CHAPTER I
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INTRODUCTION

Polymer chemistry is the chemistry of giant molecules. This includes the synthesis, characterisation and physical chemistry of organic polymers. Polymers are a large class of materials consisting of many small molecules that can be linked together to form long chains. Natural and synthetic polymers can be produced with a wide range of stiffness, strength, heat resistance, density, etc. With continued research into the science and applications of polymers, they are playing an ever increasing role in society.

In recent days, the utilization of raw materials derived from renewable feedstock is in spotlight of the chemical industry. Natural oils are considered to be the most important class of renewable resources due to their universal availability, inherent biodegradability and low price. Renewable resources are recently gaining a lot of attention as a substitute of petroleum for producing polymers on a low-cost performance basis with high eco-friendliness values. Polymers are obtained from renewable resources such as starch, lignin, protein, cellulose, chitosan, shellac, rosin, alginate, wool fibres and vegetable oils. They find innumerable industrial applications such as plasticizers, biodiesel, lubricants, adhesives, biodegradable packaging materials, printing inks, paints and coatings. Depending on their usage area, they exhibit some specific properties such as high strength, lightweight, thermal stability, flexibility and resistance to chemicals, gas permeability, electrical conductivity, non-flammability, biocompatibility and biodegradability.
Natural fibres have received great interest as reinforcing material for polymer-based matrices because of the environmental issues in combination with their low cost and some intrinsic properties include density, shape ratio and mechanical behaviour. The incorporation of low cost natural fibres into polymeric matrices widens the use of these materials to new different applications. Thus, the new trend in the polymer composite industry and academy is the search for alternative products that can be prepared from renewable resources, offering also the possibility to decompose by biodegradation.

1.1 Natural oils

Natural oils derived from both plant and animal sources make up a large proportion of the current consumption of renewable raw materials. Therefore, preparation of polymeric materials from renewable resources is of great economic and ecological significance\(^1,2\). Natural oils have excellent properties that can be used to produce valuable polymeric materials such as epoxy resins, polyurethanes, biocomposites and nanocomposites. It ranges from soft rubbery materials to ductile or rigid plastics and to high-performance biocomposites and nanocomposites\(^3,4\). Natural oils can be received from naturally occurring plants such as linseed, sunflower, soybean, castor, etc. It consists predominantly of triglycerides\(^5-7\). Because they are relatively unreactive, they must be functionalized to serve as building blocks for polymers. Introduction of hydroxyl groups at the position of double bonds opens the whole area of applications in polyurethanes. If the triglyceride structures were preserved, polyols usually would have functionality greater than two, giving with diisocyanates thermosetting polyurethane networks\(^8\).
1.2 Cashew Nut Shell Liquid (CNSL)

The cashew tree (*Anacardium occidentale* L.) is a native of Brazil and the Lower Amazons\(^9\). The tree is mostly grown in India and East Africa\(^{10}\). The tree consists of the cashew apple, cashew nut, leaf and bark (Fig 1.1). The cashew apple is a pseudofruit because it is only the swollen stalk of the true fruit and it is bright yellow or red in colour. The true fruit is the cashew nut. The nut has two walls or shells, the outer one being smooth and somewhat elastic and green in colour before maturity. The honeycomb is housed between the inner and outer shells. The kernel is present inside the shell and covered with a brown skin known as testa is shown in Fig 1.2. Cashew nut shell liquid occurs as a reddish brown viscous liquid in the soft honeycomb structure of cashew nut shell\(^{11-13}\).

![Fig 1.1](Anacardium_occidentale_L.jpg)

*Fig 1.1*  
*Anacardium occidentale* L.
CNSL is obtained as an agricultural byproduct of the cashew industry. The main constituents of CNSL are phenolic compounds with long side chain substitution at meta position. These compounds give most of the reactions of phenol and can be the basis for producing a number of polymeric substances of wide utility in industrial applications.

1.2.1 Constituents of CNSL

On the basis of the mode of extraction from cashew nut shell, CNSL is classified into two types, solvent-extracted CNSL and technical CNSL. A typical solvent-extracted CNSL contains anacardic acid, cardol, cardanol and traces of 2-methyl cardol. Table1.1 shows the typical chemical composition of CNSL. Technical CNSL is obtained by roasting shells at 180-200°C. The anacardic acid is thermally unstable and easily decarboxylated during the extraction process and transformed into cardanol. Thus technical CNSL contains mainly cardanol (60-65%), cardol (15-20%), polymeric material (10%) and traces of 2-methyl cardol. Depending on the condition of the roasting processes, the composition of technical CNSL can change and reach higher cardanol content (83-84%), less
cardol (8-11%) and maintaining polymeric material as 10% and 2-methyl cardol content as 2%. Each component phenol contains saturated, monoene, diene and triene constituents. The industrial significance of CNSL are its use in producing low cost phenol, possibilities in the development of high performance polymers, versatility in polymerization and chemical modification and good impact resistance, flexibility etc.\textsuperscript{20-28} The properties of cashew nut shell and Indian Standard (IS) Specification for CNSL (IS: 840-1964) are shown in Table 1.2.

### Table 1.1

**Typical chemical composition of CNSL**

<table>
<thead>
<tr>
<th>Component</th>
<th>Content in CNSL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anacardic acid (1)</td>
<td>60-65</td>
</tr>
<tr>
<td>Cardol (2)</td>
<td>15-20</td>
</tr>
<tr>
<td>Cardanol (3)</td>
<td>10</td>
</tr>
<tr>
<td>2-methyl cardol (4)</td>
<td>Traces</td>
</tr>
</tbody>
</table>
Where,

\[ n = 0, 2, 4 \text{ or } 6 \]
Table 1.2
Indian Standard Specification for CNSL (IS: 840-1964)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Properties</th>
<th>Specified values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Colour</td>
<td>Smoky and mild phenolic</td>
</tr>
<tr>
<td>2.</td>
<td>Specific gravity g/cc at 30°C</td>
<td>0.950 - 0.970</td>
</tr>
<tr>
<td>3.</td>
<td>Viscosity at 30°C (cps)</td>
<td>550</td>
</tr>
<tr>
<td>4.</td>
<td>Moisture content (% by weight)</td>
<td>1.0</td>
</tr>
<tr>
<td>5.</td>
<td>Matter insoluble in toluene (% by weight)</td>
<td>1.0</td>
</tr>
<tr>
<td>6.</td>
<td>Loss in weight on heating (% by weight)</td>
<td>2.0</td>
</tr>
<tr>
<td>7.</td>
<td>Ash content (% by weight)</td>
<td>1.0</td>
</tr>
<tr>
<td>8.</td>
<td>Iodine value (Wij’s method)</td>
<td>250</td>
</tr>
</tbody>
</table>

1.3 Applications of CNSL

CNSL has innumerable applications in polymer-based industries such as phenolic resins, epoxy resins, friction materials, brake linings, rubber compounding, etc.

1.3.1 Phenolic resins

CNSL is used in the manufacture of special phenolic resins for coatings, lamination and as friction materials. Phenolic resins are the synthetic polymers often referred to as phenol-formaldehyde condensation polymers and they have a wide range of applications, from commodity and construction materials to high technology aerospace industry.
1.3.2 Epoxy resins

CNSL can be used as a low-cost curing agent for epoxy resin\textsuperscript{32}. Epoxy resins are a class of important thermosetting materials, which have been extensively used as adhesive in the aerospace and surface coatings industries, electronic encapsulating materials\textsuperscript{33} and as matrices in reinforced composites because of their high performance including excellent thermal and mechanical properties\textsuperscript{34}.

1.3.3 Friction materials

CNSL resin is known to increase friction properties of the base thermoset resin which otherwise has a hard smooth finish and also makes it abrasion resistant\textsuperscript{35}. The friction material plays essential roles in various aspects of the brake performance such as counter disk wear, pedal feel, stopping distance and brake induced vibrations\textsuperscript{36}.

1.3.4 Brake linings

CNSL contains high proportions of phenolic compounds which are used in the manufacture of brake lining compounds. Brake linings have the property of absorbing the heat generated by friction in the braking action while retaining their braking efficiency longer\textsuperscript{37}.

1.3.5 Rubber compounding

CNSL could be adopted as alternatives to plasticizers in rubber compounds\textsuperscript{38}. The use of CNSL in rubber compositions has been found to improve the performance of rubber products. It helps in processing and enhances the vulcanisation properties.
1.3.6 Medicinal applications

Chlorinated and copperised CNSL found to have pesticidal effects on insects and fungi\(^39\). CNSL by itself is useful as an anti-termite\(^40\). CNSL exhibits potent antibacterial activity against gram-positive and weak antifungal activity against molds. Traditionally, it is used to treat ailments such as scurvy, sores, warts, ringworm and psoriasis\(^41\).

1.3.7 Miscellaneous applications

The applications of various derivatives of CNSL are used for plastic materials, additives, polyurethane-based polymers, surfactants and wood preservative\(^42\)\(^-\)\(^44\). The resins from CNSL are used in laminating for papers, cloths and glass fibres, or impregnating materials where oil or acid resistance is required. Other uses include the manufacture of lacquers, printing inks, electrical insulation material, water proofing compounds and anti-corrosive for metals\(^45\).

1.4 Cardanol

Cardanol is a phenolic compound with a C\(_{15}\) unsaturated aliphatic side chain in the meta position\(^46\) obtained from cashew nut shell liquid\(^47\). The aliphatic chain usually consists of mixtures one, two and three double bonds in a linear chain with saturated 5.4\%, monoolefin 48.5\%, diolefin 16.8\% and triolefin 29.3\%\(^48\). That confers attractive properties to cardanol derivatives such as good processability and high solubility in organic solvents but, also the possibility to influence many chemical transformations introducing novel functionalities\(^49\). Cardanol and its derivate are examples of such compounds and present significant antioxidant characteristics, being applied for lubricants, polymers and rubber industries, in addition to like antifungal, antibacterial and antitumor products\(^50\)\(^-\)\(^55\). Polymers from
cardanol are prepared either by condensation with active hydrogen-containing compounds such as formaldehyde, or by chain-reaction polymerization through the unsaturation in the side chain using acid catalysts or functionalization at the hydroxyl group and subsequently oligomerization to get functionalized prepolymer. The resulting prepolymer acts as a multifunctional additive.\textsuperscript{56}

### 1.4.1 Applications of Cardanol

It is a commonly available component which has been used in many applications such as paints and varnishes, foundry core oil, phenol-formaldehyde resins, polymers with surface activity and distilled cardanol for epoxy resins. They are used in the manufacture of special phenolic resins for adhesives, lamination and as friction materials.\textsuperscript{57-59} It has been used in the preparation of different materials such as cross-linkable polyphenols, nanotubes, liquid crystalline polyesters and a range of other specialty polymers and additives.\textsuperscript{60-68} Cardanol based polymers have wide applications in polyurethanes, composites and surface coatings.\textsuperscript{69-72}

### 1.5 Castor oil

The plant from which the castor oil is extracted can be found throughout the world, is mainly explored in Brazil and India (Fig 1.3). Castor oil is obtained from the seeds of castor plant (\textit{Ricinus communis} L.) by pressing and solvent extraction as shown in Fig 1.4. It constitutes approximately 90\% of triglycerides of ricinoleic acid (12-hydroxy-\textit{cis}-octadec-9-enoic acid). This aliphatic carboxylic acid presents an 18-carbon chain, having a double bond between carbon 9 and 10 and a hydroxyl group on the C-12. Owing to the presence of a hydroxyl group at C-12, castor oil possesses several unique chemical and physical properties. Castor oil (5) is a low-
cost, abundantly available and renewable raw material. It is clear, almost colourless or pale yellow coloured viscous oil. As a vegetable oil with reactive hydroxyl functional groups, it can be used as a polyol to develop new and “green” macromolecular architectures\textsuperscript{73-75}. The percentage of fatty acids present in castor oil is shown in Table 1.3\textsuperscript{76,77}.

Fig 1.3

\textit{Ricinus communis} L.

Fig 1.4

Seeds of \textit{Ricinus communis}
Table 1.3
Percentage of fatty acids

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ricinoleic acid (6)</td>
<td>89.5</td>
</tr>
<tr>
<td>Linoleic acid (7)</td>
<td>4.2</td>
</tr>
<tr>
<td>Oleic acid (8)</td>
<td>3.0</td>
</tr>
<tr>
<td>Stearic acid (9)</td>
<td>1.0</td>
</tr>
<tr>
<td>Palmitic acid (10)</td>
<td>1.0</td>
</tr>
<tr>
<td>Dihydroxystearic acid (11)</td>
<td>0.7</td>
</tr>
<tr>
<td>Eicosanoic acid (12)</td>
<td>0.3</td>
</tr>
<tr>
<td>Linolenic acid (13)</td>
<td>0.3</td>
</tr>
</tbody>
</table>
1.5.1 Applications of Castor oil

Castor oil has found applications in various industries including the production of plastics, skin moisturisers (including lotions for solar burnings and dermatitis), cosmetics, fungicides, textile, lubricants, contraceptive gels, herbal preparations for labour stimulation, systems of drug controlled release and
encapsulating compounds. When dehydrated, it is converted into a fast drying oil widely applied in paints and varnishes. Its high water resistance makes it ideal for the use in all types of wrappings and packages for the food industry\textsuperscript{78-83}.

It has been also used in isocyanate reactions to make polyurethane elastomers, castable polyurethanes, polyurethane foams and polyurethane adhesives\textsuperscript{84-88}. Castor oil has also found application as a softener and as a raw material source for polyamides\textsuperscript{89}.

1.6 Polyurethanes

Polyurethanes (PUs) are polymeric materials varying from thermoplastic to thermosetting plastics\textsuperscript{90}, which are the reaction products of diisocyanates (aromatic and aliphatic) with hydroxyl-containing materials such as oils, fabrics or with partial glycerides prepared from oil and glycerol\textsuperscript{91}. PUs is characterised by the presence of urethane linkages (14) in their repeat units:

\[
\begin{array}{c}
\text{O} \quad \text{H} \\
\text{H} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{H} \\
\text{C} - \text{N} - \text{R} \rightarrow \text{N} - \text{C} - \text{O} - \text{R} \rightarrow \text{O} \\
\end{array}
\]

(14)

The flexibility of PUs was increased by the presence of additional oxygen in the chain\textsuperscript{92}. PUs consists of alternating hard and soft segments, the hard segment being the isocyanate with a macroglycol soft segment. These segments are reacted together to form units which are then linked by other molecules known as chain extenders. By varying the constituent parts of the polymer, PUs exhibit versatile properties in all fields of polymer applications\textsuperscript{93,94}. 

14
Achary et al.\textsuperscript{95} reported the new biobased polymer blends were synthesised from polyurethanes which are derived from glycerol modified linseed oil and diphenyl methane-4,4’-diisocyanate and cardanol based dyes with aminophenols. Corcuera et al.\textsuperscript{96} synthesised novel segmented polyurethanes with a high percentage of components derived from castor oil and different chain extenders, petrochemical-based 1,4-butanediol and corn sugar-based 1,3-propanediol. Polyurethanes based polymers were obtained by mixing castor oil as polyl to diisocyanate at different NCO/OH ratios have been studied by Santos et al.\textsuperscript{97}.

Polyurethane films for biomedical applications were prepared from poly(ethylene glycol) with different molecular weight (PEG 1500, 3000 and 8000) and castor oil by one-shot bulk polymerization method using hexamethylene diisocyanate and 1,4-butane diol as chain extender have been investigated by Bonfil et al.\textsuperscript{98}. Medical grade polyurethane film based on castor oil without any additives has been developed by Najafabadi et al.\textsuperscript{99}.

1.6.1 Applications of polyurethanes

Polyurethane products are used everywhere in people’s daily lives and in engineering applications such as automobiles, industries, structural materials, insulations, packaging and footwear, as a result there is an increase in consumption worldwide\textsuperscript{100-102}. They have advantages such as excellent mechanical properties, good biocompatibility, design flexibility, light weight and low cost, possessing applications such as sealants and composites\textsuperscript{103}. Polyurethanes can be classified as rigid, flexible, foams, elastomers, adhesives and coatings\textsuperscript{104}. 

1.6.2 Rigid and Flexible Polyurethanes

Rigid polyurethanes has many desirable properties such as low thermal conductivity, low density, excellent dimensional stability, high strength-to-weight ratio, low moisture permeability and low water absorption. So, it is suitable for the application in household refrigerators, construction and industrial insulation, flotation in boats, life preservers, buoys and other marine equipment\(^{105}\). The flexibility of polyurethane chemistry translates into substantial flexibility in terms of polyurethane polymer\(^{106}\). They are industrially important materials with widespread use in household furniture and car seat\(^{107,108}\).

Rigid polyurethanes synthesised using hydroxyalkylated cardanol-formaldehyde resins and 4,4'-dicyclohexylmethane diisocyanate have been investigated by Sathiyalekshmi \textit{et al.}\(^{109}\). Hard and soft polyurethanes developed by treating cardanol-furfural resin with toluene diisocyanate, keeping the isocyanate index (NCO/OH mole ratio) constant at 1.4 have been reported by Gopalakrishnan \textit{et al.}\(^{110}\).

1.6.3 Polyurethane Foams

Polyurethane foams are low-density cellular polyurethane materials with limited and reversible resistance to compression. Proper selection of catalyst formulation in the preparation of polyurethane foams influences the properties which are required for a number of applications in upholstery for furniture, bedding, mattresses, transportation seating and also used in every type of vehicles including automobiles, from buses to aircrafts\(^{111,112}\). They have wide applications traditionally in furniture, packaging, footwear and thermal insulation\(^{113}\).
Ayo et al.\textsuperscript{114} observed the performance analysis of castor oil-based polyurethane foam using toluene diisocyanate in comparison with the conventional polyol based foam. The effects of matrix mixing on the properties of castor oil-based polyurethane foams using toluene diisocyanate have been studied by Adogbo and Atiwurca\textsuperscript{115}.

### 1.6.4 Polyurethane Elastomers

Polyurethane elastomer is a linear segmented block composed of hard and soft segments. The soft segment polyurethane is aliphatic polyester polyols or aliphatic polyether polyols are coupled with hard segment formed from aromatic diisocyanates and hard diols urethane linkages\textsuperscript{116}. It is used for very wide number of applications due to their high strength with high hardness and high modulus plus high elongation at break\textsuperscript{117}.

Ghatge and Phadke\textsuperscript{118} reported the castor oil has been used to synthesis milliable polyurethane elastomers using 2,4-toluene diisocyanate, 4,4’-diphenylmethane diisocyanate and 1,5-naphthalene diisocyanate respectively. Millable polyurethane elastomers based on difunctional castor oil and poly(propylene glycol), 2,4-toluene diisocyanate and 1,4-butane diol were synthesised by Yeganeh and Mehdizadeh\textsuperscript{119}.

Polyurethane elastomers from castor oil based polyol, polyethylene glycol of various molecular weight (200, 400 and 600) and toluene diisocyanate were prepared in the form of transparent sheets have been reported by Bharadwaj et al.\textsuperscript{120}. Segmented polyurethane elastomers based on a mixture of castor oil and poly(propylene glycol), 4,4’-diphenylmethane diisocyanate and 1,4-butandiol were prepared by Saxena et al.\textsuperscript{121}.
Petrovic and Fajnik\textsuperscript{122} synthesised polyurethane elastomers using diphenylmethane diisocyanate and castor oil as the polyol. Polyurethane elastomers obtained by reacting poly(1,4-butanediol) using aliphatic 1,6-hexamethylene diisocyanate and castor oil as a trifunctional crosslinker at stoichiometric ratios have been investigated by Oprea\textsuperscript{123}.

1.6.5 Polyurethane Adhesives

Polyurethane adhesives can be prepared as single or multi-component and the former are the moisture-curing or hot melt types in which reactive groups exposed to air moisture react to crosslink the structure and the latter being the components must be mixed prior to use and one of the components is usually a prepolymer. Since polyurethane adhesives cure rapidly at room temperature, they are used in many areas such as transport, building, packing, goods and furniture industries.

Castor oil-based polyurethane adhesives prepared with different NCO/OH molar ratios were applied to two different substrates, wood-wood and foam-foam joints have been reported by Silva \textit{et al.}\textsuperscript{124}. Biomaterial based novel polyurethane adhesives for wood to wood and metal to metal bonding from castor oil-based polyols, polyester polyols and epoxy based polyols with isocyanate adducts has been developed by Patel \textit{et al.}\textsuperscript{125}.

Hong-Quan and Jun-Shi\textsuperscript{126}, Somani \textit{et al.}\textsuperscript{127} studied the NCO/OH molar ratio and the mechanical property relationships of castor oil-based PU adhesives with solvents exhibited an increase in the NCO/OH molar ratio up to 2.0 increases the chain crosslink density, which improves the adhesive bond strength. Azambuja and
Dias\textsuperscript{128} investigated the use of castor oil-based polyurethane adhesive in the production of glued laminated timber beams.

1.6.6 Polyurethane Coatings

Polyurethane coatings are based on polymers which contain two or more urethane groups per molecule\textsuperscript{129}. They have suitable properties such as high adhesion, high resistance to corrosion especially microbial corrosion, flexibility, very good friction and stroke resistance, high chemical resistance and good resistance in high temperature, have various applications in transitional water tanks, external surface of urban pipes, internal surface of swedge pipes, internal surface of carrying limy and abrasive solution, mobile concrete coating and upper ground pipes coating\textsuperscript{130}.

Thakur and Karak\textsuperscript{131} developed polyurethanes as advanced surface coating materials from castor oil and toluene diisocyanate using simple polymerization technique. Polyurethane coating from castor oil and toluene diisocyanate was transformed into an antimicrobial coating by covalently attaching monomethylol hydantoin, a potential N-halamine derivative with regenerable antimicrobial properties have been studied by Bisquera and Sumera\textsuperscript{132}. High solids polyurethane coatings were developed by reacting three different castor oil-based polyester-polyols with aromatic as well as aliphatic isocyanate adducts in different NCO/OH ratios have been reported by Somani et al.\textsuperscript{133}.

1.6.7 Biomedical Applications of Polyurethanes

Polyurethanes find applications especially in the biomedical field which include synthesis of catheters of wide range, cardiovascular devices, artificial ducts, artificial heart valves, contraceptives and pacemaker lead insulation\textsuperscript{134-140}.
PUs appear to be an ideal for use in vascular grafts\textsuperscript{141} with excellent blood and tissue biocompatibility combined with good compliance characteristics, self-sealing properties, relatively good strength and an attractive surface for endothelial cell seeding\textsuperscript{142,143}. They have the properties such as durability, elasticity, elastomer-like character, fatigue resistance, compliance and acceptance or tolerance in the body during the healing, became often associated with polyurethanes\textsuperscript{144}.

1.7 Natural fibres

In the last decade, there is a growing interest in natural fibre-reinforced composites because of their high performance in terms of mechanical properties, significant processing advantages, chemical resistance and low density ratio\textsuperscript{145-147}. The natural fibres can be used to reinforce both thermosetting and thermoplastic matrices\textsuperscript{148}. They are more environmental friendly and completely biodegradable. Thus it can play a key role in the emerging “Green Composites”\textsuperscript{149}. Natural fibre composites include baggase, bamboo, jute, cotton, pineapple, banana, oil palm, sisal, coir, flax, hemp and remi\textsuperscript{150-157}. All these fibres are grown as agricultural plants in various parts of the world such as India, Sri Lanka, Thailand, Indonesia, Bangladesh, Philippines, Brazil, China and South Africa. They are commonly used for making bags, carpet backing, ropes, etc. The components of natural fibres are cellulose microfibrils spread in an amorphous matrix of lignin and hemicelluloses\textsuperscript{158,159}. The products obtained from these fibres have low-cost, increased impact strength and other mechanical properties such as tensile strength, percentage elongation, tear strength and hardness\textsuperscript{160}. They are used as reinforcing agents in plastic materials and have many substantial advantages over synthetic
fibres. Still, incorporation of fibres will form elastomeric composites exhibit combined behaviour of soft, elastic rubber matrix and firmly strong fibrous reinforcement.

1.7.1 Classification of natural fibres

Fibres are the principal constituents in a fibre-reinforced composite material. They occupy the largest volume fraction in a composite and share the major portion of the load acting on a composite structure. Natural fibres include those made from plant, animal and mineral sources. They can be classified according to their origin as: plant fibres, animal fibres and mineral fibres.

1.7.2 Plant fibres

Plant fibres are generally comprised mainly of cellulose such as cotton, jute, flax, ramie, sisal, coir and hemp. This fibre can be further categorized into the following:

(a) Stem fibre

Fibres are collected from the skin or bast surrounding the stem of their respective plant. These fibres have higher tensile strength than other fibres. Therefore, these fibres are used for durable yarn and fabric some examples are flax, jute, banana, hemp, kenaf and ramie.

(b) Leaf fibre

Fibres are collected from the leaves including sisal, abaca, pineapple, fique, henequen and palm.

(c) Seed fibre

Fibre is collected from the seed, e.g. cotton.
(d) Fruit fibre

Fruit fibre is collected from the fruit of the plant, e.g. coconut (coir) fibre.

(e) Stalk fibre

Fibres are actually the stalks of the plant such as straws of wheat, rice, barley and other crops including bamboo and grass. Tree wood is also such a fibre.

1.7.3 Animal fibres

Animal fibre generally comprises proteins. It is taken from animals or hairy mammals including goat hair, alpaca hair, horse hair, silk and wool.

1.7.4 Mineral fibres

Mineral fibres are naturally occurring fibre or slightly modified fibre procured from minerals. These can be further categorized into the following categories:

(a) Asbestos

Asbestos is the only naturally occurring mineral fibres. They include serpentine and amphiboles, anthophyllite.

(b) Ceramic fibre

Ceramic fibres include glass fibres (glass wood and quartz), aluminum oxide, silicon carbide, and boron carbide.

(c) Metal fibre

The example of metal fibre: aluminum fibre.

1.7.5 Applications of Natural Fibres

The use of natural fibres as a reinforcement in a cement matrix has also been practised for making low cost building materials such as panels, claddings, roofing sheets and tiles, slabs and beams166.
1.8 Polyurethane Composites

Composites are hybrid materials made of a polymer resin reinforced by fibres, combining the high mechanical and physical characters of the fibres\textsuperscript{167}. Nowadays, the fibres resulting from wood, animals, leaves, grasses and other natural sources are commonly used as reinforcement in composites used for various applications such as automotive (interior and exterior), ship, etc., due to their unusual properties compared to other synthetic fibres\textsuperscript{168}.

Calo \textit{et al.}\textsuperscript{169} synthesised cardanol based matrix biocomposites in combination with cellulose based materials such as jute fibres. Flexural behaviour of castor oil-based polyurethane composites using sisal fibre has been studied by Milanese \textit{et al.}\textsuperscript{170}. Influence of fibre surface treatment and length on physico-chemical properties of short random banana fibre-reinforced castor oil polyurethane composites has been developed by Merlini \textit{et al.}\textsuperscript{171}.

Frollini \textit{et al.}\textsuperscript{172} explained the use of castor oil and sodium lignosulfonate glutaraldehyde to prepare polyurethane composites which resulted with high impact strength. Polyurethane composites derived from castor oil-based polyol (castor oil by alcoholysis with triethanolamine) and wood flour has been studied by Mosiewicki \textit{et al.}\textsuperscript{173} as wood flour content increased then compression modulus and yield strength decrease. Ahmed\textsuperscript{174} and Azmi \textit{et al.}\textsuperscript{175} investigated the polyurethane composites based on glass and coconut coir fibres respectively.

New composites based on castor oil with isophorone diisocyanate polyurethanes and cellulose fibres extracted from Alfa plant with different cellulose contents (5, 10, 15, 20, 30 and 40 wt\%) have been reported by Ganetri \textit{et al.}\textsuperscript{176}. Microcellular polyurethane composites reinforced with pine
wood-fibres or with hemp, which can be applied to the manufacture of car interior panels, or acoustic insulation panels for the construction industry were prepared by Aranguren et al.\textsuperscript{177}. Particulate composite based on coconut fibre and castor oil polyurethane adhesive presented sufficient mechanical properties for use in civil and agricultural constructions, besides its use in homes, farm buildings and structural applications has been explained by Fiorelli et al.\textsuperscript{178}.

1.8.1 Applications of Polyurethane Composites

Polyurethane composites have good wear resistance and excellent mechanical properties and it is easy to adjust their hardness by changing the ratio of hard and soft segments. As a result, they are an important class of materials for structural and tribological applications that is, to do with interactions of moving surfaces such as friction or lubrication.

They are used in a wide range of applications areas such as bearings, gears, aerospace, automobiles, construction, biomedical, commercial and domestic sectors including sports industry, household appliances, packaging, etc.\textsuperscript{179-182}.

1.9 Polyurethane Nanocomposites

Nanocomposites are combinations of two or more materials present as separate phases where one of the phases has at least one dimension in the nanometer range ($10^{-9}$ m). They are combined to form desired structures with certain desirable properties of each component. The main advantages are low weight, high specific strength and stiffness, environmental resistance and long shelf-life\textsuperscript{183,184}.

Polyurethane nanocomposites prepared from castor oil with organically modified layered-silicates (organoclays) showed a higher improvement of tensile
modulus with better dispersion and intercalation of the nanoparticles in a polymer matrix have been reported by Swagatika et al.\textsuperscript{185}. Pradhan and Nayak\textsuperscript{186} synthesised polyurethane nanocomposites from castor oil using hexamethylene diisocyanate and modified clay exhibited that the nanocrystals become pseudosperical and the size increases or decreases depending on diisocyanate concentration.

Kaushik \textit{et al.}\textsuperscript{187} investigated a series of 1,4-butane diol chain extended polyurethane nanocomposites based on castor oil, 4,4-diphenylmethane diisocyanate with modified clay (Cloisite 30B) as a filler. Polyurethane nanocomposites by mixing polypropylene glycol polyol and dehydrated castor oil (15\%), enforced with C30B nanofillers at different weight percentages depicted an improvement of \textasciitilde240\% in tensile strength and decrease of \textasciitilde30\% in elongation with 5 wt. \% organoclay respectively have been investigated by Alaa \textit{et al.}\textsuperscript{188}.

\textbf{1.9.1 Applications of Polyurethane Nanocomposites}

The primary application of nanocomposites is used in food packaging systems. Some particles can have multiple applications such as immobilized enzymes which can act as antimicrobial components, oxygen scavengers and biosensors\textsuperscript{189}.

\textbf{1.10 Scope of the Present Investigation}

Current and future development in biodegradable polymers and renewable input materials focus relate mainly to the scaling up of production and improvement of product properties. Renewable resource is an organic natural resource which can replenish to overcome usage and consumption, either through biological reproduction or other naturally recurring processes. Among the
renewable resources, cashew nut shell liquid (CNSL), obtained as a byproduct of the cashew industry, it contains a natural phenolic distillate, cardanol. It has been found that cardanol and castor oil have interesting structural features for chemical modification and polymerization into specialty polymers.

Polyurethanes (PUs) are important polymeric materials formed through the polyaddition reaction between organic isocyanates and compounds containing hydroxyl groups. Polyurethanes play a major role in construction, flexible packaging, footwear, synthetic leather and automotive industry. The development of advanced polymer composite materials based on natural fibre such as coir fibres have improved properties such as corrosion resistance, electrical insulation, easy processability at relatively less energy requirement in tooling and assembly costs, higher stiffness and strength, fatigue resistance. They are widely used in structural applications because of their excellent mechanical properties.

1.11 Objectives of the Present Investigation

The main objectives of the present investigation are

- to synthesise and characterise cardanol-formaldehyde novolac and resole resins.
- to synthesise and characterise polyols from cardanol-formaldehyde novolac and resole resins.
- to synthesise and characterise glycol-glycoside from corn starch and ethylene glycol.
- to synthesise and characterise rigid and tough polyurethanes and its composites based on cardanol-formaldehyde resins and polyols.
- to synthesise and characterise castor oil based-polyurethanes and its composites.
- to synthesise and characterise chain extended polyurethanes and its composites from castor oil using chain extender.
- to synthesise and characterise polyurethanes and its composites based on glycol-glycoside.
- to evaluate the material properties and the performance of the newly developed polyurethanes and its composites under ageing studies.
REFERENCES


