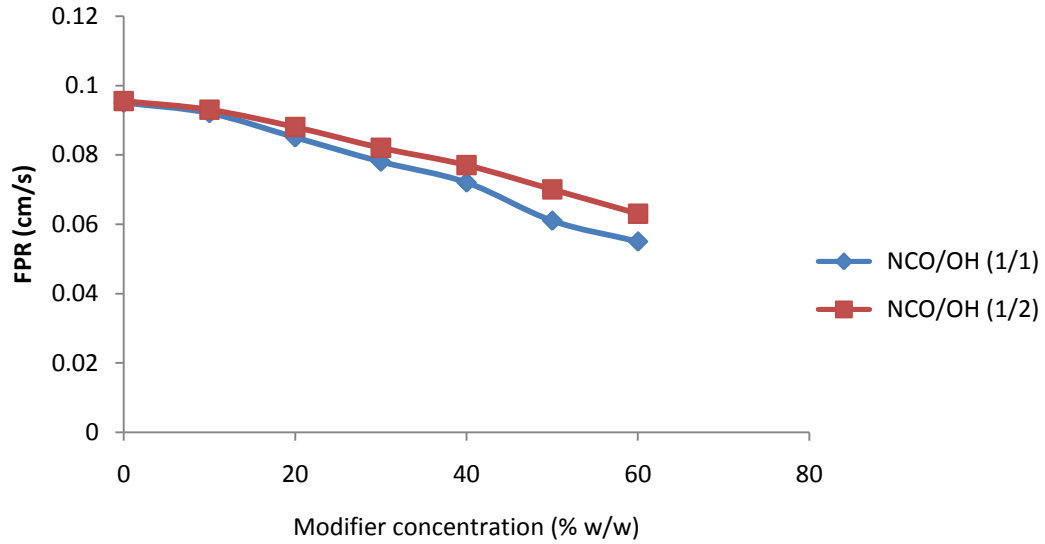


Fig.: 4.38: Flame propagation rate *versus* modifier concentration in GMFs

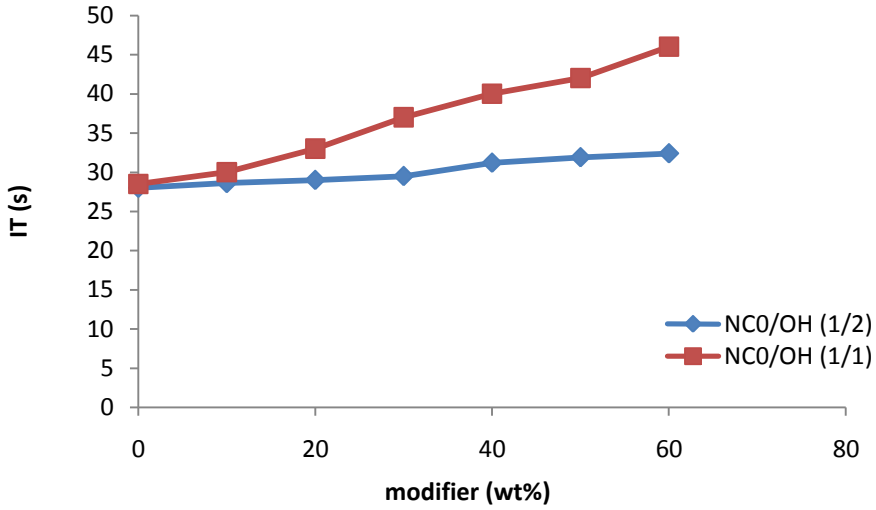


Fig. 4.39: Ignition time *versus* modifier concentration for GMFs treated with 50:50 (HCTD:HCHD) blends

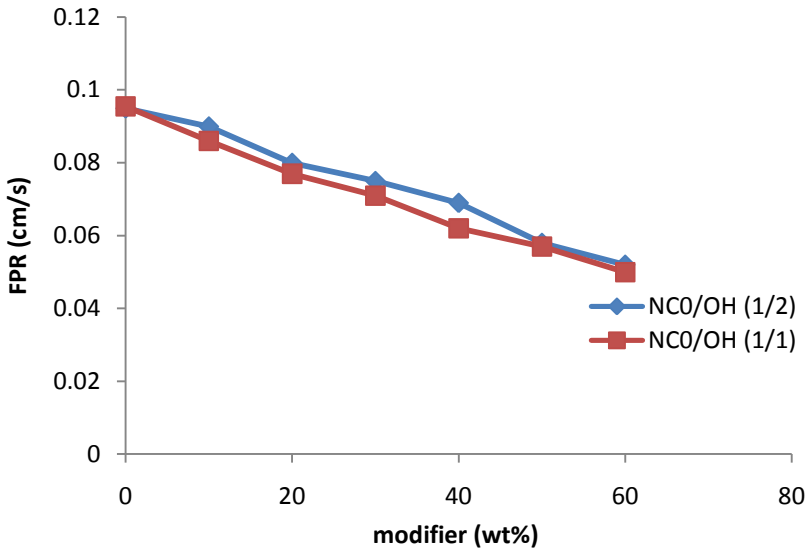


Fig. 4.40: Flame propagation rate *versus* modifier concentration in GMFs treated with 50:50 (HCTD:HCHD) blends

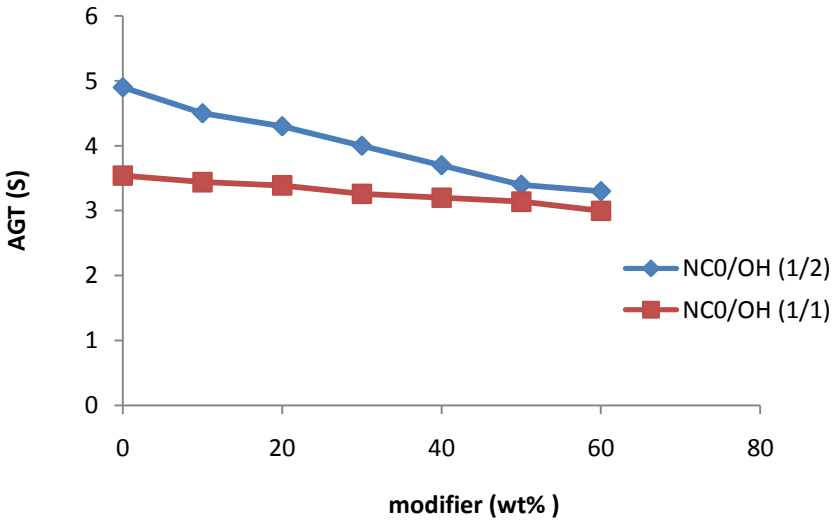


Fig. 4.41: After-glow time *versus* modifier concentration in GMFs treated with 50:50 (HCTD:HCHD) blends

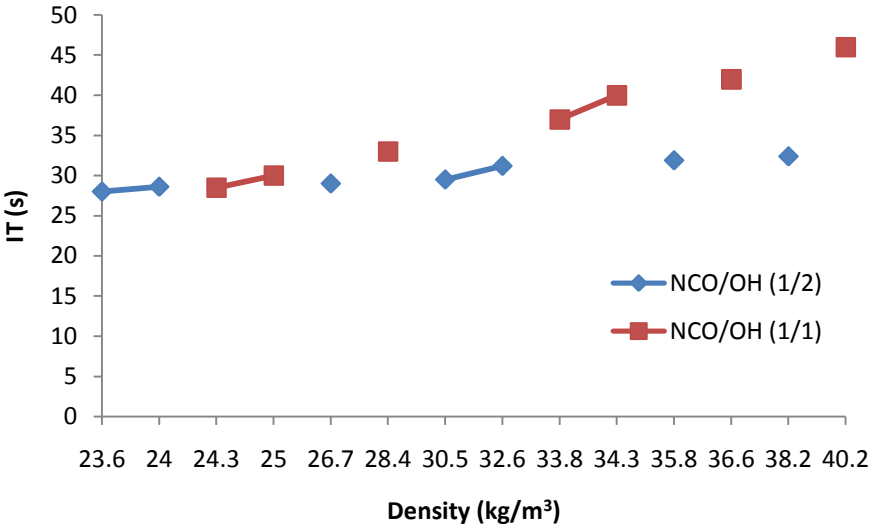


Fig. 4.42: Ignition time *versus* density of GMFs treated with 50:50 (HCTD:HCHD) blends

4.5.2 Effect of flame retardant (FR) concentration on flame properties of COPUFs

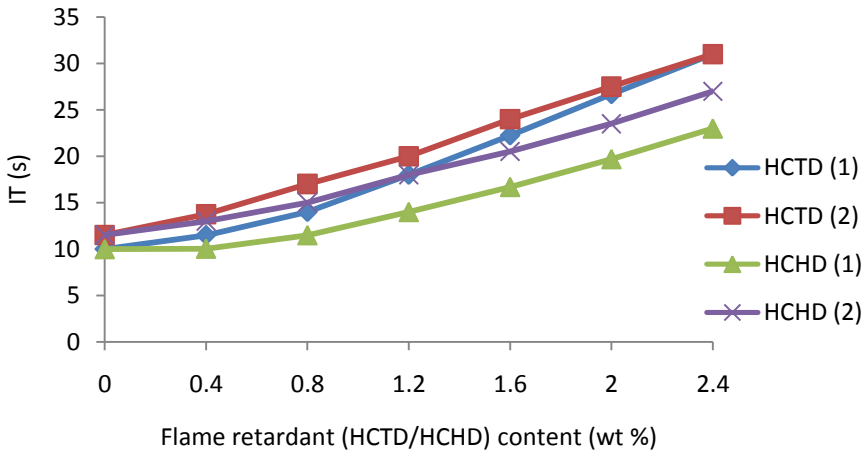


Fig. 4.43: Ignition time *versus* flame retardant concentration for COPUFs

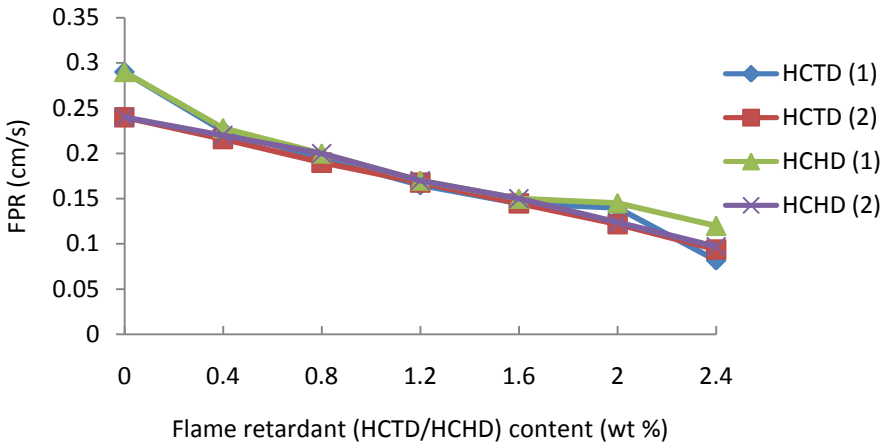


Fig. 4.44: Flame propagation rate *versus* flame retardant concentration for COPUFs

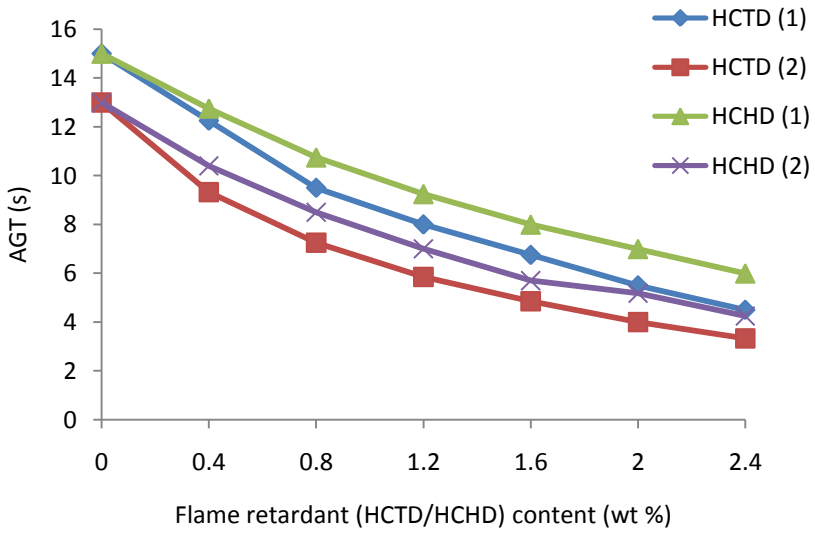


Fig. 4.45: After-glow time *versus* flame retardant concentration for COPUFs

4.5.3 Effect of HCTD/HCHD blending on flame properties of COPUFs

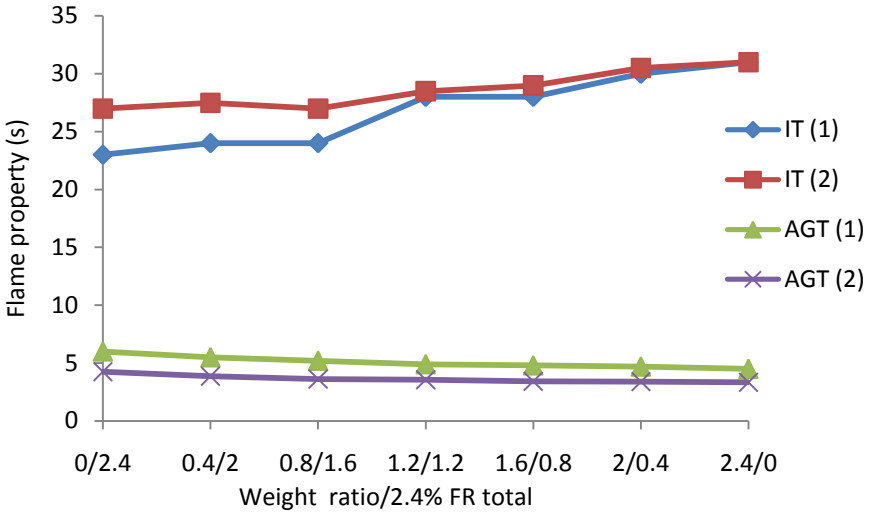


Fig. 4.46: Ignition/after glow-time *versus* flame retardant (HCTD/HCHD) weight ratios for COPUFs

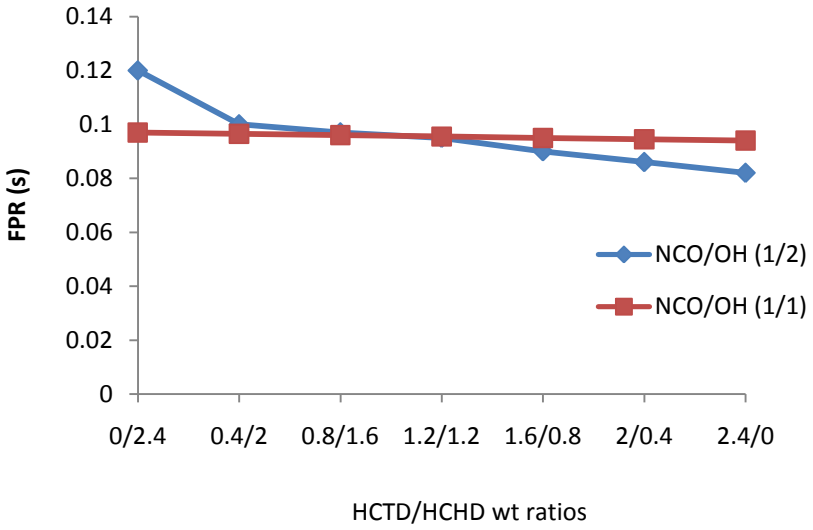


Fig. 4.47: Flame propagation rate *versus* flame retardant (HCTD/HCHD) weight ratios for COPUFs

4.5.4 Effect of filler loading on flame properties of COPUFs

Table 4.19: Flame properties of COPUFs filled with $CaCO_3$

Filler content (wt%)	NCO/OH of 1/2			NCO/OH of 1/1		
	IT (s)	FPR (cm/s)	AGT (s)	IT (s)	FPR (cm/s)	AGT (s)
0	10	0.29	15.0	11.5	0.24	13.0
2	11.25	0.26	12.4	12.25	0.20	11.3
4	11.75	0.23	10.5	13.0	0.18	9.9
6	12.0	0.21	9.38	14.0	0.16	9.0
8	12.1	0.185	8.5	15.18	0.14	8.0
10	12.32	0.173	7.8	16.5	0.125	7.2
12	13.3	0.155	7.2	18.25	0.11	6.66
14	16.0	0.14	6.8	20.25	0.10	6.0
16	20.0	0.125	6.4	22.4	0.09	5.5
18	23.0	0.115	6.2	24.77	0.085	5.2
20	25.5	0.11	5.8	27.25	0.08	5.0

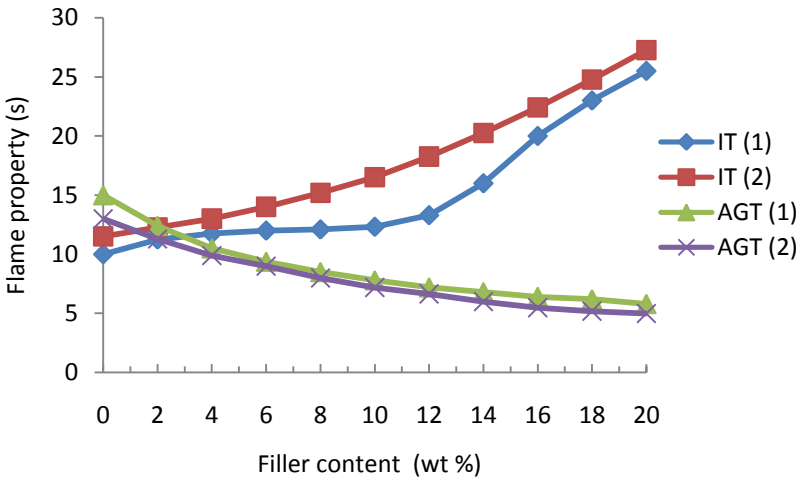


Fig. 4.48: Ignition/after-glow time *versus* filler concentration in COPUFs

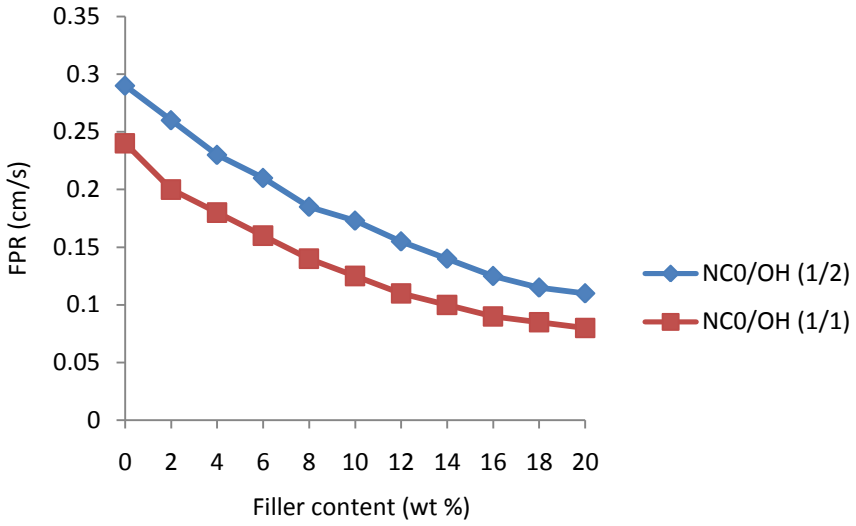


Fig. 4.49: Flame propagation rate *versus* filler concentration in COPUFs

4.6 Morphological Characteristics of COPUFs

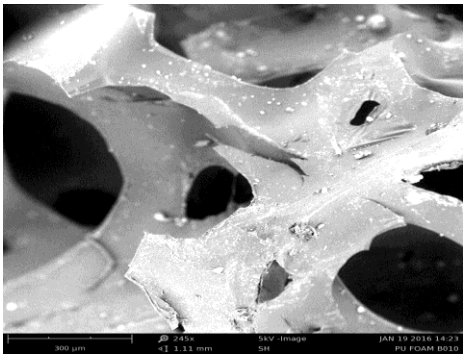


Plate I: SEM image for neat COPUF (NCO/OH of 1/2) Magnification (250 X)

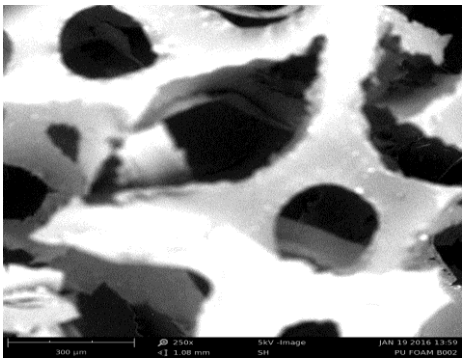


Plate II: SEM image for neat COPUF (NCO/OH of 1/1) Magnification (250 X)

4.6.1: Effect of modifier concentration on the morphology of GMFs

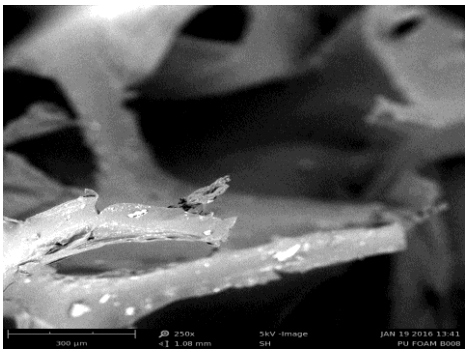


Plate III: SEM image for GMF-10 (NCO/OH of 1/2) Magnification (250 X)

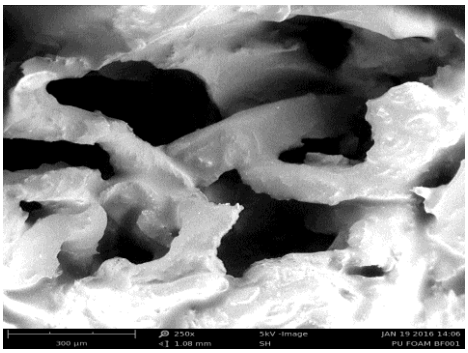


Plate IV: SEM image for GMF-10 (NCO/OH of 1/1) Magnification (250 X)

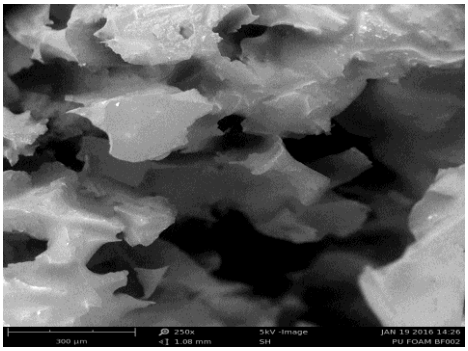


Plate V: SEM image for GMF-20 (NCO/OH of 1/2)

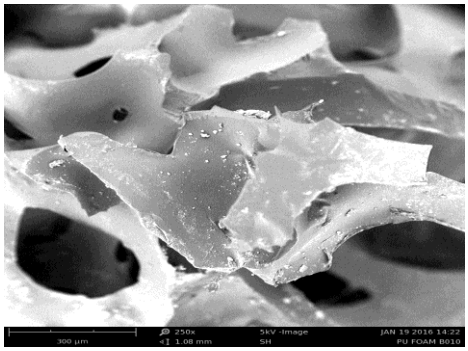


Plate VI: SEM image for GMF-20 (NCO/OH of 1/1)

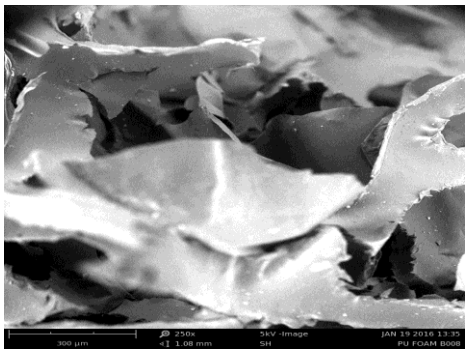


Plate VII: SEM image for GMF-40 (NCO/OH of 1/2)

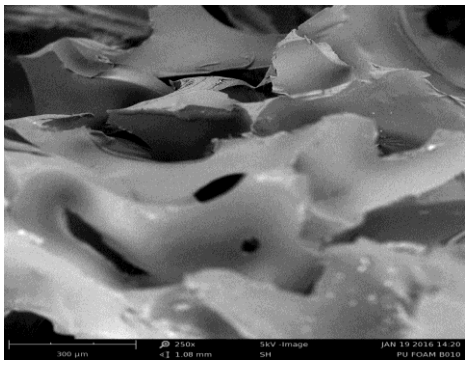


Plate VIII: SEM image for GMF-40 (NCO/OH of 1/1)

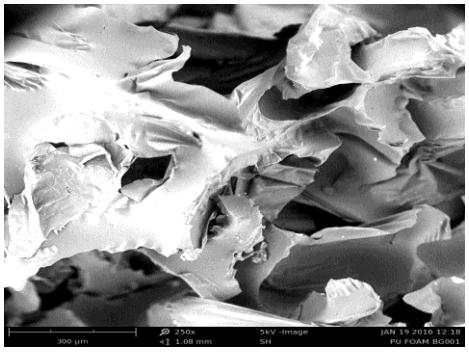


Plate IX: SEM image for GMF-60 (NCO/OH of 1/2)

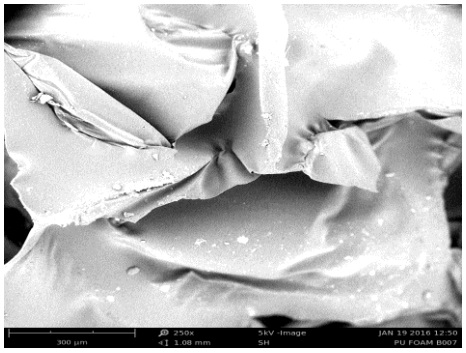


Plate X: SEM image for GMF-60 (NCO/OH of 1/1)

4.6.2: Effect of filler concentration on the morphology of CFFs

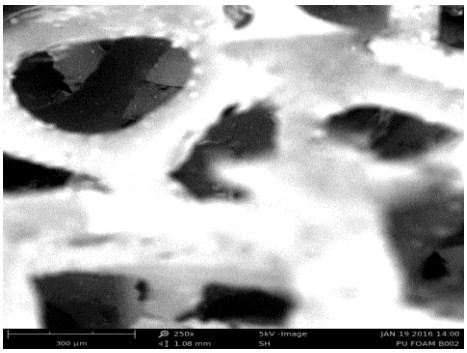


Plate XI: SEM image for CFF-4 (NCO/OH of 1/2)

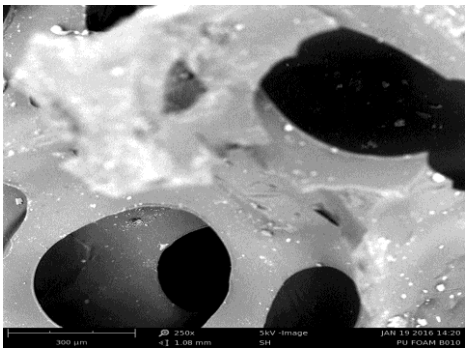


Plate XII: SEM image for CFF-4 (NCO/OH of 1/1)

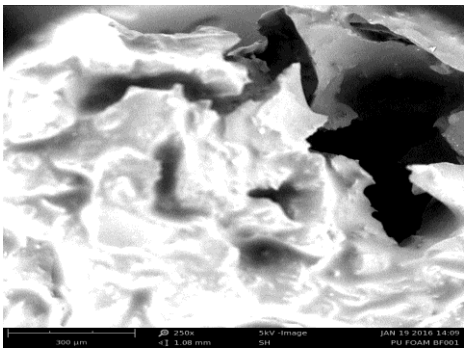


Plate XIII: SEM image for CFF-8 (NCO/OH of 1/2)

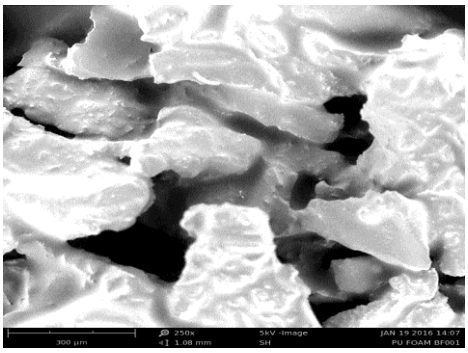


Plate XIV: SEM image for CFF-8 (NCO/OH of 1/1)

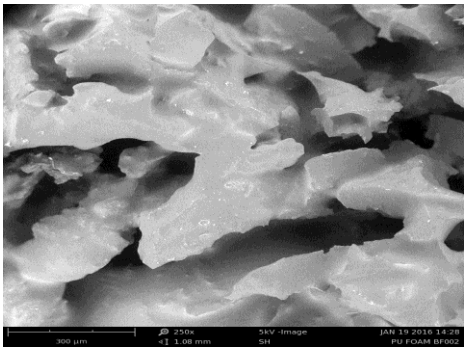


Plate XV: SEM images for CFF-12 (NCO/OH of 1/2)

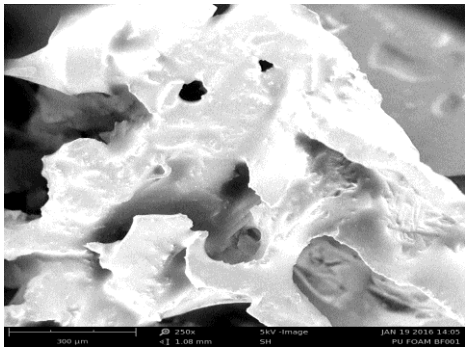


Plate XVI: SEM image for CFF-12 (NCO/OH of 1/1)

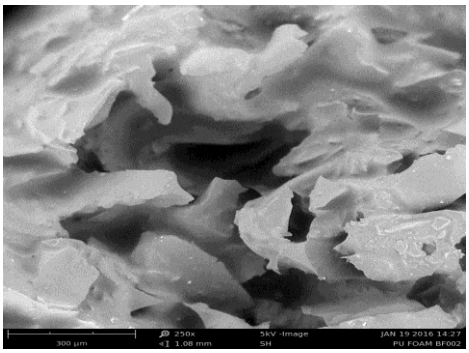


Plate XVII: SEM images for CFF-16 (NCO/OH of 1/2)

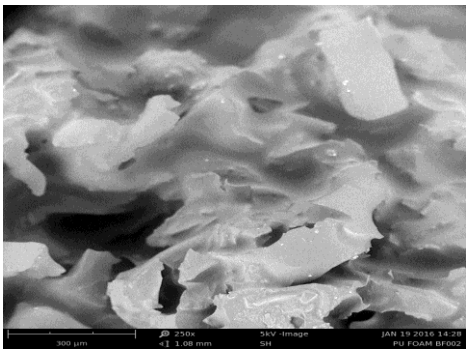


Plate XVIII: SEM images for CFF-16 (NCO/OH of 1/1)

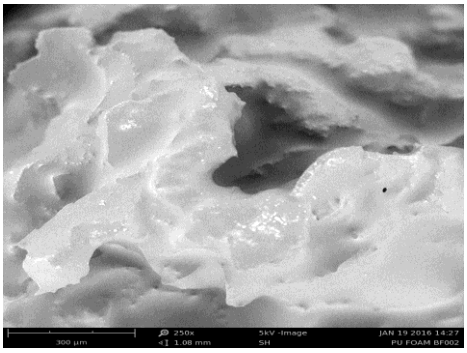


Plate XIX: SEM images for CFF-20 (NCO/OH of 1/2)

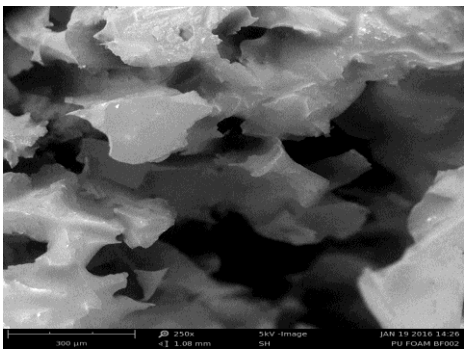


Plate XX: SEM images for CFF-20 (NCO/OH of 1/1)

4.6.3: Effect of HCTD/HCHD plasticisation on the morphology of COPUFs

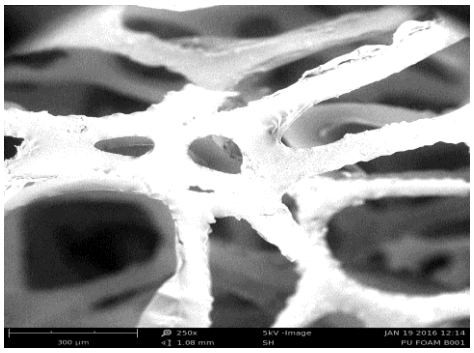


Plate XXI: SEM image for 2.4 wt% HCTD-plasticised COPUF (NCO/OH of 1/2)

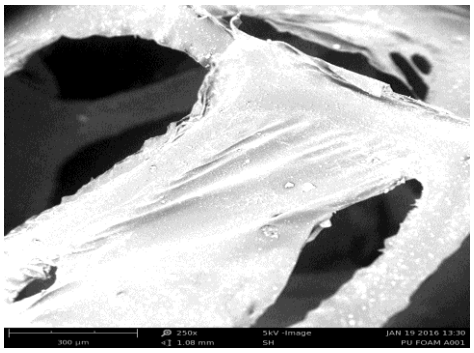


Plate XXII: SEM image for 2.4 wt% HCHD-plasticised COPUF (NCO/OH of 1/2)

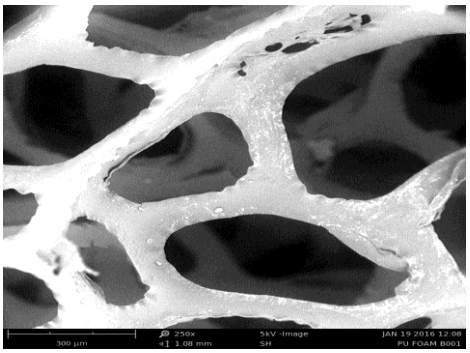


Plate XXIII: SEM image for COPUF containing 50:50 (HCTD: HCHD) blend per 2.4 wt% plasticiser (NCO/OH of 1/2)

4.6.4: COPUF pore dimensions

Table 4.20: COPUF pore and wall sizes

COPUF	PS (mm)	MPS (mm)	WT (µm)	MWT (µm)
Neat	0.15-0.33	0.19	25-40	32.40
GMFs	0.10-0.25	0.15	30-50	35.20
CFFs	0.12-0.32	0.16	20-35	26.50
HCTD/HCHD (treated)	0.20-0.35	0.24	18-26	22.70

CHAPTER FIVE

DISCUSSION

5.1 Physico-chemical Properties for the Castor Seed Oil

5.1.1 physico-chemical parameters

Determined physico-chemical properties evaluated for the oil are presented in table 4.1. Percentage oil content (cold-press) for the seeds (39.43) is generally lower than yields reported for hot-press methods (Ayo *et al*., 2012; Bhatol, 2013, Imasuen *et al*., 2014). However, the yield of 39.43% is quite reasonable considering reported maximum yield of 45% for mechanically pressed castor oil in general (Ogunniyi, 2006). Apart from preserving the natural properties of vegetable oils, the cold-press method is also known to yield castor oil of light colour, low impurity level and low light absorbance (Carr, 1976; Ogunniyi, 2006; Bhatol, 2013). These qualities ensure immediate end-use application of the oil even without refining.

Evaluated physico-chemical parameters for the oil include low acid number (2.07), low iodine number (84.18), low peroxide number (38.00), but moderately high specific gravity (0.959), hydroxyl (163.64), and saponification (175.31) numbers. These numbers compare favourably with ASTM standards and general specifications for industrial grade castor oil (WHC, 2012). Low acid number and pH value of 6.16 suggest low free fatty acid (FFA) content in the oil.

Acid number is a measure of the FFA content in the oil. Iodine number on the other hand, is a measure of the oil's unsaturation level, while peroxide number is related to its oxidation level as a result of hydroperoxide formation at double bond positions. Double bond unsaturation in oils therefore is one of the most important parameters that influence lipid oxidation. In castor oil though, the double bond on C-9 of ricinoleic acid

is believed to be protected against hydroperoxide formation by the hydroxyl group on C-12 (ICOA, 2013).

Low value of iodine number observed for the seed oil is suggestive of low unsaturation level typical of non-drying oils. This means that the oil may not be suitable as alkyd resin for paint formulation or used as vanishes (Kyari, 2008), though it could be used as lubricant or hydraulic brake fluid. Again, relatively high saponification number of 175.31 indicates that the oil has the potential to be used in the soap and cosmetics industries.

In effect, the combination of high hydroxyl number, low iodine and peroxide numbers observed for the seed oil largely account for the stability of castor oil against oxidative rancidity - the oil not turning rancid unless exposed to excessive heat.

5.1.2 Results of FTIR analysis

FTIR spectroscopic analysis has been used to identify certain functional groups in vegetable oils. These oils, irrespective of their origin, contain both saturated fatty acids (SFAs) and unsaturated fatty acids (UFAs). The UFAs may be monounsaturated FAs (MUFAs) or polyunsaturated FAs (PUFAs).

FTIR spectrum (4500-350cm^{-1}) of the castor seed oil (Fig.4.1) reveals major functional group absorption bands, notably for hydroxyl, carbonyl, olefinic, methylenic groups etc. The broad band peaking at 3414.12cm^{-1} represents O-H stretching vibration for hydrogen bonded OH groups. The large band area suggests high concentration of OH groups.

This is consistent with the moderately high hydroxyl value (163.64) determined for the oil by chemical analysis. Other well defined peaks are those for C=O stretching of triglyceride ester linkage (1739.85cm^{-1}), C-H stretching (CH_2) (2925.15cm^{-1}), CH_3 bending (twisting) (1452.45cm^{-1}), out-of-plane bending vibration of *cis*-disubstituted

olefins (1164.08cm^{-1}), overlapping of CH_2 rocking vibration and out-of-plane vibration of *cis*-disubstituted olefins (721.40cm^{-1}), as well as C-O-C bending vibration (401.21cm^{-1}). The shoulder at 1656.80cm^{-1} is for C=C stretching vibration, one of two distinct absorption bands typically observed in oils containing UFAs. The other is at about 3010cm^{-1} (Yousef *et al*., 2001).

5.1.3 Results of GC-MS analysis

(a) Fatty Acid (FA) composition

In Fig. 4.2, seven peaks representing seven major constituent FAMEs in the oil's chemical composition are evident. Peak identification involved noting peak retention time and comparing with authentic reference standards for individual FAMEs. Identified peaks were used to determine fatty acid composition, since peak area (recorded by data processing unit of the GC) is proportional to the concentration of the constituent FAME represented by the peak.

Peak 5 (retention time 18.817 min) represents ricinoleic acid (*cis*-12-hydroxyoctadeca-9-enoic acid) (74.10%) as the major constituent fatty acid in the oil. Other fatty acids are linoleic acid (10.32%) (Peak 2), Oleic acid (7.55%) (Peak 3), stearic acid (2.81%) (Peak 4), palmitic acid (2.59%) (Peak 1), erucic acid (1.70%) (Peak 7) and eicosadienoic acid (0.93%) (Peak 6). The detailed fatty acid profile for the oil is given in Table 4.2, while Table 4.3 presents the SFA, MUFA and PUFA contents (% w/w) for the seed oil.

GC-MS suggested structure for methyl ester of ricinoleic acid (methyl ricinoleate) is given in Fig. 4.3 (double bonds appear as thicker, dark lines).

Ricinoleic acid content (74.10%) for the seed oil is substantially lower than values reported in literature (up to 84-95%) for most castor oil samples (Akpan *et al.*, 2006; Ogunniyi, 2006; Conceicao *et al*., 2007), but falls within the range (70-90%) reported by Foglia *et al.* (2000) for castor oil samples in USA. Variations in percentage chemical content and composition among naturally occurring renewable resources are not uncommon, especially where there are differences in species or varieties, geographical origin, climatic conditions, soil types etc (Lochab *et al.*, 2012). Alirezalu *et al.* (2011) who studied the effect of climatic factors on the production and quality of castor oil among 10 different climatic regions in Iran, reported significant differences in physico-chemical properties of the oil in the regions. Similarly, Salimon *et al.* (2010) reported differences in ricinoleic acid and UFA contents among Malaysian, Brazilian and Indian castor oil samples. In Nigeria, Bello and Anjorin (2012), and Nangbes *et al.* (2013) have reported ricinoleic acid contents of 89.50% and 83.97% for castor oil samples from Akure (Ondo state) and Pankshin (Plateau State) respectively.

SFA total for the oil sample in this study was 5.40%, while the UFA total, made up of MUFA (83.35%) and PUFA (11.25%), was 94.60%. UFA content in our sample is much higher than that for palm oil (Boyle and Anderson, 2007) and compares well with reported values for UFA-rich edible vegetable oils like sunflower, safflower, linseed and soybean oils (Chowdhury *et al.*, 2007; Kostik *et al.*, 2013).

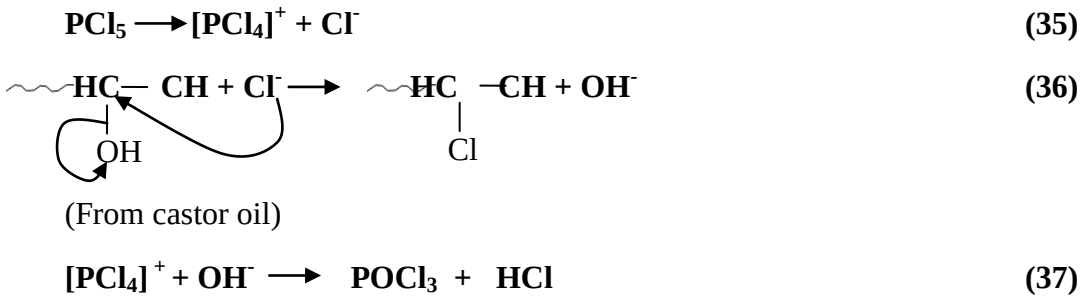
5.2 Physico-chemical Properties of MCOPs

Tables 4.4 - 4.6 describe the physico-chemical properties determined for the glycerol modified castor oil polyols (GMCOPs), PCl_5 modified castor oil polyols (PMCOPs) and sulphated castor oil (SLCO).

5.2.1 Variation of hydroxyl number (HN) and relative viscosity (RV) in MCOPs

Figs 4.4 and 4.5 depict changes in HN and RV of castor oil respectively with increase in modifier concentration. For the GMCOPs, there is steady rise in HN (Fig. 4.4), but gradual fall in RV (Fig. 4.5) with increasing concentration of the modifier (glycerol). The chemistry of this transformation is discussed in Scheme 1 (Chapter One).

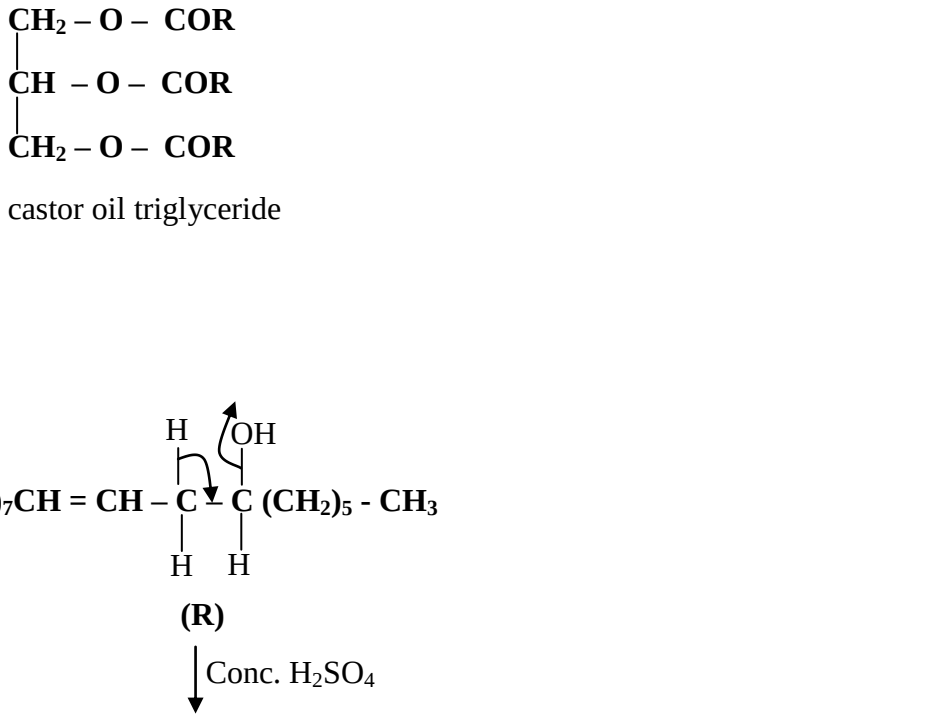
Increase in HN for the GMCOPs is due to increase in hydroxyl functionality of polyol as a result of castor oil hydroxylation via glycerolysis, while fall in viscosity resulted from the splitting of castor oil into mono- and diglycerides (Scheme 1). Higher viscosity of GMCOPs relative to PMCOPs and SLCO is mainly the result of increased H-bonding due to added hydroxyl functionality in oil. For the PMCOPs, both HN and RV decreased monotonically as modifier (PCl_5) concentration was increased, because PCl_5-chlorination of castor oil is known to proceed by nucleophilic substitution in which hydroxyl groups are replaced with chlorine (Naughton, 1974) (Scheme 3). This translates to diminishing hydroxyl functionality in oil as concentration of PCl_5 modifier increased. However, viscosity of castor oil would increase if chlorinated by addition across its double bonds (Yousef *et al*., 2001; Ali *et al*., 2005).



Scheme 3: Chlorination of castor oil by substitution using PCl_5 as chlorinating agent

With regard to sulphated castor oil (SLCO) or Turkey-red oil, hydroxyl number of oil at 60 wt% sulphuric acid modifier was only 10mgKOH/g. This is due to dehydration of

the three ricinoleic acid esters (or ricinoleates) in castor oil as per Scheme 4 (below), to create additional double bond unsaturations in the oil.



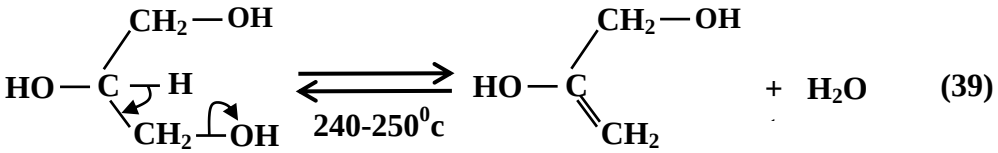
Scheme 4: Sulphation (dehydration) of castor oil using conc. H_2SO_4

Very low hydroxyl number in SLCO implies very low conversion to PU if reacted with diisocyanate. Fall in castor oil RV for SLCO of 60 wt% modifier concentration (Fig.4.5) is consistent with reported reduction in viscosity of oils with increasing degree of unsaturation (Ali *et al*., 2005).

5.2.2 Variation of iodine number (IN) in MCOPs

High iodine number (98.6) observed for SLCO (Fig.4.6) is the result of increased double bond unsaturation in oil. Iodine number for the GMCOPs was constant up to 20 wt% modifier concentration, but thereafter increased slightly with increased modifier

concentration. The slight increase in iodine number at higher glycerol concentrations is probably due to the formation of unsaturated species via thermal dissociation of remaining (unreacted) glycerol (as side reaction), since glycerol is known to be susceptible to high temperatures because of the presence of hydrogen atoms in positions β relative to hydroxyl group in the glycerol molecule (Ramirez *et al*., 2008).



1,2,3- propanetriol (glycerol)

2,3-propenediol

Scheme 5: Probable mechanism for the thermal dissociation of glycerol

Similarly, iodine number for the PMCOPs was constant up to 20 wt% modifier concentration, but surprisingly decreased slightly thereafter. This is unusual, since as stated earlier, PCl_5 chlorination of castor oil proceeds via substitution, and therefore should have no effect on iodine number. However, observed trend might be the result of some free radical addition reaction at the oil double bond positions occurring at random, and involving the HCl molecule generated as by-product via Scheme 2. This could happen at high concentrations of the chlorinating agent (PCl_5) and at very high temperatures that can promote the thermal dissociation or homolytic cleavage of the HCl molecule.

5.2.3 Variation of hydroxyl number with reaction time during polyol synthesis

Fig. 4.7 shows changes in the hydroxyl number of polyol with reaction time for the GMCOPs, while Fig. 8 describes the same variables for the PMCOPs.

Observed monotonic increase of HN (GMCOPs), but monotonic decrease of same (PMCOPs) with modification time suggest good thermal stability for the alcoholysis (glycerolysis) and chlorination reactions involving castor oil. In both cases, the rate of HN rise or fall depended on the modifier concentration.

5.2.4 Results of FTIR and GC-MS analyses for the MCOPs

FTIR and GC-MS analytical techniques were used as complementary methods (after chemical/titrimetric methods discussed earlier) for the structural characterisation of the MCOPs.

(a) GMCOPs

The alcoholysis/transesterification of castor oil using glycerol in presence of traces of PbO catalyst results in the splitting and hydroxylation of the castor oil triglyceride molecule to yield mono- and diglycerides (Scheme 1). In the GMCOPs (Figs 4.9 a-f), FTIR was employed for the identification of key functional groups such as carbonyl (C=O) (1728-1738 cm^{-1}), hydroxyl (OH) (3376-3393 cm^{-1}) and double bond unsaturation (C=C) (1649-1656 cm^{-1}). In addition, this study was also interested in monitoring the growth of hydroxyl absorption peaks in the GMCOPs with increase in the wt% concentration of the hydroxylating agent (glycerol). Peak intensity and peak area were used to gauge the strength of hydroxyl absorption (Dole *et al*., 2011), and therefore the amount or concentration of hydroxyl groups in GMCOPs. The observed trend was that of increasing hydroxyl concentration (indicated by growth of OH peak at 3376-3393 cm^{-1}) with increase in wt% concentration of the modifier.

(b) PMCOPs

According to Naughton (1974), there are three sites for the chlorination of castor oil or its ricinoleic acid namely

(i) At the ester linkage (using thionyl chloride – $SOCl_2$) to produce fatty acid chlorides

(ii) At the hydroxyl groups (PCl_5) to produce chlorinated castor oil by substitution

(iii) At the double bonds (using Cl_2 or HCl) to produce chlorinated castor oil by addition.

Mechanism for the chlorination of castor oil by substitution using PCl_5 has been described earlier (Scheme 2). Both FTIR and GC-MS were employed for the characterisation of the chlorinated castor oil polyols.

(i) FTIR

Figs 4.10 (a-f) represent the FTIR spectra for PMCOPs containing 10-60 wt% concentration of the chlorinating agent or modifier (PCl_5). The particular absorption peaks of interest here are the carbon-chlorine (C-Cl) absorption peak which usually features between 600-500 cm^{-1} (Abdul Qadir *et al*., 2011) and of course, hydroxyl absorption which usually features as a broad band between 3600-3300 cm^{-1}. The appearance of absorption peaks within the frequency range 582-500 cm^{-1} in the FTIR spectra of the PMCOPs is, therefore, a confirmation of castor oil chlorination. The chlorinated castor oil polyols were thus characterized by simultaneously monitoring the growth of C-Cl absorption (582-500 cm^{-1}) and the diminishing hydroxyl presence

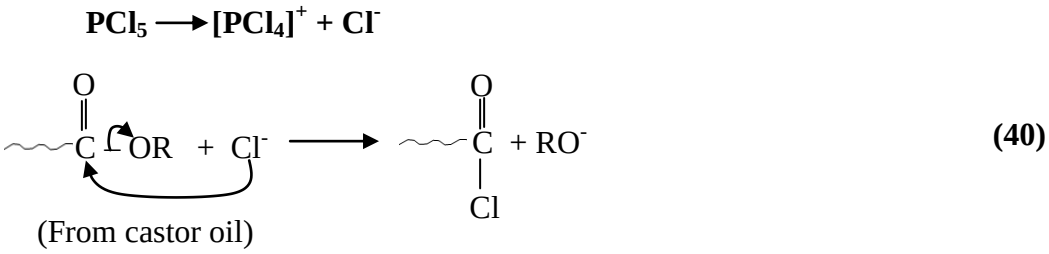
(3453-3291 cm^{-1}) with increase in concentration of the chlorinating agent (PCl_5) (Figs 4.10a-f).

(ii) GC-MS

GC-MS chromatograms for the PMCOPs (Figs 4.11 a-f) show signals for chlorinated products of the pyrolysis of castor oil at various peaks and corresponding to different retention times.

The chlorinated products identified by mass spectral library matching against reference standards were 9,12-octadecadienoyl chloride, linoleoyl chloride, lineoleoyl chloride, linoleic acid chloride, hexanoyl chloride, n-hexanoyl chloride, caproyl chloride, n-caproyl chloride, caproic chloride and caproic acid chloride.

Number of peaks, peak intensity and peak area in respect of the chlorinated products all generally increased with increase in concentration of the chlorinating agent (PCl_5) in polyol, with the polyol containing 60 wt% PCl_5 recording six such peaks having peak areas of 4.91, 8.89, 4.58, 2.30, 3.37 and 37.28% respectively. The presence of small quantity of acid chlorides (linoleic and caproic acid chlorides) in the polyols is unexpected, though this might suggest the possibility of chloride ions from PCl_5 dissociation (Scheme 2) reacting (at random) with castor oil triglycerides at ester linkages (Scheme 4). Presence of acid chlorides is also supported by the appearance of weak IR absorption peaks at 1810-1750 cm^{-1}(Fig.4.10f) and 1000-910 cm^{-1}(Fig.4.10b). However, chlorination at the oil's hydroxyl groups is the major feature, and is predominant.



Scheme 6: Probable PCl_5-chlorination of castor oil triglyceride at ester linkages.

(c) Sulphated castor oil (SLCO)

FTIR spectrum for SLCO (Fig.4.13) shows absorption peaks at 945.15 cm^{-1}(=C-H twisting) and 736.83 cm^{-1}(XHC=CHX out-of-plane vibration) suggestive of unsaturation, but no hydroxyl absorption in the frequency range 3600-3300 cm^{-1}. The disappearance of hydroxyl absorption band in SLCO spectrum corroborates the very low hydroxyl value obtained for this species by chemical analysis. For this reason, SLCO or Turkey-red oil was not considered further as potential polyol for the synthesis of castor oil-based PUFs. However, the oil can be utilized extensively in the production of paints and vanishes (Wiley and Oeitmann, 1991; Ogunniyi, 2006).

5.3 Physical Properties of COPUFs

In Table 4.8, foam colour depended either on the natural colour of the base polyol (castor oil) which is pale yellow, or on the influence of the polyol modifier, or both. For instance, foams from PCl_5 chlorinated CO polyols were of light-to-dark brown colour (the higher the PCl_5 concentration, the darker the colour), those from glycerolysed CO were all white, while those from HCTD/HCHD treated CO were pale yellow (HCTD, HCHD and CO being of pale yellow colour). Initial foam colour, even if not desired, is

not of much practical consequence since bleaching or selective dyeing could yield the desired (final) foam colour.

5.3.1 Process parameters for the synthesised COPUFs

Process parameters (Tables 4.9 - 4.12) namely cream, free-rise, gel and tack–free times were determined sequentially during foam synthesis, but foam rise, density and water absorption were determined post-cure. The parameters were defined as follows:

(i) Cream/initiation time - time taken (seconds) to form cream-coloured bubbles that just began to rise above the level of the reaction mixture.

(ii) Free rise time - time taken (seconds) for the freely rising foaming product to stop rising.

(iii) Gel time - time taken (seconds) for the foaming product to form semi-solid or gel.

(iv) Tack free time - time (seconds) when outer surface of the solidifying foam lost its stickiness.

(v) Foam rise - maximum foam height (cm) attained in an open mould.

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, 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. The latter is evident from generally shorter free-rise times and higher foam rise 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 and polyester polyols. This is understandable on the basis of the much lower hydroxyl value for castor oil (160-166mgKOH/g) (WHC, 2012) compared to 400-500mgKOH/g for conventional polyether and polyester polyols (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 (Kim *et al*., 2008, Luo *et al.*, 2008). This confirms the role of glycerol in this system essentially as 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^{0}C), suggesting that the CO-based foams are of good dimensional stability within this temperature range.

However, attempts at producing PMF PU foams across the modifier compositional range (10-60%) was not successful. Only PMF foams containing 10 and 20% modifier could be produced (Tables 4.11 and 4.12), and even these were characterized by delayed cream time, very poor foam rise, relatively lower densities and foam embrittlement. Chlorination of CO was primarily intended to impart fire retardancy

characteristics on the synthesised COPUF. However, PCl_5 chlorination of CO is known to proceed by substitution at OH group on C-12 of ricinoleic acid (Naughton, 1974). The higher the concentration of PCl_5, the more the depletion of hydroxyl functionality (by substitution), and generally the lower is the conversion of polyol into PUF. This is because hydroxyl value in polyol is directly related to the extent of gelation during foam synthesis (Firdaus, 2011). Highly chlorinated CO polyols obtained by this method are better used as plasticiser in nitrile rubber formulations (Yousef *et al.*, 2001). Nevertheless, PUFs have been reportedly produced from chlorinated polyols via epoxidation, followed by ring opening using HCl (Petrovic, 2008), but these are less thermally stable than PUFs obtained from unchlorinated polyols (Sharmin *et al.*, 2012).

In Fig. 4.14, 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. This is mainly due to crosslinking reactions engendered by higher hydroxyl functionality in polyol. Highest densities were recorded for GMFs containing 60% modifier, and of NCO/OH ratio 1/1. High density of GMFs is directly related to network formation and foam rigidity.

It is also observed that both gel time and tack-free time were substantially influenced by NCO/OH ratio in foam formulation. While gel time decreased, tack-free time actually increased with an increase in NCO/OH ratio.

5.3.2 Density and water absorption of COPUFs

Fig. 4.15 depicts rapid fall in water absorption of GMFs with increased modifier concentration. This is as a result of the formation of more rigid, crosslinked structures at higher hydroxyl content in polyol as discussed earlier. In other words, water absorption of foam is inversely related to foam crosslink density. Water absorption of PU foams 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 polymer foams. Resistance to water/moisture permeability is therefore an important quality of PU foams, especially those meant for outdoor application (Singh and Jain, 2008).

5.3.3 Effect of filler incorporation on the physico-chemical properties of COPUFs

Decrease in cream time with increased filler content (Fig. 4.16) implies that the introduction of $CaCO_3$ filler substantially influenced foam reaction time. Consequently, the higher the filler concentration (up to 20 wt%), the shorter the cream and free rise times, and the higher the foam rise. Density of foam was found to improve as filler content increased from 2-20%. This is in agreement with the results of the work of Usman *et al.* (2012) on the effects of $CaCO_3$ filler on flexible PU foam. Foam density also improved at the higher NCO/OH ratio of 1/1 likely due to the formation of more hard segments in form of allophanate crosslinks and urea linkages in the foam matrix (Dusek *et al.*, 1991; Luo *et al*., 2008). $CaCO_3$ filler would tend to disperse and fill voids in the PU matrix, resulting in increased foam density (Latinwo *et al.*, 2010).

Fig. 4.17 shows the water absorption of neat COPUF produced using two different NCO/OH ratios in foam formulation, while Figs 4.18 & 4.19 compare the water absorption levels of GMF, PMF and CFF foams of 20 wt% modifier composition, but varying NCO/OH ratios. GMFs exhibited lowest water permeability due to their rigid, crosslinked structures as discussed earlier. Generally, higher water sorption observed for the PMFs might be due to their coarse and porous nature. Lower water absorption of $CaCO_3$-filled PU foam, compared to the control (neat COPUF), is explained in terms of

the effective dispersal of this water-insoluble filler to fill voids in the CFF foam matrix. But water resistance exhibited by the control itself is largely on account of the hydrophobic nature, as well as the hydrolytic and thermal stability of the base polyol (castor oil). Similarly, higher density foams of NCO/OH ratio of 1/1 were found to have relatively lower water absorption values.

5.3.4 Effect of plasticisation on the physical properties of COPUFs

It is observed that foam density generally decreased with increased plasticiser content (Fig. 4.20), while water absorption generally increased slightly at higher plasticiser concentration (Fig. 4.21).

The effect of plasticisation is to reduce the cohesive intermolecular forces between polymer chains and create greater free volume between them (Fox, 2008). This explains the lower foam density and increased water sorption observed for HCTD/HCHD - plasticised COPUFs, compared to the control foam. However, relatively lower density and higher water sorption in respect of the HCHD – plasticised CPUFs (Figs 4.20 & 4.21) suggest that HCHD is a better plasticiser than HCTD in the COPUF system.

HCTD and HCHD (Fig. 3.1), which are chlorinated paraffins (CPs), are known to be compatible with oils generally. They are also known to have the advantage of increasing the flexibility and extensibility of materials, in addition to enhancing their fire retardancy and low temperature strength (Klorfin, 2012). According to Houghton (2003), the physico-chemical properties of CPs are determined by their carbon chain length and their chlorine content. Both HCTD (C-14) and HCHD (C-17) have moderately long carbon chains compatible with castor oil. It is thought that the fairly long carbon chains in HCTD and HCHD (Fig.3.1) when incorporated into CO polyols

could increase the flexibility and extensibility of the produced PU foam through an internal plasticisation mechanism in which they break the cohesive intermolecular forces of attraction between polymer chains, and at the same time mask or block interaction sites along the chains to prevent re-formation (Amato *et al.*, 2001; Fox, 2008). Typically, these cohesive forces involve mono – and bidentate hydrogen bond formation (Yilgor, 2000) around urethane and urea units in PU matrix largely responsible for foam rigidity. By this mechanism, greater free volume is created between the PU chains, resulting in greater segmental mobility within the PU matrix. This is consistent with observed density decline and greater water uptake for the HCTD /HCHD treated foams, compared to the untreated ones. The observed greater plasticising ability of HCHD compared to HCTD perhaps lies with the ability of the longer chain (C_{17}) HCHD to mask or block greater number of interaction sites along the polymer chains, to prevent re-formation of cohesive intermolecular bonds.

5.4 Mechanical properties of COPUFs

5.4.1 Compressive strength

In Fig. 4.22, compressive strength of GMFs increased steadily up to about 30 wt% modifier concentration, followed by a sharp, steep rise thereafter up to 60 wt%, with foams prepared using formulation II (NCO/OH ratio of 1/1) yielding higher values. COPUFs prepared using the higher NCO/OH ratio of 1/1 and from glycerolysed CO polyol containing 60 wt% modifier gave the highest compressive strength value of up to 450KN/m^2 (Fig. 4.22).

Higher isocyanate content resulted in increased hard segment content (through allophanate linkages) in the PU foam matrix. Similarly, higher hydroxyl functionality in polyol also resulted in increased crosslinking reactions and formation of interchain networks (Lim *et al*., 2008). Both could result in increased foam crosslink density and greater rigidity in foam structure, making foam harder to compress.

(a) **Effect of filler loading on the compressive strength of COPUFs**

The effect of $CaCO_3$ filler on the compressive strength of the PU foams is depicted in Fig. 4.23. Increased filler loading and higher NCO/OH ratio gave higher compressive strength values. Compressive strength of filled PU foams (Fig.4.23) shows gradual increase from 65.40 - 100.2 KN/m^2 with increase in filler loading from 2 - 20 wt% $CaCO_3$. It is considered that increased $CaCO_3$ filler loading has the effect of increasing foam density by filling interstitial voids in the polymer foam matrix.

(b) Effect of plasticiser concentration on the compressive strength of COPUFs

Variation in compressive strength of HCTD/HCHD plasticised CO-based foams is presented in Fig. 4.24. Increased plasticiser concentration in foam formulation resulted in lower compressive strength of PU foam. Foams containing same plasticiser concentration in formulation, but different NCO/OH ratios had different compressive strength values; with the higher ratio of 1/1 yielding higher values. In other words, the lowest compressive strength values were obtained from the highest plasticiser concentration of 2.4 wt%, and the lower NCO/OH ratio of 1/2.

In terms of plasticiser effectiveness, HCHD yielded lower compressive strength values making it a better plasticiser for the CO-based PU system. This is explained in terms of the longer chain HCHD constituting a greater impediment to inter-chain polymer interactions that produce rigid foams, and at the same time offering more free volume in polymer matrix for segmental mobility. 50:50 blend of HCTD/HCHD produced a synergistic effect by yielding the lowest foam density (19.50 Kg/m^3) (Fig. 4.25) and the lowest compressive strength (48.8 KN/m^2) (Fig. 4.26), both lower than the weighted average for the two components. These results suggest a very close relationship between foam density and compressive strength.

5.4.2 Creep recovery

Creep recovery describes the extent to which a 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 structurally rigid GMFs (Fig. 4.27) decreases steadily with increase in modifier concentration. These foams produced the lowest % creep recovery of 18.5 and 20 respectively for NCO/OH ratios of 1/1 and 1/2 (at 60% modifier concentration) (Fig. 4.27). Filler ($CaCO_3$) loading led to substantial fall in % creep recovery from 38 (neat foam) to 26 (CFF-20) for CFFs of NCO/OH ratio of 1/2 (Fig. 4.28). For the HCTD/HCHD plasticised foams, the 50:50 blend of HCTD/HCHD produced synergistic creep recovery values of 45.8 and 36.1% for NCO/OH ratios of 1/2 and 1/1 respectively (Fig. 4.30). However, the highest creep recovery was recorded with respect to HCHD plasticised PU foam of NCO/OH ratio of 1/2, and containing 2.4 wt% plasticiser (Fig. 4.29).

5.4.3 Effect of density on mechanical properties of COPUFs

Mechanical properties of PUFs such as tensile strength, compressive modulus, compressive strength, creep recovery etc, are known to depend strongly on density (Saint–Michel *et al*., 2006; Song *et al*., 2009) as well as on the material composition. Foam density is a very important physical property which has great influence on the mechanical properties of PUFs (Thirumal *et al*., 2008). For a foamed polymer generally, compressive properties are important because they describe the behaviour of the foam when it is subjected to compressive load. Compressive strength represents the ability of a material to resist compression under an applied force or compressive load. Both compressive strength and compressive modulus are support factors that are related to load - bearing capacity, while creep recovery is an indicator of foam resilience. These parameters are very important especially in PU foam applications that require high energy impact absorption such as packaging, sporting foot-wears etc (Linul *et al.*, 2013).

The relationship between density and mechanical properties of COPUFs has informed the graphical representation of this relationship in this study (Figs 4.31-4.33). In particular, the close relationship between density and compressive strength of PU foams has been noted. In Figs 4.31 and 4.32, there is steady, monotonic increase in compressive strength with increase in density for GMF, CFF, as well as the HCTD and HCHD plasticised COPUFs. In Fig. 4.34, 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. Still, with regard to the GMFs whose densities are directly related to the hydroxyl functionality in the CO polyol, a plot of compressive strength of foam against hydroxyl number of polyol (Fig.4.35) also shows a direct relationship. This is in

agreement with the works of Kanner and Decker (1969), Chan (2008) and Firdaus (2011) on soybean oil-based polyurethane foams (SPUFs).

5.5 Comparison of Physico-mechanical Properties of COPUFs with Standard Values for the Conventional Polyurethane Foam

Tables 4.15 and 4.16 compare the physico-mechanical properties of flexible and rigid COPUFs obtained in this study with corresponding values for the conventional polyurethane foam. Worldwide, flexible polyurethane foams are mainly used for cushioning (upholstered furniture, mattresses, pillows, automotive interiors, footwears etc.) and packaging applications, while rigid PUFs are mainly used as thermal/electrical insulation (in building and construction) and flotation materials. The properties compared are density (a factor of foam support, durability and ignition resistance), water absorption (related to water resistance and foam longevity), compressive strength (measure of foam firmness or load-bearing capacity) and creep recovery (foam resilience).

For the rigid PUFs, values for COPUF density, water absorption and compressive strength are within the prescribed American Society for Testing and Materials (ASTM) standards for the conventional PUF, while no universally accepted standards for PUF creep recovery are available. Similarly, density and water absorption values for the flexible COPUFs in our study also fall within the prescribed ASTM standards, but were of lower compressive strength. This suggests that by the ASTM standards, the produced flexible COPUFs in our study are inferior to the standard conventional polyurethane foam in terms of load-bearing capacity. Further studies are therefore needed to address this shortcoming, especially with regard to optimising plasticiser application in the

COPUF system, or incorporating filler into the flexible foam formulation to give more solidity to the flexible COPUF.

5.6 Flame Properties of COPUFs

Flammability characteristics such as ignition time (IT), flame propagation rate (FPR) and after-glow time (AGT) were used to assess the fire behaviour of FR-treated and untreated PU foam samples (Tables 4.15 - 4.17). Add-on, i.e. the weight of FR absorbed by foam sample was also evaluated (Equation 34) for the FR treated samples. For these samples, add-on increased steadily with FR content in foam formulation (Fig. 4.36).

5.6.1 Effect of foam density on flame properties of COPUFs

For both the treated and untreated samples, it is observed that IT was higher, while FPR and AGT were lower at the higher NCO/OH ratio of 1/1. This is likely due to greater foam density at higher NCO/OH ratios as discussed earlier. According to Vanspeybroeck *et al.* (1993), density is a key variable in controlling ignition resistance. Decrease in FPR and AGT with increase in foam density is probably due to thermal stability enhancement of the PU foams at higher densities. In other words, the thermal stability and ignition behaviour of PU foams mainly depend on density and material composition (Lefebvre *et al.*, 2005). The effect of density on flammability is implied from Figs 4.37 - 4.41 because increase in modifier concentration has been shown to result in density enhancement for the GMFs. A direct plot of IT against foam density for the GMFs (Fig. 4.42) corroborates this assertion. Thus, ignition time increased while FPR and AGT decreased with increase in foam density in GMFs.

5.6.2 Effect of FR concentration on flame properties of COPUFs

For treated samples, IT generally increased while both FPR and AGT decreased with increase in FR concentration. The untreated foam samples generally showed shorter ignition times, but longer FPR and AGT values than the FR treated samples. For these foam samples, while FPR and AGT reduced, IT increased with increase in foam density. The effect of FR additive is to reduce or delay the ignitability of the foam samples, and reduce the speed or rate of their burning (Figs 4.43 - 4.45).

Substantial AGT decrease is likely due to diminished char formation as a result of the FR treatment. This is because according to Arinze *et al*. (2015), glow is a heterogeneous surface oxidative process that depends on char formation, as well as the availability of oxygen. For a particular NCO/OH ratio, the higher the FR concentration, the higher the add-on, and the greater the influence of FR on foam fire behaviour. However, HCHD, with longer carbon chain, seems to be less absorbed than HCTD. Overall result suggests that irrespective of NCO/OH ratio in formulation, HCTD is more effective than HCHD as FR for the CO-based PU system. The former (C_{14}) is likely to be less thermally stable on thermal agitation than the latter (C_{17}), and therefore expected to yield more chlorine radicals per mole of FR according to equation (6).

$$\underset{\textbf{(HCTD)}}{\mathbf{C_{14}H_{23}Cl_7}} \rightarrow \mathbf{\bullet C_{14}H_{23}} + \mathbf{7\ Cl\bullet} \qquad \textbf{(41)}$$

$$\underset{\textbf{(HCHD)}}{\mathbf{C_{17}H_{29}Cl_7}} \rightarrow \mathbf{\bullet C_{17}H_{29}} + \mathbf{7\ Cl\bullet} \qquad \textbf{(42)}$$

The effect of HCTD and HCHD on the flammability characteristics of the CO-based PU foam system can be explained on the basis of the general mechanism of action of halogenated FRs on polymer substrate i.e. chemical gas phase radical quenching (Dufton, 2003; Papazoglou, 2004; L; Kirk-Othmer, 2001; Weil and Levchik, 2009; Laoutid *et al.*, 2009). In this process, high energy hydrogen (H•) and hydroxyl (HO•) radicals formed at the onset and at later stages of PU foam combustion (and which have the potential to propagate radical oxidation reactions of combustion) are effectively removed or quenched by the action of the chlorine radicals above, thus

$$\mathbf{Cl\bullet + H\bullet \rightarrow HCl} \qquad \mathbf{(43)}$$

$$\mathbf{HCl + H\bullet \rightarrow H_2 + Cl\bullet} \qquad \mathbf{(44)}$$

$$\mathbf{HCl + HO\bullet \rightarrow H_2O + Cl\bullet} \qquad \mathbf{(45)}$$

The higher the absorbed HCTD/HCHD concentration, the greater their potential to release chlorine radicals, and the more effective the FR is in gas phase radical quenching.

5.6.3 Effect of HCTD/HCHD blending on flame properties of COPUFs

In Figs 4.46 and 4.47, the treatment of COPUFs with blends of HCTD and HCHD at total FR concentration of 2.4 wt% also enhanced the flammability characteristics (i.e. IT, FPR and AGT) of the COPUFs. Blending of the two FRs in various weight ratios has produced improvements in flammability characteristics compared to those of the untreated COPUFs. However, there was no observable synergism in these characteristics as a result of blending of the two FRs.

5.6.4 Effect of filler loading on flame properties of COPUFs

Table 4.17 and Figs 4.48 and 4.49 show the variation of IT, FPR and AGT with filler ($CaCO_3$) loading. Foam samples show improvement in the flame properties studied, i.e. longer ignition times, shorter flame propagation rates and shorter after-glow times as a result of increased filler loading from 0 - 20 wt%. Indeed, $CaCO_3$ filler is known to enhance the fire retardancy of various PUFs (Singh and Jain, 2008), in addition to enhancement of their load-bearing properties and modulus characteristics (Nunes *et al*., 2000; Chen *et al*., 2002; Latinwo *et al*., 2010). This trend is even more pronounced in the higher NCO/OH ratio of 1/1 in formulation.

Increased filler loading means greater interstitial void filling by highly dispersed inert filler particles across PU foam matrix. Latinwo *et al*. (2010) who studied compositions and particle size distributions on the mechanical properties of flexible PUFs reported among others that finely divided filler material increased the hardness characteristics of the foam to compositions of up to 35 wt%. In filled polymer composites generally, strong interfacial adhesion between filler and polymer is very important. For this to be achieved, the reinforcing filler must be compatible with polymer matrix, and must show strong interaction with matrix at filler-matrix interfaces. Thus, good filler particle dispersion across foam matrix and strong particle-matrix adhesion (either by adsorption, electrostatic attraction, chemical bonding or mechanical adhesion) at interfaces are very important towards attaining enhanced foam mechanical property and fire resistance (Anna *et al*., 2008).

5.7 Morphological Characteristics of COPUFs

SEM analysis (Plates I - XXIII) has shed light on the cellular morphologies and microstructural characteristics of the COPUFs. The foams exhibited wide variation in

pore size (0.10-0.35mm) and shape (mainly spherical, oblong and polyhedral), while wall thicknesses ranged from 18-50μm. The control or neat COPUFs of NCO/OH ratio 1/2 (Plate I) and 1/1 (Plate II) both show a semi-rigid morphology with almost even closed and open cell content, but with the latter exhibiting thicker cell walls and struts. There are also differences in pore shape; the neat COPUF with higher NCO/OH ratio has smaller and more rounded (spherical) pores, while the lower NCO/OH ratio neat COPUF has slightly bigger oblong or polyhedral pores. These differences are as a result of the influence of NCO/OH ratio on the morphology of the COPUFs.

5.7.1 Effect of modifier concentration on the morphology of GMFs

GMF SEM micrographs (Plates III - X) are characterised by decreasing pore size and increasing solid content morphology with increasing modifier concentration from 10 - 60 wt%, confirming the rigid structure and texture of these foams. However, this trend is even more pronounced at the higher NCO/OH ratio of 1/1.

The 60 wt% GMFs (Plates IX and X) show a fibre-like morphology, suggesting heavy network formation due to extensive crosslinking and hydrogen bonding within the PU foam matrix. This is consistent with the reported ability of hard urea domains in COPUFs to undergo self assembly to alter the entire segmented morphology of the foam matrix (Sharma *et al.*, 2014).

5.7.2 Effect of filler concentration on the morphology of CFFs

SEM images for CFFs (NCO/OH ratio 1/1) (Plates XI - XX) depict increasing dispersion of filler particles, but decreasing pore size with increase in filler concentration. Low filler-containing COPUFs (Plates XI and XII) have bigger pores and a more porous or less dense structure. Observed changes in morphology of

COPUFs are because filler incorporation alters foam cellular structure (Zhu *et al*., 2011).

Morphology of the CFFs is generally less rigid than that of the GMFs because of crosslinking reactions in the latter engendered by added hydroxyl functionality via glycerolysis.

5.7.3 Effect of HCTD/HCHD plasticisation on the morphology of COPUFs

The morphologies of plasticised COPUFs of 1/1 NCO/OH ratio (Plates XXI-XXIII) reveal flexible or semi-flexible cellular arrangement comprising large, open - polyhedral cells. Morphology of COPUF plasticised with 50:50 blend (NCO/OH 1/2) of HCTD/HCHD (Plate XXIII) has the most open, evenly distributed cells with large pores, but smaller wall thicknesses.

Table 4.18 descibes the dimensions of foam pores including pore size (PS) or pore diameter (PD) and foam wall thickness (WT) visible in the images of the sections under a Phenom (Pro) scanning electron microscope and their arithmetic means.

CHAPTER SIX

SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1 Summary

In this study, polyurethane foams based on 100% castor oil polyol component were produced using two different formulations with NCO/OH ratios of 1/2 and 1/1 respectively. This avoids the use of mixed polyol (castor oil: conventional polyol) formulations experimented by many researchers with the view of obtaining soft, flexible PU foams needed mainly for cushioning and impact absorption. The mixed polyol formulations were obtained by blending conventional petroleum-based polyether or polyester polyols with varying proportions of castor oil as replacement of the base polyol. This was because neat castor oil and indeed other vegetable oils when used directly as polyol are known to produce rigid or semi-rigid PUFs. However, the mixed polyol recipes were not quite successful as the castor oil proportion needed to produce soft, flexible PUFs was no more than 20-25% (Ogunniyi *et al*., 1998; Ogunfeyitimi *et al*., 2012; Dalen *et al*., 2014). Moreover, in such mixed polyol recipes, the compatibility question between the constituents is a very important one, and could significantly impact on whether or not this goal can be achieved. A 100% castor oil polyol recipe on the other hand, could result in substantial reduction of production cost and the maximal exploitation of castor oil as a renewable bioresource for flexible COPUF production. Effort has been made in this study to obtain flexible COPUFs from 100% castor oil polyol in formulation by *in-situ* plasticisation during foam synthesis using varying weight concentrations (0.4 - 2.4 wt%) of two straight-chain chlorinated paraffin plasticisers (HCTD and HCHD) both as separate, individual plasticisers, and as blends

of different weight ratios. This yielded flexible COPUFs in some instances, and semi-rigid COPUFs in others.

Castor oil for PUF synthesis was extracted from the seeds of Nigerian wild castor plant (*Ricinus communis* Linn) obtained from Katsina, Katsina State, and its determined physico-chemical properties were found to be comparable with ASTM standards and those of general specifications for industrial grade castor oil (WHC, 2012). However, before use, oil was purified and chemically modified by sulphation (using conc. H_2SO_4), chlorination (via substitution using PCl_5) and transesterification/alcoholysis (using glycerol). Physico-chemical and structural characterisations of the modified oils were also carried out using titrimetric methods, as well as FTIR and GC-MS techniques. Sulphation of castor oil produced Turkey-red oil suitable for the production of paints and varnishes (Wiley and Oeitmann, 1991; Ogunniyi, 2006), but unsuitable for PUF production. Alcoholysis (glycerolysis) of castor oil yielded polyols with higher hydroxyl functionality than the control (neat castor oil), while chlorination (by substitution of OH groups) generated polyols poorer in hydroxyl functionality than the control.

Castor oil-based polyurethane foams (COPUFs) of wide ranging structural strengths (rigid, semi-rigid and flexible) were prepared using neat castor oil, as well as PCl_5-modified (or chlorinated) castor oil polyols (PMCOPs) and glycerol-modified (or glycerolysed) castor oil polyols (GMCOPs) containing 10 - 60 wt% of modifier. PMCOPs produced PU foams only at 10 and 20 wt% modifier concentrations, and the foams so produced were found to be coarse, brittle and of poor mechanical integrity, and therefore of little or no practical value. No PU foams were produced with this polyol at modifier concentrations above 20 wt%. This is very likely due to low hydroxyl functionality in the highly chlorinated polyols resulting in low conversion to

PUF, hence the poor foam properties. 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 (Kanner and Decker, 1969; Firdaus, 2011). Treatment of the polyols with 0.4 - 2.4 wt% HCTD/HCHD plasticiser or flame retardant (FR) and 2 - 20 wt% $CaCO_3$ filler at two different NCO/OH ratios of 1/2 and 1/1 yielded COPUFs with unique, wide ranging physico-mechanical and flammability characteristics. Among physico-mechanical properties of the foams studied were cream, free-rise, gel and tack-free times, foam rise, density, water absorption, compressive strength and creep recovery. COPUF synthesis generally involved delayed cream time and less vigour during foaming reaction than PUF synthesis using conventional polyether polyols due to relatively lower hydroxyl numbers compared to the conventional polyether or polyester polyols with hydroxyl numbers as high as 400 – 500mgKOH/g (Narine *et al*., 2007). Foam density ranged from 19.50 - 50.50 Kg/m^3, compressive strength from 48.80 - 450.20 KN/m^2, while creep recovery values were in the range 18.5 - 47.60%.

In-situ plasticisation of COPUFs using HCTD/HCHD has yielded flexible COPUFs especially at the lower NCO/OH ratio of 1/2, and at 50:50 (HCTD: HCHD) weight ratios. These foams exhibited the lowest densities and compressive strengths, but the highest % creep recovery. $CaCO_3$-filled COPUFs have shown improvement in density and compressive strength, but reduction in creep recovery as filler loading was increased from 2 - 20 wt%, compared to the control (neat COPUF). Also, incorporation of HCTD/HCHD as FRs in COPUFs has resulted in improved flame properties such as longer ignition times (ITs), and shorter flame propagation rates (FPRs) and after-glow times (AGTs) compared to those of the neat COPUF. This is particularly significant towards enhancing the fire safety of COPUFs in their various applications as cushioning

and seating materials, packaging materials, insulators in buildings etc. SEM analysis has provided microstructural evidence of the characteristic cellular morphologies of the COPUFs. The control or neat COPUF has a semi-rigid structure, the GMFs a rigid structure, while the CFFs showed a gradually increasing dispersed morphology and stiffness with increasing filler concentration. SEM images for COPUF plasticised with 50:50 blend of HCTD/HCHD reveal large and open cell morphology typical of flexible PU foams.

6.2 Conclusion

This study has investigated the structure-property relationships of castor oil-based polyurethane foams (COPUFs). Physicochemical and structural characterisations of the neat castor oil used and its polyol derivatives (10 - 60 wt% PMCOPs and GMCOPs) using titrimetric, FTIR and GC-MS methods have confirmed the characteristic properties of the oil, and the modification of its structure. Among key physico-chemical characteristics of this oil are high specific gravity, high saponification number, moderately high hydroxyl number, but low iodine and peroxide numbers. The oil's FA composition as confirmed by this study is 74.10% (ricinoleic), 10.32% (linoleic), 7.55% (oleic), 2.81% (stearic), 2.59% (palmitic), 1.70% (erucic) and 0.93% (ecosadienoic). GMCOPs had quantitatively more hydroxyl moiety in their structures than neat CO, while PMCOPs were poorer in hydroxyl moiety than CO. By this, polyols with wide - ranging physico-chemical and structural characteristics were generated for COPUF synthesis.

COPUFs produced were of wide-ranging structural strengths (rigid, semi-rigid and flexible). PMCOP-based PUFs (or PMFs) produced from 10 and 20 wt% PCl_5

concentration were coarse, hard and brittle (irrespective of NCO/OH ratio), and therefore considered of no practical value. Poor foam structure and poor mechanical integrity of the PMFs is attributed to very low conversion to COPUF as a result of low hydroxyl content in PMCOPs. Hydroxyl-rich GMCOPs on the other hand yielded rigid COPUFs whose rigidity increased with higher modifier concentration and NCO/OH ratio. Increased rigidity enhanced foam physico-mechanical properties such as density, moisture resistance and compressive strength, while reducing creep recovery. Foam rigidity adversely limited foam creep recovery, as foam lacked needed resilience to recover its original shape and foam on release of applied force/load. Wide-ranging physico-mechanical properties of the GMFs, as revealed by this study, are potentials of their applicability across the entire utility spectrum of rigid PUFs, especially as insulation, packaging, refrigeration, flotation etc materials. SEM micrographs reveal increasing solid content and closed-cell morphology of the GMFs with increasing modifier concentration and NCO/OH ratio. It is concluded that rigidity in structure of the GMFs is largely due to network formation likely resulting from allophanate and urea crosslinking reactions during foam synthesis.

The use of low concentrations (0.4 - 2.4 wt%) of two straight-chain chlorinated paraffin plasticisers (HCTD and HCHD) individually and as blends (incorporated *in- situ* during COPUF synthesis) as well as the use of low NCO/OH ratios in foam formulation, has yielded soft, flexible foams suitable for cushioning and impact absorption applications. This window could be further explored and exploited to make the production of soft, flexible PUFs from 100% vegetable oil-based polyols an industrial reality.

$CaCO_3$-filled COPUFs have shown improvement in density and compressive strength, but reduction in creep recovery as filler loading was raised from 2 - 20 wt%. SEM images of CFFs show gradually increasing particle-dispersed morphology and stiffness

with increasing filler concentration. Similarly, $CaCO_3$-filling has resulted in marked improvement in flammability characteristics of the CFFs i.e. increased ignition time and reduced flame propagation rate and after-glow time.

On the flammability characteristics of COPUFs, the use of $CaCO_3$ filler and HCTD / HCHD (as flame retardants) has resulted in the enhancement of the fire retardancy characteristics of untreated COPUFs. Higher filler concentration, effective dispersion of filler particles across COPUF matrix and strong filler-matrix interaction and adhesion drastically reduced ignitability and fire spread in the CFFs. Despite low FR concentrations (0.4 - 2.4 wt%) used in this study, FR-treated foams exhibited less ignitability, lower flame propagation rates and shorter after-glow durations, without impairment of the physical properties of the untreated COPUF. FR treatment results indicate HCTD as the more effective FR (than HCHD) based on greater absorbability (higher add-on) during foam synthesis, and its superior fire-retarding ability. Blending HCTD with HCHD achieved improvement in fire retardancy characteristics of the untreated COPUFs, but produced neither synergistic nor antagonistic effects on COPUF flame properties. In order to achieve maximum fire retardancy in this system, blending of HCTD with synergists such as antimony oxides is recommended. Again, despite potential toxicity concerns about halogenated FRs, these compounds are generally very effective, have not been totally prohibited from use, and are still relevant in material fire retardancy.

6.3 Recommendations/Suggestions for further studies

In view of the tremendous potentials and prospects of castor oil in polyurethane (PU) development, continued research on this versatile, renewable resource especially on how to improve its PU products for industrial application is needed on a sustainable

basis. Further, in the light of the experiences and prospects offered by this study, the following specific recommendations are made:

(i) Further research is needed on the flame properties of COPUFs using cone calorimetry, and employing different FR additives (including synergists like Sb_2O_3) of higher concentrations than the ones used in this study.

(ii) Varied internal plasticisers and plasticiser concentrations should be further tested on the COPUF system, towards obtaining soft, flexible PU foams with compressive strength comparable to those of conventional flexible polyurethane foams used for cushioning and impact absorption applications.

(iii) There is need for close collaboration and effective linkage between researchers on PUF development and foam-manufacturing industries to harmonise product quality standards, and to foster commercialisation of research results.

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APPENDICES

Appendix I

Data for the Variation of Compressive Strength of GMFs with wt% Modifier and NCO/OH ratio

	NCO/OH (1/2)			NCO/OH (1/1)		
Pu Foam	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)
GMF - 0	23.6	3.00	65.40	24.3	4.00	87.21
GMF - 10	24.5	3.60	89.20	25.8	4.38	95.50
GMF - 20	26.8	4.80	115.50	26.9	5.50	130.00
GMF - 30	30.4	5.90	128.00	33.5	6.90	150.50
GMF - 40	34.0	9.70	190.70	36.7	11.46	250.00
GMF - 50	39.2	12.40	260.00	44.2	16.54	360.80
GMF - 60	45.8	15.80	330.00	50.5	20.63	450.20

Appendix II

Data for the variation of Compressive Strength of CFFs with wt% Modifier and NCO/OH ratio

	NCO/OH (1/2)			NCO/OH (1/1)		
PU Foam	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)
CFF - 0	23.6	3.00	65.40	65.40	24.3	87.21
CFF - 2	23.62	3.10	66.00	66.00	24.35	89.00
CFF - 4	23.65	3.20	66.50	66.50	24.40	91.20
CFF - 6	23.73	3.20	67.20	67.20	24.46	93.00
CFF - 8	23.80	3.25	68.00	68.00	24.52	94.70
CFF - 10	23.90	3.32	70.10	70.10	24.60	95.90
CFF - 12	24.02	3.41	73.50	73.50	24.68	97.50
CFF - 14	24.10	3.68	80.60	80.60	24.75	99.10
CFF - 16	24.25	3.77	88.40	88.40	24.83	102.60
CFF - 18	24.32	3.85	92.00	92.00	24.92	110.00
CFF - 20	24.50	4.00	100.20	100.20	4.72	118.00

Appendix III

Data for the variation of Compressive Strength of COPUFs with Plasticiser and plasticiser concentration (NCO/OH of 1/2)

% Plasticiser in COPUF	HCTD Plasticised			HCHD Plasticised		
	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)
0	23.60	3.00	65.40	23.60	3.00	65.40
0.4	23.50	3.00	62.20	23.30	2.90	60.00
0.8	23.35	2.80	58.00	22.90	2.70	57.20
1.2	23.10	2.50	55.00	22.40	2.50	54.00
1.6	22.80	2.30	53.50	21.60	2.20	52.00
2.0	22.20	2.20	52.00	20.60	2.11	51.30
2.4	21.45	2.10	51.00	19.80	2.00	50.00

Appendix IV

Data for the variation of Compressive Strength of COPUFs with Plasticiser and plasticiser concentration (NCO/OH of 1/1)

% Plasticiser in COPUF	HCTD Plasticised			HCHD Plasticised		
	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)
0	24.30	4.00	87.21	24.30	4.00	87.21
0.4	24.10	4.00	86.50	24.00	4.00	86.00
0.8	23.90	3.80	85.90	23.90	3.72	85.20
1.2	23.70	3.50	80.20	23.80	3.48	80.00
1.6	23.40	3.20	74.60	23.50	3.00	70.20
2.0	23.00	2.90	69.30	23.20	2.80	65.00
2.4	21.70	2.75	64.10	21.05	2.64	60.00

Appendix V

Data for the variation of Compressive Strength of COPUFs with HCTD/HCHD weight ratios per 2.4 wt% plasticiser and NCO/OH ratio of 1/1.

% Plasticiser in COPUF	HCTD Plasticised			HCHD Plasticised		
	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)	Foam density (Kg/m^3)	Maximum compressive load (KN)	Compressive strength (KN/m^2)
0/2.4	19.80	2.00	50.00	21.05	2.07	50.90
0.4/2.0	20.05	2.00	50.20	21.15	2.08	51.00
0.8/1.6	20.08	2.00	50.30	21.10	2.08	50.95
1.2/1.2	19.05	1.95	48.80	21.00	2.07	50.90
1.6/0.8	20.10	2.02	50.40	21.30	2.15	51.40
2.0/0.4	20.80	2.08	50.85	21.60	2.28	52.50
2.4/0	21.45	2.10	51.80	21.70	2.32	53.80

Appendix VI

Data for the Variation of Compressive Strength of COPUFS with hydroxyl value of GMF polyol and NCO/OH ratio.

PU foam	Hydroxyl value of polyol (mg KOH/g)	NCO/OH (1/2)		NCO/OH (1/1)	
		Maximum compressive load (KN)	Compressive strength (KN/m^2)	Foam density (Kg/m^3)	Compressive strength (KN/m^2)
GMF - 0	20	3.00	65.40	4.00	87.21
GMF - 10	20	3.60	89.20	4.38	95.50
GMF - 20	20	4.80	115.50	5.50	130.00
GMF - 30	20	5.90	128.00	6.90	150.50
GMF - 40	20	9.70	190.70	11.46	250.00
GMF - 50	20	12.40	260.00	16.54	360.80
GMF - 60	20	15.80	330.00	20.63	450.20

Appendix VII

Data for the variation of Creep recovery of GMFs with modifier concentration and NCO/OH ratio.

PU foam	Applied load (N)	NCO/OH (1/2)	NCO/OH (1/1)
		Creep recovery (%)	Creep recovery (%)
GMF - 0	20	38.00	30.40
GMF - 10	20	28.50	23.40
GMF - 20	20	25.20	21.90
GMF - 30	20	23.90	21.00
GMF - 40	20	22.20	20.50
GMF - 50	20	21.40	19.30
GMF - 60	20	20.00	18.50

Appendix VIII

Data for the variation of Creep recovery of CFFs with wt% $CaCO_3$ filler and NCO/OH ratio.

PU foam	Applied load (N)	NCO/OH (1/2)	NCO/OH (1/1)
		Creep recovery (%)	Creep recovery (%)
CFF - 0	20	38.00	30.40
CFF - 2	20	36.20	29.80
CFF - 4	20	35.00	29.20
CFF - 6	20	32.90	28.50
CFF - 8	20	30.00	27.70
CFF - 10	20	29.30	26.30
CFF - 12	20	28.90	25.60
CFF - 14	20	27.20	24.40
CFF - 16	20	26.80	23.60
CFF - 18	20	26.20	22.90
CFF - 20	20	26.00	22.50

Appendix IX

Data for the variation of Creep recovery of COPUFs (NCO/OH of 1/2) with plasticiser and plasticiser concentration.

% Plasticiser in COPUF	Applied load (N)	HCTD Plasticised	HCHD Plasticised
		Creep recovery (%)	Creep recovery (%)
0	20	38.00	38.00
0.4	20	38.00	38.20
0.8	20	40.50	42.30
1.2	20	41.60	43.80
1.6	20	42.70	44.80
2.0	20	43.50	46.10
2.4	20	44.20	47.60

Appendix X

Data for the variation of Creep recovery of COPUFs (NCO/OH of 1/1) with plasticiser and plasticiser concentration.

% Plasticiser in COPUF	Applied load (N)	HCTD Plasticised	HCHD Plasticised
		Creep recovery (%)	Creep recovery (%)
0	20	30.40	30.40
0.4	20	30.50	30.60
0.8	20	31.30	32.20
1.2	20	32.50	33.90
1.6	20	33.20	35.40
2.0	20	35.10	36.50
2.4	20	35.00	37.60

Appendix XI

Data for the variation of Creep recovery of COPUFs with HCTD/HCTD weight ratios and NCO/OH.

HCTD/HCHD Wt. ratios per 2.4wt% plasticiser	Applied load (N)	NCO/OH (1/2) Creep recovery (%)	NCO/OH (1/1) Creep recovery (%)
0/2.4	20	47.60	37.60
0.4/2.0	20	47.00	37.10
0.8/1.6	20	46.30	36.50
1.2/1.2	20	45.80	36.10
1.6/0.8	20	45.20	35.70
2.0/0.4	20	44.70	35.30
2.4/0	20	44.20	35.00

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