

# Raw and Renewable Polymers

Seena Joseph, Maya Jacob John, Laly A. Pothen, and Sabu Thomas

**Abstract** Biopolymers from renewable resources have attracted much attention in recent years. Increasing environmental consciousness and demands of legislative authorities have given significant opportunities for improved materials from renewable resources with enhanced support for global sustainability. High-performance plastics are the outcome of continuous research over the last few decades. The real challenge of renewable polymers lies in finding applications, which will result in mass production, and price reduction. This can be attained by improving the end performance of the biodegradable polymers. The structure, properties, and applications of polymers derived from natural resources are discussed in this article.

**Keywords** Cellulose, Natural polymers, Natural rubber, Renewable materials

## Contents

- 1 Introduction
- 2 Polymers Derived from Renewable Resources
  - 2.1 Hydrocarbon Polymers
  - 2.2 Carbon Oxygen Polymers

---

S. Thomas (✉) and S. Joseph  
School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O, Kottayam  
686 560, Kerala, India  
e-mail: sabut552001@yahoo.com

M.J. John  
Polymers and Composites Competence Area, Materials Science and Manufacturing, CSIR, Port  
Elizabeth, South Africa  
e-mail: mjohn@csir.co.za

L.A. Pothen  
Department of Chemistry, Bishop Moore College, Mavelikara, Kerala, India

2.3	Carbon Oxygen Nitrogen Polymers
3	Monomers Derived from Renewable Resources
3.1	Natural Monomers Already Polymerized
4	Conclusions
	References

## Abbreviations

CNSL	Cashew nut shell liquid
DNA	Deoxy ribonucleic acid
DPNR	Deproteinized natural rubber
FRP	Fiber reinforced plastic
NR	Natural rubber
OENR	Oil extended natural rubber
PAN	Polyacrylo-nitrile
PMMA	Polymethyl methacrylate
PRI	Plasticity retention index
PS	Polystyrene
PVA	Polyvinyl alcohol
RNA	Ribo nucleic acid
RSS	Ribbed smoked sheet
SIR	Standard Indonesian rubber
SMR	Standard Malaysian rubber
SSR	Standard Singapore rubber
TPNR	Thermoplastic natural rubber
TSR	Technically specified rubber

## 1 Introduction

Nature has been using natural polymers to make life possible on this earth for a long time. We do not think of natural polymers in the same way as synthetic polymers because we cannot take credit for them as marvels of our own ingenuity, and chemical companies cannot sell them for profit. However, that does not make natural polymers less important; it turns out in fact, that they are more important in many ways. Naturally occurring polymers were used by early humans to meet their material needs. A variety of materials made from wood bark, animal skin, cotton, wool, silk, natural rubber (NR), etc., played key roles in early civilization [1].

Natural polymers include the RNA and DNA that are so important in genes and life processes. While proteins are the basic building units, enzymes help to control

the chemistry inside living organisms and peptides make-up some of the more interesting structural components of skin, hair, and even the horns of rhinos. Other natural polymers include polysaccharides (sugar polymers) and polypeptides like silk, keratin, and hair. NR is another polymer, made from just carbon and hydrogen. Two important polymers, which have influenced human civilization during the last century, are rubbers and plastics. They have challenged the old materials for their well-established uses and have become part and parcel of everyday life [2]. The use of NR was well-established by the start of the twentieth century while the major growth period of the plastic industry has been since 1930. These natural polymers have found applications in various fields [3].

In ancient Egypt, mummies were wrapped in cloth dipped in a solution of bitumen in oil of lavender, which was known as Syrian Asphalt, or Bitumen of Judea. On exposure to light, the product hardened and became insoluble. This process involved the action of chemical cross-linking, which became important in the vulcanization of rubber and production of thermosetting plastics.

Depending on the nature of the heteroatom inserted in the main chain, polymers can be classified into four major types, i.e. hydrocarbon polymers, carbohydrates, carbon oxygen nitrogen polymers and carbon, oxygen, nitrogen and phosphorus containing polymers. Of these polymers, polysaccharides, proteins, and nucleic acids are polymers having pronounced physiological activity.

An in-depth review of polymers from renewable resources has been given by Gandini [4]. The author gives a critical review of polysaccharides in terms of development and an account of future biopolymers that can be used.

## 2 Polymers Derived from Renewable Resources

### 2.1 Hydrocarbon Polymers

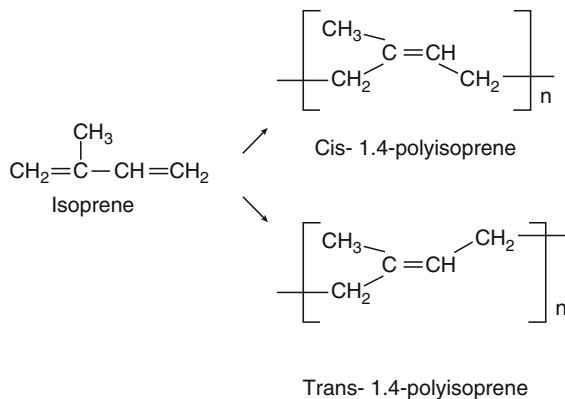
#### 2.1.1 Natural Rubber

NR belongs to a class of compounds known as elastomers [5]. NR was used for centuries by the Mayans in the Western hemisphere before it was introduced into Europe by Columbus. The term rubber was, however, coined by Joseph Priestly. NR is indispensable in our daily lives. The main uses of NR are concentrated in four key areas, namely: medical devices, industrial products, domestic and recreational goods, and foremost automobile products. The current elastomer consumption in the world is 18 million t per year [6]. NR supplies about one-third of the world demand for elastomers. It is also used as an industrial raw material. NR is a naturally occurring elastomeric polymer of isoprene (2-methyl-1,3-butadiene). It can be extracted from latex of only one kind of tree, *Hevea brasiliensis*. Hevea rubber is produced in many tropical regions of Southeast Asia, Africa and Central and South America. There is practically only one other potential source of NR, that is the guayule shrub (*Parthenium argentatum*).

NR occurs as particles dispersed in an aqueous serum, i.e., latex, which are contained in bundles of tubular vessels in the trunk of the tree [7]. Latex is harvested from the tree by a process called tapping. The latex of the *Hevea brasiliensis* tree has been described as a cytoplasmic system containing rubber and nonrubber particles dispersed in an aqueous serum phase. Freshly tapped Hevea latex has a pH of 6.5–7 and a density of  $0.98 \text{ g cm}^{-3}$ . The total solids of fresh field latex vary typically from 30 to 40%, depending on weather and tapping frequency and other factors. The dry rubber content is approximately 3 wt% less than the total solids [8].

Polyisoprene exists naturally in the form of two stereo-isomers, namely *cis*-1,4-polyisoprene and *trans*-1,4-polyisoprene (Fig. 1).

Chemically NR is *cis*-1,4-polyisoprene [9]. A linear, long-chain polymer with repeating isoprenic units ( $\text{C}_5\text{H}_8$ ), it has a density of 0.93 at  $20^\circ\text{C}$ . Natural *trans*-1,4-polyisoprene is a crystalline thermoplastic polymer, which is mainly used in golf ball covers, root canal fillings in dentistry, special adhesives and to a lesser extent in wire and cable coverings. It is obtained as gutta percha from *Palaquium oblongofolium* in South East Asia. It is much harder and less soluble than Hevea rubber. Certain trees like Chicle (*Achras sapota*) produce latex, which is a physical mixture of *cis* and *trans* polyisoprene. *Cis*-1,4-polyisoprene can be produced synthetically by stereo-specific polymerization reaction using Ziegler–Natta heterogeneous catalyst. The important components of NR are given in Table 1.



**Fig. 1** Structure of *cis* and *trans* poly isoprene

**Table 1** Typical analysis of NR [3]

Components	%
Rubber hydrocarbon	93.3
Acetone extract	2.9
Protein	2.8
Moisture	0.6
Ash	0.4

**Table 2** Properties of NR

Property	Approximate values
Glass transition temperature (°C)	-72
Density (g/cc)	0.97
Solubility (J m <sup>-3</sup> )	16.2
Nitrogen content (%)	0.4
Dirt (%)	0.03
Volatile matter (%)	0.5
Ash content (%)	0.4
Plasticity (P <sub>0</sub> )	40
Plasticity retention index (PRI)	75

The most important factor governing the properties of polyisoprene is the stereoregularity of the polymer chain. The very unique characteristic of NR is the ability to crystallize under strain, the phenomenon known as strain-induced crystallization. Stretching of vulcanizates of polyisoprene having at least 90% *cis* content leads to crystallization, which in turn leads to strengthening of rubber [10].

Another interesting aspect of isoprene rubbers is their low hysteresis, giving low heat buildup during flexing [11]. The combination of high tensile properties and low hysteresis explains the requirement of NR as the primary rubber in heavy vehicle tires. In addition to this, NR has excellent tensile and tear properties, good green strength and building tack. However, NR is not very resistant to oxidation, ozone, weathering, and a wide range of chemicals and solvents, mainly due to its unsaturated chain structure and nonpolarity. The properties of NR are given in Table 2.

All types of NR that are not modified [such as oil-extended NR (OENR)] or technically specified rubbers (TSR's) are considered to be international grades. Grade designations usually use color or how the rubber was made; conventional grade descriptions are pale crepe, ribbed smoke sheet (RSS), air dried sheet, Michelin sheets, sole crepe, brown and blanket crepes. The main disadvantage of this system is that grading is done on visual aspects. Almost exclusively, the darker the rubber, the lower the grade. Other grading criteria such as the presence or absence of rust, bubbles, mold and cut spots are subjective in nature. Perhaps the most valid assumption is that the darker the rubber the more dirt it contains. In the 1960s, Malaysia developed a grading scheme that was more sophisticated and useful to customers. A major criticism of NR was the large and varying dirt content. The cornerstone of the new system was grading according to dirt content measured in hundreds of 1%. For example, Standard Malaysian rubber (SMR) is a rubber whose dirt content does not exceed 0.5%. Dirt is considered to be the residue on a 45 µm sieve after a rubber sample has been dissolved in an appropriate solvent, washed through the sieve and dried. The specification has other parameters including source material for the grade, ash and nitrogen content, volatile matter, plasticity retention index (PRI) and initial plasticity. Acceptance of these standards is vigorous and other rubber-producing countries followed suit. Letter abbreviations identify the rubber source; SMR denotes rubber from Malaysia, SIR indicates Indonesian product, SSR indicates Singapore product, and ISNR denotes Indian Standard Natural Rubber.

The main modifications of NR are:

Deproteinized rubber (DPNR) – this is very useful when low water absorption is wanted, vulcanizates with low creep are needed, or more than ordinary reproducibility is required. Normally NR has between 0.25 and 0.5% nitrogen as protein; DPNR has only about 0.07%. A drawback is that since protein matter in the rubber accelerates cure, DPNR requires more acceleration. DPNR is made by treating NR latex with bioenzyme, which hydrolyzes the proteins to water-soluble forms. A protease like *Bacillus subtilis* is used at about 0.3 phr. When the enzymolysis is completed the latex is diluted to 3% total solids and coagulated by adding a mixture of phosphoric and sulfuric acid. The coagulated rubber is then pressed free of most of the water, crumbed, dried, and baled.

Another modification is OENR. There are three ways to make this kind of rubber; (1) co-coagulation of latex with oil emulsion, (2) banbury mixing of oil and rubber, (3) allowing the rubber to absorb the oil in pans until almost all is absorbed, then milling to incorporate the remaining oil. Recently rubber and oil have been mixed using an extruder. A comparatively new modification of NR is epoxidized NR. The rubber molecule is partially epoxidized with the epoxy groups randomly distributed along the molecular chain. The main advantage of ENR over NR is improved oil resistance and low gas permeability. Another new modification is thermoplastic natural rubbers (TPNR) [12–14].

These are physical blends of NR and polypropylene, mixed in different proportions to give rubbers with different stiffness properties. The method of dynamic vulcanization is possible in TPNR [15]. They are suitable for injection molding into products for automotive applications such as flexible sight shields and bumper components. Grafting is another method used for the modification of NR. The properties of PMMA-g-NR, PS-gg-NR, and PAN-g-NR have been analyzed by Thomas and co-workers [16, 17].

Other modified rubbers are tire rubber, peptized rubber, powdered rubber, skim rubber, and superior performing rubber (SP) (made by blending normal latex and pre-vulcanized latex before coagulation and drying by conventional methods). SP rubbers confer superior extrusion properties such as better surface smoothness and lower die swell when blended with natural and synthetic rubbers.

Many other chemically modified forms of NR were available in the past. These included cyclized rubber, chlorinated rubber, hydrochlorinated rubber, and depolymerized rubber.

With such a wide range of useful properties NR can be used in a large variety of applications. These include tires, mechanical goods like hoses, conveyer belts, rubber linings, gaskets, rubber soles etc., and engineering products in dynamic applications such as springs, antivibration moldings, brushings and so forth. High fatigue resistance, good strength, and durability are other points in favor of NR. NR is now accepted as suitable for use in bridge bearings. NR-based natural fiber composites are used for the fabrication of a wide variety of products such as V-belts [18], hoses [19] and complex shaped articles. Many researchers have studied the properties of NR-based composites [20–25].

## 2.2 *Carbon Oxygen Polymers*

### 2.2.1 Cellulose

Cellulose is the most abundant natural polymer on the planet. The chief source of cellulose is plant fibers. Certain types of bacteria also synthesize cellulose, which can be obtained as a continuous film by cultivating the bacteria in a glucose solution. Cellulose is also secreted by such marine chordates (truncates) as the sea squirt [26].

Cellulose is found not to be uniformly crystalline. However, the ordered regions are extensively distributed throughout the material and these regions are called crystallites [27]. Cellulose exists in the plant cell wall in the form of thin threads with an indefinite length. Such threads are cellulose micro-fibrils, playing an important role in the chemical, physical, and mechanical properties of plant fibers and wood.

The plasma membrane of the plant cells has been considered the likely site for the synthesis and assembly of cellulosic micro-fibrils [28]. These micro-fibrils are found to be 10–30 nm wide, less than this in width, and indefinitely long containing 2–30,000 cellulose molecules in cross section. Their structure consists of predominantly crystalline cellulose core.

These are covered with a sheath of para-crystalline polyglucosan material surrounded by hemicellulose [29]. In most natural fibers, these micro-fibrils orient themselves at an angle to the fiber axis called the micro-fibril angle. The ultimate mechanical properties of natural fibers are found to be dependent on the micro-fibrillar angle. Gassan et al. have performed calculations on the elastic properties of natural fibers [30].

A discrepancy in the size of the crystalline regions of cellulose, obtained by X-ray diffractometry and electron microscopy, led to differing concepts on the molecular organization of micro-fibrils. Frey-Wyssling regarded the micro-fibril itself as being made up of a number of crystallites, each of which was separated by a para-crystalline region and later termed the “elementary fibril” [31]. The term “elementary fibril” is therefore applied to the smallest cellulosic strand. Electron micrograph studies of the disintegrated micro-fibrils, showing the crystalline nature of cellulose micro-fibrils ( $\times 100$  nm) taken by diffraction contrast in the bright field mode.

Reports on the characterization and the make-up of the elementary fibrils and on their association while establishing the fiber structure – usually called fibrillar or fringed fibril structure – are present in the literature [32].

According to this concept, the elementary fibril is formed by the association of many cellulose molecules, which are linked together in repeating lengths along their chains. In this way, a strand of elementary crystallites is held together by parts of the long molecules reaching from one crystallite to the next, through less ordered inter-linking regions. Molecular transition from one crystallite strand to an adjacent

one is possible, in principle. Apparently, in natural fibers this occurs only to a minor extent, whereas in man-made cellulosic fibers such molecular transitions occur more frequently.

The coherence of the fibrils in their secondary aggregation is given either by hydrogen bonds at close contact points or by diverging molecules. Access into this structure is given by large voids formed by the imperfect axial orientation of the fibrillar aggregates, interspaces of nanometer dimensions between the fibrils in the fibrillar aggregations, and by the less ordered inter-linking regions between the crystallites within the elementary fibrils. Dufresne [33] has reported on whiskers obtained from a variety of natural and living sources. Cellulose micro-fibrils and cellulose whisker suspension were obtained from sugar beet root and from tunicin. Typical electron micrographs obtained from dilute suspensions of sugar beet are shown in Fig. 2.

Individual micro-fibrils are almost 5 nm in width while their length is of a much higher value, leading to a practically infinite aspect ratio of this filler. They can be used as a reinforcing phase in a polymer matrix.

In terms of chemical structure, cellulose is among the simplest of natural polymers in that it contains a single repeating unit, D-glucose, linked through carbons 1 and 4 by  $\beta$  linkages. The ring substituents other than hydrogen, including the bonds linking the glucose rings together, are all-equatorial.

The crystallinities of cellulose are obtained from X-ray diffraction techniques, which give the most direct results, although their interpretation and evaluation is still under discussion and widely based on convenience. On the basis of the two-phase fringed-micellar structure, Hermans and Weidinger derived a theory on the proportionality of the intensity or amplitude of scattering from the amorphous and

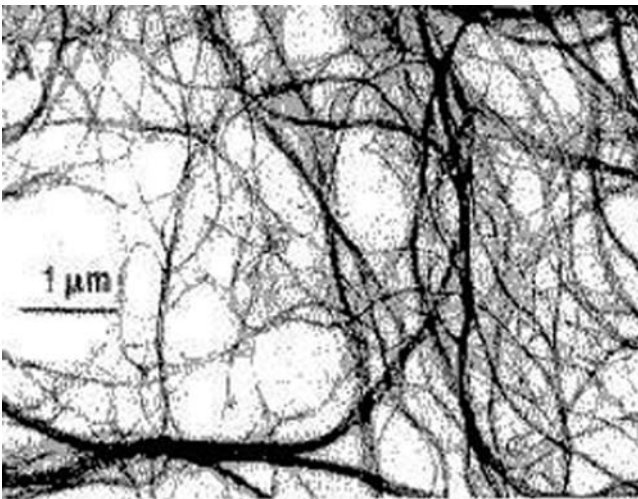
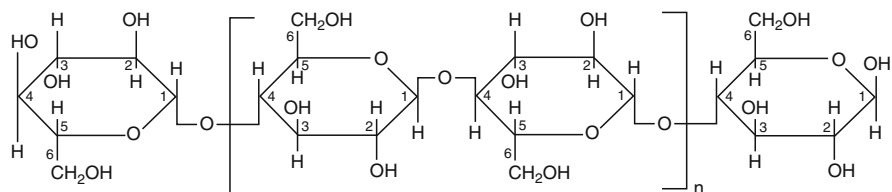


Fig. 2 Transmission electron micrograph of a dilute suspension of a sugar beet cellulose





**Fig. 3** Haworth projection formula for cellulose, Reproduced with permission from American Institute of Physics

crystalline phases of cellulose [34]. The respective crystallinities are based on certain expressions (Fig. 3).

Cellulose can be considered as a syndiotactic poly acetal of glucose. Terminal hydroxyl groups are present at both ends of the cellulose chain molecule. However, these groups are quite different in nature. The C (1) hydroxyl at one end of the molecule is an aldehyde hydrate group with reducing activity and originates from the formation of the pyranose ring through an intermolecular hemi acetal reaction. In contrast to this, the C (4) hydroxyl on the other end of the chain is an alcoholic hydroxyl and is nonreducing. The chemical character of the cellulose molecule is determined by the sensitivity of the β-glucosidic linkages, between the glucose repeating units, to hydrolytic attack and by the presence of three reactive hydroxyl groups, one primary and two secondary, in each of the base units. These reactive hydroxyl groups are able to undergo etherification and esterification reactions. The main cause for the relative stiffness and rigidity of the cellulose molecule is the intra molecular hydrogen bonding, which is reflected in its high viscosity in solution, its high tendency to crystallize and the ability to form fibrillar strands. The β-glucosidic linkage further favors the chain stiffness.

The molecular structure of cellulose is responsible for its supramolecular structure and this, in turn, determines many of its physical and chemical properties. In the fully extended molecule, their mean planes are at an angle of 180° to each other and orient adjacent chain units. The mechanical properties of natural fibers also depend on the cellulose type, because each type of cellulose has its own cell geometry and the geometrical conditions determine the mechanical properties. The crystal structure of natural and regenerated cellulose is known as cellulose I and II, respectively. In cellulose I the chains within the unit cell are in parallel configuration, while they have an anti-parallel configuration in cellulose II [35]. In addition to the cellulose component, natural fibers contain hemicelluloses, which consist of a group of polysaccharides that remain associated with the cellulose after lignin has been removed. The hemicelluloses differ from cellulose, in that they contain several sugar units whereas cellulose contains only glucopyranose units. Hemicellulose also exhibits considerable chain branching whereas cellulose is strictly linear. The degree of polymerization of native cellulose is also 10–100 times higher than that of hemicellulose. Unlike cellulose, the constituents of hemicellulose differ from plant to plant.

Cellulose in the form of natural fibers is finding enormous application in various fields. Plant fibers obtained from the leaf, seed, and stem of plants are used as reinforcement in various matrices and the resulting composites, which are eco friendly, are finding application in various fields like automobile, building etc. Satyanarayana et al. reviewed the potential of natural fiber as a resource for industrial materials [36, 37].

Various reports are present in the literature on the usage of cellulose fibers in the preparation of composites. Cellulose fibers like banana, sisal, oil palm, jute, pine apple leaf fiber were found to have a very good reinforcing effect on polymer matrices [38–42]. The mechanical properties and water absorption were found to be dependent on the amount of micro-fibrils.

### **2.2.2 Shellac**

Among the natural resins used in varnishes and molding compounds, shellac is the best known. Shellac is the only commercial resin of animal origin [43]. It is the hardened secretion of a tiny insect, popularly known as the lac insect. It is a hard brittle resinous solid, heavier than water. Shellac is the refined form of lac, the secretion of the lac insect which is a parasite on certain trees in India, Burma, Thailand, and to a minor extent in south east Asian countries [44].

Lac incrustations deposited by the insects on trees are separated from the twigs by scraping. Lac, thus gathered is known as stick lac. It contains lac resin together with woody materials, sand, dust and other water-soluble impurities. This is subjected to various refining processes. The various refined forms of sticklac are seedlac, shellac, buttonlac, garnet lac, bleached lac, and decolorized lac.

#### **Seedlac**

Seedlac is obtained from sticklac. Sticklac is crushed into small grains, sieved, winnowed, washed with water and dried. This semi-refined product is known as seedlac.

#### **Shellac**

Shellac is obtained from seedlac, usually in the form of thin flakes, by stretching the heat-softened resin by solvent refining or by squeezing it out of cloth bags.

#### **Button Lac**

This is also shellac but in the form of buttons.

## Garnet Lac

The impurities that remain in the cloth bag during the preparation of shellac contain a substantial amount of lac. This is reclaimed by solvent extraction as a dark colored lac called garnet lac.

## Bleached Lac

The color of the lac is the result of the presence of alcohol soluble dye erythro-laccin. Bleached lac is produced by bleaching a soda solution of seedlac with sodium hypochlorite under controlled conditions [45].

The chemical nature of shellac is not completely understood. Gas chromatographic analysis of the products of chemical degradation of shellac has shown the presence of several saturated and unsaturated long-chain aliphatic acids together with other hydroxyl-substituted acids and nonaliphatic compounds [46]. Dewaxed, decolorized wax approaches most nearly lac resin in its pure form. Shellac is apparently a mixture of polyesters made up of various hydroxy aliphatic and sesquiterpenic acids. It has free carboxyl, hydroxyl, and aldehyde groups and is unsaturated. The lac resin is associated with two lac dyes, lac wax and odiferous substance, and these materials may be present to a variable extent in shellac. The resin itself appears to be a polycondensate of aldehydic and hydroxy acids either as lactides or inter-esters [47]. The resin constituents can be placed into two groups, an ether-soluble fraction (25% of the total) with an acid value of 100 and molecular weight about 550, and an insoluble fraction with an acid value of 55 and a molecular weight of about 2,000.

Hydrolysis of the resin will produce aldehydic acids at mild concentration of alkali (0.5N); using more concentrated alkalis (5N) hydroxy acids are produced, probably via the aldehydic acids. Unfortunately most of the work done in order to analyze the lac resin was carried out before the significance of the hydrolysis conditions was fully appreciated. It does, however, appear to be agreed that one of the major constituents is aleuritic acid. This is present to the extent of about 30–40% and is found in both the ether-soluble and ether-insoluble fractions. Both free hydroxyl and carboxyl groups are to be found in the resin.

The presence of free hydroxy and carboxyl groups in lac resin makes it very reactive, in particular to etherification involving either type of group. Of particular interest is the inter-etherification that occurs at elevated temperatures ( $>70^{\circ}\text{C}$ ) and leads to an insoluble “polymerized” product. Whereas ordinary shellac melts at about  $75^{\circ}\text{C}$ , prolonged heating at  $125\text{--}150^{\circ}\text{C}$  will cause the material to change from a viscous liquid, via a rubbery state, to a hard solid. One of the indications that the reaction involved is etherification is that water is evolved. The reaction is reversible and if heated in the presence of water the polymerized resin will revert to the soluble form. Thus shellac cannot be polymerized under pressure in a mold since it is not possible for the water to escape. Polymerization may be retarded by basic materials, some of which are useful when the shellac is subjected to repeated heating operations.

These include sodium hydroxide, sodium acetate, and diphenyl urea. Polymerization may be completely inhibited by esterifying the resin with mono basic saturated acids. A number of accelerators are also known, such as oxalic acid and urea nitrate. Unmodified lac polymerizes in about 45 min at 150°C and 15 min at 175°C. Shellac is soluble in a very wide range of solvents, of which ethyl alcohol is most commonly employed. Aqueous solution may be prepared by warming shellac in a dilute caustic solution. The resin is too brittle to give true meaning to mechanical properties. The thermal properties are interesting in that there appears to be a transition point at 46°C. Above this temperature, specific heat and temperature coefficient of expansion are much greater than below it. The specific heat of hardened shellac at 50°C is lower than that of unhardened material. From the point of view of the plastics technologist the most important properties of shellac are the electrical ones.

Stability of shellac to UV radiation is the most important optical property. The principal application of shellac was in gramophone records. The resin acts as a binder for about three times its weight of mineral filler. Today, the most important application of shellac is in surface coatings. It is also used in some French polish as adhesives and cements including valve capping and optical cements. Shellac is also used in the manufacture of sealing wax.

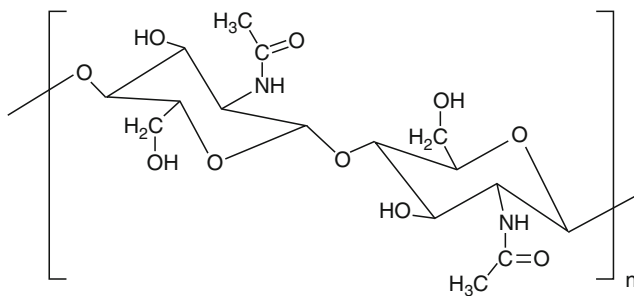
In an interesting study, shellac was used to coat jute fibers by Ray et al. [48]. The authors observed that low-cost natural resins such as shellac in small quantities can be utilized effectively, in their virgin form or in some suitably modified form, for the surface treatment of natural fibers.

### 2.2.3 Chitin

Chitin is one of the most abundant organic compounds on earth. It is present in both animals and fungi, and characteristically it is absent in plants. In nature, the most abundant crystalline form of the polymer is  $\alpha$ -chitin, which occurs in the form of micro-fibrils. In the cell walls of fungi, chitin micro-fibrils constitute the skeleton responsible for their rigidity [49]. It makes up the shells of crawfish, shrimp, crabs, lobsters, and other crustaceans. It is hard, insoluble and yet somehow flexible. Chitin is a long unbranched polysaccharide, which may be regarded as a cellulose derivative in which the hydroxyl group on the C-2 position has been replaced by the acetyl amino group. Chitin, along with collagen is one of the major constituents of cartilage and the blood anticoagulant heparin.

Functionally, chitin is related both to cellulose and to collagen [50]. Chitin and collagen form the basis of the two principal skeletal systems of animals. It is present in the exoskeleton eye lenses, tendons and the linings of the gastrointestinal and respiratory tracts of arthropods, the largest phylum of the animal kingdom, a phylum including insects, arachnids, and crustaceans. Among plants, chitin is found in the cell walls of some fungi.

Chitin always occurs in combination with various other substances such as proteins, calcium carbonate or various pigments. Varying amounts of protein are always found in association with chitin [51]. The chitin of arthropods is  $\alpha$ -chitin.



**Fig. 4** Structure of Chitin

But  $\alpha$ -chitin occurs in structures of animals from other phyla, the most notable example being the skeletal pen or internal horny shell of squids. Purified chitin is a white material resembling paper pulp. It is insoluble in water, dilute acids, dilute and concentrated alkalis and all organic solvents, but is soluble in anhydrous formic acid, in hypochlorite solution and in mineral acids.

Chemically, chitin is poly(*N*-acetylglucosamine) (Fig. 4).

The crystal structure of chitin has been studied by means of X-ray diffraction and IR spectra. The unit cell of  $\alpha$ -chitin is similar to that of cellulose in that it contains four gluco pyranose rings linked by two pairs of (1-4)- $\beta$ -glucosidic bonds.

Chitin is known to be biodegradable, biocompatible, and nontoxic. It is used in drug delivery and bio medical applications. It also used in the purification of water especially for the absorption of toxic dyes. Chitin has limited solubility in solvents but chitosan is readily soluble in acidic aqueous solutions and has more tendency to be chemically modified. Chitosan can readily be spun into fibers, cast into films, or precipitated in a variety of micromorphologies from acidic solutions. Min and Kim have reported on the adsorption of acid dyes from wastewater using composites of PAN/chitosan [52]. Shin et al. has reported on copolymers composed of PVA and poly dimethyl siloxanes cross-linked with chitosan to prepare semi IPN hydrogels for application as biomedical materials [53]. Chen and Liu have reported on the usage of regenerated chitosans as wood dressing [54].

In another interesting research work, it was shown that the deposition of chitosan films of different thicknesses on uncoated paper sheets improves the optical properties, printability and permeability properties as well [55].

The antifungal activity of chitosan is well documented by several authors. Li et al. have reported on the manufacture and properties of fibers with antibacterial properties developed from chitosan and viscose rayon [56]. However, there are only some papers describing the antifungal activity against wood decaying fungi. In general, chitosan acts by reducing the radial growth of fungi, and as a fungicide at higher concentrations. Several theories are established to explain this phenomenon. Chitosan, which is a polycationic polymer, interferes with fungal cell wall membranes causing alterations in the permeability of the membrane and

promoting internal osmotic imbalances. This results in leaching of electrolytes and proteins.

#### **2.2.4 Amber**

Amber is the generic name for all fossil resins secreted in prehistoric times by certain types of evergreens, now extinct. This resin was produced in the Oligocene age by exudation from a now extinct species of pine.

The chemical nature of amber is complex. Amber consists of complex mixtures of sesquiterpenoids, diterpenoids, and triterpenoids that have undergone polymerization and molecular reorganization during fossilization. Phenolic units may also be present. Baltic coast deposits, which contain about 8% succinic acid, are often called succinite. Amber is amorphous, and its infrared spectrum closely resembles those of nonvolatile resins from extinct pine trees. It is believed not to be a high polymer, the resinous state being accounted for by the complexity of materials present. Amber also serves as a repository for a variety of extinct species of insects.

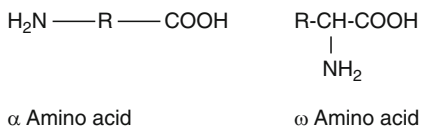
#### **2.2.5 Asphaltenes**

Asphaltenes are also called bitumens. They are resinous materials widely used in highway construction as aggregate binders and as binders for roofing and flooring composition and for water proofing buildings. They occur in natural deposits, but are obtained principally from the residue of petroleum distillation.

### **2.3 *Carbon Oxygen Nitrogen Polymers***

#### **2.3.1 Proteins and Polypeptides**

Proteins were the first examples of polyamides (a fancy word for nylon). Both share many common traits but they are very different in how they are made and in their physical properties. They are alike in that both contain amide linkages in the backbone. Amides are made from carboxylic acid groups and amine groups through the loss of water. The amide molecular segment is unique in its structure and intermolecular interactions. Because of the hybridization of the nitrogen, carbon, and oxygen of the amide group, the segment is basically flat. More importantly, the hydrogen on the nitrogen and the carbonyl oxygen are capable of a strong interaction called a hydrogen bond. Because of this, the amide groups attract each other so much that they form strong associations that give amide-containing polymers unusual properties.

**Fig. 5** Structure of amino acid

The differences between how nature does nylons and how we do it is striking. We mostly make nylons from molecules that have lots of  $\text{CH}_2$  groups in them. They possess four, five, or six  $\text{CH}_2$  groups between amide units. Nature, however, is much more economical, choosing to use only a single carbon between amide groups. What nature does differently is to substitute this carbon with lots of different functional segments and groups.

Most polypeptides and proteins are water-soluble or water swellable. Enzymes are proteins that catalyze all chemical reactions of biological origin. Enzyme functions include oxygen transport, muscle movement, nerve response, nutrient digestion and storage, hormonal regulation gene expression, and protein synthesis.

Despite the large number of functions, all proteins are similar with repeating structures along the backbone chosen from 20 amino acid monomers. These polymers, the structures of which are assembled from a template coded by messenger RNA, are monodisperse. Each protein has a unique sequence and molecular weight.

The 20 amino acids capable of appearing in various microstructural combinations of sequence lengths, and total molecular lengths, allow assembly of an infinite number of distinct proteins [57]. The side chain R may be hydrophobic, polar, acidic, or basic. The structure of the amino acid is given in Fig. 5.

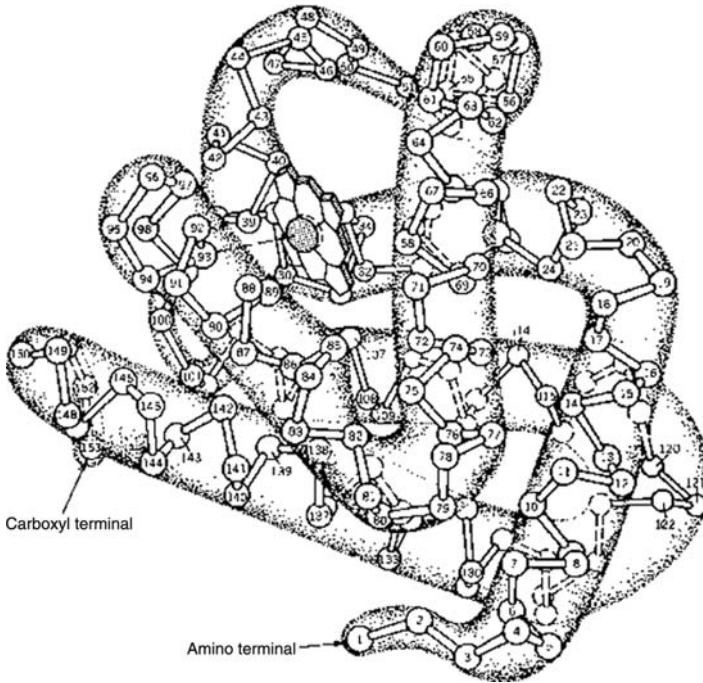
Primary structure (covalent bond lengths and bond angles) is determined by microstructure of the amino acid repeating units along the chain. Numerous procedures, including sequential degradation, gel electrolysis, dye binding, and immunoassays have been used to determine sequences.

Secondary structure of proteins is determined by configuration and conformation along the backbone of the polymer. The resistance to bond rotation of the C–N bond of the peptide unit, the configuration about the chiral carbon, and conformational restrictions to rotation by short-range charge–charge interactions or intermolecular hydrogen bonding play major roles in secondary structure.

The three-dimensional structure or tertiary structure depends strongly on primary structure with the added elements of long-range intramolecular hydrogen bonding, polar and ionic effects, and chain solvation. An example of the three-dimensional structure of myoglobin is shown in Fig. 6 [58]. The compact structure illustrates the hydrophobic interior, helical features from intramolecular hydrogen bonding and the L-amino acids, and polar external groups for hydration.

Many proteins exist in subunits of a composite structure. The organization of these subunits is termed the quaternary structure and is particularly important in enzyme-mediated reactions. The tertiary and quaternary structure of native protein in water can be distributed by addition of electrolytes, alkali solutions, urea, or detergents and increasing temperature. The properties change markedly; for example enzyme activity is often lost. In most cases this denaturation is not reversible.





**Fig. 6** Three-dimensional structure of myoglobin

The solubilities of proteins vary considerably based on compositions and conditions of ionic strength, pH, and concentrations. Those with highest density of polar groups or electrolyte character are most soluble. Therefore, solubility in water is lowest at the isoelectric point and increases with increasing basicity and acidity.

Protein biosynthesis is complex, involving 300 macromolecules. Five stages can be identified involving (1) activation of amino acid monomers and transfer to ribosomes, (2) initiation of polymerization, (3) propagation, (4) termination and release, and (5) folding and processing. Ordering of monomers is dictated by operation of the triplet code in which a sequence of these consecutive nucleotide units on messenger RNA positions specific amino acids for polymerization.

Synthetic polypeptides can be made by sequential addition of protected amino acids on to a solid support. This procedure pioneered by Merrifield, has been used to prepare hundreds of peptides of varying sizes and functions [59]. The development of recombinant DNA techniques has led to cloning of a number of genes and their expression in the form of protein products from bacterial or yeast cells [60]. Large numbers of proteins are being produced with enormous commercial potential. Among the first available genetically engineered proteins are insulin, the pituitary growth hormone and interferon [61].

In addition to the rapid growth of genetically engineered enzymes and hormones for medical and agricultural applications, other water-soluble proteins are isolated



**Table 3** Typical analysis of cow's milk

Water	87%
Fat	3.5–4%
Lactose	5
Casein	3%
Globulin + albumin	0.5–1%
Other ingredients	0.5–1%

from biological sources in a more traditional manner for commercial application. Enzymes are used as detergent additives, for hydrolyzing polysaccharides and proteins, to isomerize various glucose and sucrose precursors, for wine and beer making, for leather tanning, and for mineral recovery. Support-bound enzymes are becoming commercially significant for large-scale substrate conversion.

### 2.3.2 Casein

Casein is a protein found in a number of animal and vegetable materials but only one source is of commercial interest, cow's skimmed milk. The amount of casein in milk will vary but a typical analysis of cow's milk is given in Table 3 [62].

Plastics materials may be produced from casein by plasticizing with water followed by extrusion and then cross-linking with formaldehyde (formalization). The resultant products have a pleasant horn-like texture and are useful for decorative purposes.

Casein is one member of the important group of natural polymers, the proteins. These materials bear a formal resemblance to the polyamides in that they contain representing  $-\text{CONH}$  groups and could be formally considered as polymers of amino acids. Unlike polymers such as nylon 6 and nylon 11 a number of different  $\alpha$ -amino acids are found in each molecule whereas the nylons 6 and 11 have only one  $\omega$  amino acid molecule (Fig. 5).

Over 30 amino acids have been identified in the hydrolysis product of casein of which glutamic acid, hydroxyglutamic acid, proline, valine, leucine, and lysine comprise about 60%. The residues of the amino acid arginine also appear to be of importance in the cross-linking of casein with formaldehyde.

The presence of both acidic and basic side chains has led to protein such as casein acting as amphoteric electrolytes and their physical behavior will depend on the pH of the environment in which the molecules exist. The isoelectric point for casein is about  $\text{pH} = 4.6$  and at this point colloidal stability is at a minimum. This fact is utilized in the acid coagulation techniques for separating casein from skimmed milk.

Casein plastics are today produced by the "dry process." In this process the casein is ground so that it will pass through a 30 mesh sieve but be retained by one of a 100 mesh. The powder is then loaded into a dough mixer, usually of the Artofex type. Water is fed slowly to the mixer until the moisture present forms

**Table 4** Some physical properties of casein plastics

Specific gravity	1.35
Tensile strength	8,000–10,000 lbf in <sup>-2</sup> (55–69 MPa)
Elongation at break	2.5–4%
Modulus of elasticity	$6 \times 10^5$ lbf in <sup>-2</sup> (4,000 MPa)
Izod impact strength	1.0–1.5 ft lbf in <sup>-1</sup>
Brinell hardness	18–24
Rockwell hardness	M 75
Breakdown voltage	200 V/0.001 in
Powder factor	0.06
Water absorption	
24 h	5–7%
28 days	30%
Heat distortion temperature	80–85°C

about 20% of the total. Water has a plasticizing effect on the casein and heat is generated during the mixing operation. Mixing time for a 60 kg batch is usually about 30 min. In addition to casein and water, other ingredients like dyes, pigments, clearing agents (to enhance transparency) are added at this stage. The resultant free flowing powder should be processed soon after mixing since it will tend to putrefy. It is then extruded, so that under heat and pressure the granular powder is converted to rubbery material. The extrudate is cut up into appropriate lengths and cooled by plunging into cold water. The subsequent operations depend on the end product requirement. The rod or sheet must then be cured by a formalizing process.

Some physical properties of casein plastics are given in Table 4.

Although it is thermosetting it has a low heat distortion temperature and is not particularly useful at elevated temperatures.

In the past casein plastics were widely used for decorative purposes due to its pleasant appearance. It was also used in the button industry as well as for making buckles, slides, hairpins, knitting pin pens and pencils. These include adhesives, stabilizers for rubber latex, paper finishing agents, and miscellaneous uses in the textile industry.

### 3 Monomers Derived from Renewable Resources

#### 3.1 *Natural Monomers Already Polymerized*

There are a variety of monomers existing in nature in the free or in the combined form that can be obtained by extraction, cleavage, or depolymerization from biomass [63–65]. There are also some naturally existing monomers/oligomers, such as the amber found in fossil resources. The monomers exhibit a variety of

interesting structures that can be manipulated to obtain specialty/high-performance properties [66].

### 3.1.1 Chemically Modified Natural Monomers

#### Furans

Furans are present in xylan, one of the constituents of hemicellulose. The important products are furfural which is obtained by the steam acid digestion of corncobs, bagasse, rice husks, oat hulls, or similar materials. It acts as the precursor for the preparation of two important monomers, adipic acid and hexamethylene diamine, used in the production of nylon-66 [67]. Furfural and its derivative, furfuryl alcohol (FA), are known to polymerize to form thermosetting resins in the presence of alkaline/acid catalysts. These resins are widely used in molding compounds and in the manufacture of coated abrasives. Recently bio-based nanocomposites were produced by the in situ polymerization of FA using either montmorillonite clay (MMT) or cellulosic whiskers (CW) as the particulate phase. It was observed that FA would act as an effective surfactant for cellulose whiskers and clay particles and as the matrix precursor. Thermal stability of the nanocomposites was found to increase from the incorporation of CW and clay particles. Researchers have also used FA as a chemical treatment on bagasse and curaua fiber reinforced phenolic composites with interesting results [68].

#### Terpene Monomers

Terpene monomers are another class of interesting natural monomers because they give, on polymerization, plastic resins that exhibit a high degree of tackiness useful in pressure-sensitive tapes. They are also used for sizing paper and textile materials. Terpene-phenol resins are effective heat stabilizers for high-density polyethylene. But the current research has not seen much change in either the quality or a significant increase in their production.

#### Sorbitol

Sorbitol is an interesting natural monomer obtained from glucose (sugar waste is used for this purpose) by dehydrogenation. It easily dehydrogenates into isosorbide which is useful as a polyol for production of polymers/polyurethane [69, 70].

#### Lactic Acid and Levulinic Acid

Lactic acid and levulinic acid are two key intermediates prepared from carbohydrates. Lipinsky compared the properties of the lactide copolymers obtained from

lactic acid with those of polystyrene and polyvinyl chloride and showed that the lactide polymer can effectively replace the synthetics if the cost of production of lactic acid is made viable [71]. Poly(lactic acid) (PLA) has found increasing application particularly in packaging and fiber technology and has reached a global capacity exceeding 250,000 t per year with a steadily declining price [72]. Poly(lactic acid) and poly(l-lactide) have been shown to be good candidates for biodegradable biomaterials. Tsuji [73] and Kaspercejk [74] recently reported studies concerning their microstructure and morphology.

In an interesting piece of research, Plackett et al. [75] used commercial L-poly lactide which was first converted to film and then used in combination with jute fiber mats to generate biodegradable composites by a film-stacking technique. Degradation of the poly lactide during the process was investigated using size exclusion chromatography. The tensile properties of composites produced at temperatures in the 180–220°C range were significantly higher than those of poly lactide alone. Examination of composite fracture surfaces using electron microscopy showed voids occurring between the jute fiber bundles and the poly lactide matrix in some cases. Size exclusion chromatography revealed that only minor changes in the molecular weight distribution of the poly lactide occurred during the process.

In an innovative study, novel biodegradable films were fabricated from chitosan and PLA by Sébastien et al. [76]. It was found that composite films offered a great advantage in preventing the surface growth of mycotoxinogen strains because of their antifungal activity. However, the physico-chemical properties of such heterogeneous films dramatically limit their further use as packaging material. The crystallization behavior of composites based on PLA and different cellulose reinforcements, viz., microcrystalline cellulose (MCC), cellulose fibers and wood flour, has been reported by Mathew et al. [77]. The effect of these reinforcements on the crystallization of PLA was studied. The MCC and WF composites were found to have a better nucleating ability than CFs. The effectiveness of natural fiber as a reinforcement for PLA was studied by Oksman et al. [78]. Flax fibers were used as a reinforcement and composites were prepared using a twin-screw extruder. The extruded compound was then compression-molded. Preliminary results showed that properties of PLA and flax fiber composites are promising. Shanks et al. [79] reported on the preparation of composite materials from PLA and flax fibers. Prior to polymerization, the flax fibers were extracted with NaOH and acetone to remove lignin, pectin, and waxes from the cellulose. The surface wetting, as well as the morphology of the fibers, was studied by SEM and optical microscopy. The composites of acetone-washed fibers were found to have higher moduli than the unwashed fibers.

Lee and Wang [80] investigated the effects of lysine-based diisocyanate (LDI) as a coupling agent on the properties of biocomposites from PLA, poly (butylene succinate) (PBS) and bamboo fiber (BF). They observed that the tensile properties, water resistance, and interfacial adhesion of both PLA/BF and PBS/BF composites were improved by the addition of LDI, but thermal flow [81] was hindered due to cross-linking between polymer matrix and BF. Enzymatic biodegradability of

PLA/BF and PBS/BF composites was investigated by Proteinase K and Lipase PS, respectively. It was seen that the composites could be quickly decomposed by enzyme and the addition of LDI delayed the degradation.

### 3.1.2 Long-Chain Hydrocarbon Phenols

Long-chain hydrocarbon phenols are phenolic lipids present in plants from a number of families, notably the Anacardiaceae, found in many parts of the world [82]. They are mostly monohydric or dihydric phenols or phenolic acids with a hydrocarbon side chain at the meta position. Many of these monomers are found to be mixtures of four components varying in degree of unsaturation in the side chain. Being unsaturated these phenols can undergo oxidative coupling polymerization giving rise finally to cross-linked films and have found application in surface coatings. Thus, some have found artistic use while others have found technical use [83–85].

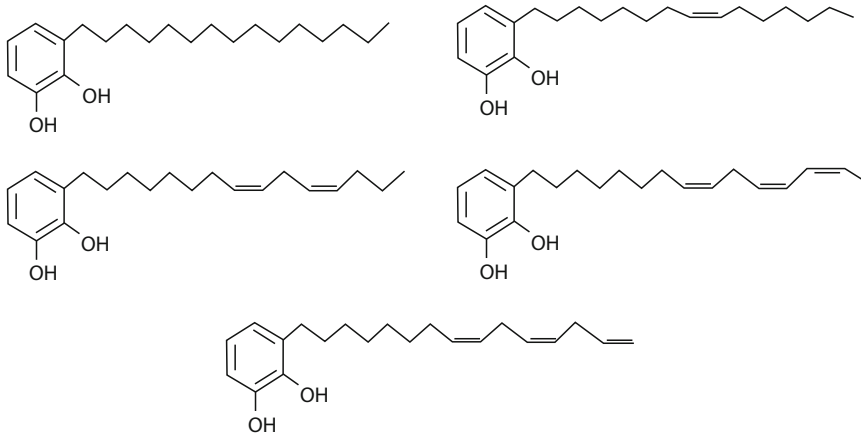
From the point of view of chemistry, phenols are interesting because of their dual aliphatic and aromatic character. The aliphatic entity gives rise to hydrophobic behavior, whereas the phenolic moiety is hydrophilic in character. From an application point of view, the reactions are (1) that of the phenolic moiety undergoing the conventional polycondensation reaction with formaldehyde to give phenolic type resins, (2) the unsaturated side chain reaction polymerization to flexible/rubbery polymers, and (3) the auto-oxidation/oxidative coupling polymerization to give rise to cross-linked polymers. Apart from these possibilities, these lipids have numerous sites such as the hydroxyl position, the aromatic ring, and the side chain that are amenable to chemical modifications. So, compared with phenols they have more opportunities for chemical modifications and polymerization for effecting structural changes for tailor-made polymers for a specific application. Among the phenolic lipids of nonisoprenoid origin, the two most important lipids of commercial significance are those available from the trees *Anacardium occidentale* and *Rhus vernicefera*.

#### *Rhus vernicefera*

The latex is collected in the same way as the rubber plant *Hevea brasiliensis*. The product is known as urushiol, which consists of dihydric phenols of structures as shown in Fig. 7 and it is used as a lacquer.

#### *Structure of Dihydric Phenols of Urushiol*

As in the case of other phenolic lipids, urushiol is also a mixture of components varying mostly in the degree of unsaturation. Thus, the urushiol from *Rhus vernicefera* has structures as shown in Fig. 5 [86]. *Rhus toxicodendron* is also known to give urushiol, but its triene component has a vinyl end group unlike that of *Rhus*



**Fig. 7** Structures of dihydric phenols of urushiol

*vernicefera* [87]. Urushiol is used largely in Japanese lacquering. The hardening of urushiol is thought to involve oxidative polymerization and cross-linking [88]. High adhesion, thermal and alkali-resistant epoxy resin paints have been made by adding the product of reaction between urushiol and hexamethylene diamine [89]. Black ointments for printing ink, plastics, and carbon paper have been obtained from urushiol and certain iron salts [90]. Salts of thiosulfate ester of urushiol have found use as lubricants and additives.

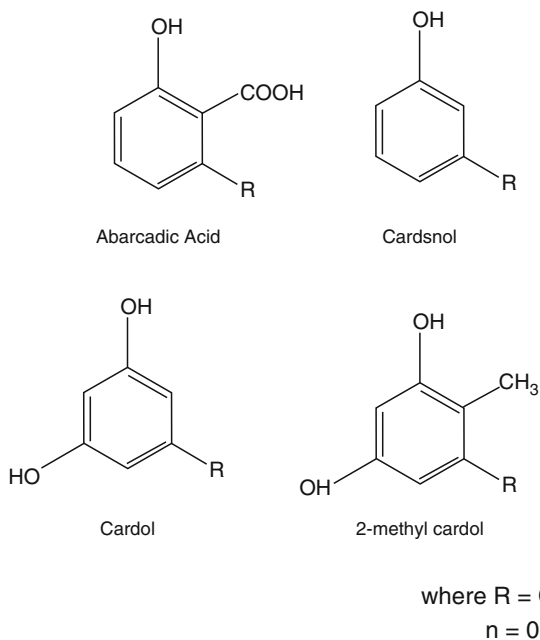
#### *Anacardium occidentale*

This is one of the most widely distributed plants cultivated to obtain cashew nut. The phenolic lipid is only a by-product known as cashew nut shell liquid (CNSL). The nut, attached to the base of the cashew nut apple consists of an ivory-colored kernel covered by a thin brown membrane (testa) and enclosed by an outer porous shell, the mesocarp which is about 3 mm thick with a honey-comb structure where the reddish brown liquid (CNSL) is stored [91]. The major components of CNSL are a phenolic acid, anacardic acid, a dihydric phenol, cardol with traces of mono hydric phenol, cardanol, and 2-methyl cardol [92–95].

A number of methods exist for the extraction of CNSL, but most industries follow the CNSL bath process. Solvent extraction processes are also used at a limited scale.

The structures of anacardic acid, cardol, cardanol, and 2-methyl cardol are given in Fig. 8.

Cardanol is generally obtained by the distillation of CNSL under reduced pressure. The structure of cardanol has many interesting features when compared to phenols. The presence of a  $C_{15}$  hydrocarbon side chain at the meta position provides additional opportunities for manipulation. For example, unlike phenol,



**Fig. 8** Structure of CNSL components

cardanol can be polymerized by a chain reaction mechanism. This gives rise to opportunities for selection of control of polymerization for a particular product. Cardanol can also undergo chemical modifications at the hydroxyl group at the reactive sites of the aromatic ring and on the side chain. Moreover, the presence of a hydrocarbon side chain imparts additional properties such as internal plasticization, flexibility, acid and alkali resistance, moisture resistance etc.

CNSL and cardanol have found extensive uses in automotive break-lining applications [96]. Break linings and clutch facings based on CNSL polymers show very low fade characteristics and very high recovery. CNSL/cardanol-based surface coatings possess excellent gloss and surface finish with a high level of toughness and elasticity [97–100]. CNSL resins are added to laminates based on phenol formaldehyde, epoxy, etc. to reduce brittleness and to improve flexibility of product. The resins also exhibit better age hardening and improved bonding to the substrate [101].

#### Natural Monomers Not Yet Studied and Utilized

There exist a large number of natural monomers that need further studies for their exploitation. Pillai and Manjula [62] have reviewed the subject and have produced a comprehensive list of potential monomers and their sources.

## 4 Conclusions

Natural monomers and polymers have complex structure and properties, which with proper modifications could be a substitute for today's high-performance plastic materials. Existing biodegradable polymers can be blended with different materials with the aim to reduce cost and to tailor the product for specific applications. NR and almost all other natural resources are discussed and possible modifications and the applications of these natural polymers as well as polymers from natural monomers are analyzed in this review. Further studies are required to improve the performance of these materials so that synthetic polymeric materials can be replaced by polymers derived from these renewable materials.

## References

1. Norbert M Bikales, Herman F Mark, Norman G Gaylord (1968) vol 9, Encyclopaedia of polymer science and technology: plastics, resins, rubbers, fibres, Wiley, New York, p 275
2. Ver Strate G, Lohse DJ (1994) In: Mark JE, Erman B, Eirich FR (eds) Science and technology of rubber. Academic, San Diego, pp 95–188
3. Barlow FW (1993) Rubber compounding, principles, materials and techniques, 2nd edn. Marcel Dekker, New York
4. Gandini A (2008) *Macromolecules* 41(24):9491–9504
5. Eirich FR (ed) (1978) Science and technology of rubber. Academic, NY
6. Brydson JA (ed) (1967) Developments with natural rubber. Maclaren, London
7. Brown RP (1986) Physical testing of rubber, 2nd edn. Elsevier, London
8. Grossman RF (1997) The mixing of rubber. Chapman and Hall, London
9. Sethuraj MR, Mathew NM (1992) Natural rubber: biology, cultivation and technology in crop science. Elsevier, Amsterdam
10. Crawford RJ (1985) Plastics and rubbers, engineering design and applications. Mechanical Engineering, London
11. Annual Book of ASTM Standards (1989) vol 09.01, American Society for Testing and Materials, Philadelphia, PA, p 529
12. Ashaletha R, Kumaran MG, Thomas S (1999) *Eur Polym J* 35:253
13. Varughese KT, De PP, Sanyal SK (1990) *Die Angewandte Macromoleculare Chemie* 182:73
14. Ashaletha R, Kumaran MG, Thomas S (1995) *Polym Plast Technol Eng* 34:633
15. Fisher WK (1973) *Rubber World* 167:49
16. Oommen Z, Thomas S (1993) *Polym Bull* 31:623
17. Ashaletha R, Kumaran MG, Thomas S (1995) *Rubber Chem Technol* 68:67
18. Rogers JW (1981) *Rubber World* 27:183
19. Goettler LA, Lambright AJ, Leib RI, Diamouro PJ (1981) *Rubber Chem Technol* 54:277
20. Derringer DC (1971) *Rubber World* 1651:4521
21. Coran AY, Boustany K, Ahmed P (1974) *Rubber Chem Technol* 4:396
22. Murthy VM, De SK (1982) *Rubber Chem Technol* 55:287
23. Setua DK, De SK (1983) *Rubber Chem Technol* 56:808
24. Varghese S, Kuriakose B, Thomas S (1994) *J Appl Polym Sci* 53:1051
25. Geethamma VG, Mathew KT, Laksmi Narayanan R, Thomas S (1998) *Polymer* 39:6
26. Yung RA, Rowell RM (1986) *Cellulose*. Wiley, New York
27. David N, Hon S, Shiraishi N (1991) Wood and cellulose chemistry. Marcel Dekker, New York



28. Preston RD (1974) *The physical biology of plant cell wall*. Chapman and Hall, London
29. Whistler RL, Richards EL (1970) *The carbohydrates*, vol 2A. Academic, New York
30. Gassan J, Chate A, Bledzki AK (2001) *J Mater Sci* 36:3715
31. Frey-Wyssling A (1954) The fine structure of cell microfibrils. *Science* 119:80
32. Krassig HA (1992) *Cellulose*. Gordon and Breach, Yverdon, Switzerland
33. Dufresne A (1998) Recent research developments in macromolecular research, vol 3. Old City Publishing, Philadelphia, p 455
34. Hermans PH, Weidinger W (1948) *J Appl Phys* 19:491
35. Marchessault RH, Sarko A (1976) *Adv Carbohydr Chem* 22:421
36. Satyanarayana KG, Kulkarni AG, Rohatgi PK (1981) *J Sci Ind Res* 40:222
37. Satyanarayana KG, Kulkarni AG, Rohatgi PK (1983) *J Sci Ind Res* 42:425
38. Sreekala MS, Kumaran MG, Joseph S, Jacob M, Thomas S (2000) *Appl Compos Mater* 7:295
39. Kumar RP, Nair KCM, Thomas S, Schitt SC, Ramamoorthy K (2000) *Compos Sci Technol* 60:1737
40. George J, Bhagawan SS, Thomas S (1998) *Compos Sci Technol* 58:1471
41. George J, Bhagawan SS, Thomas S (1998) *Compos Interfaces* 5:201
42. Pothan LA, Zimmermann Y, Thomas S, Spange S (2000) *J Polym Sci B Polym Phys* 38:2546
43. Bose PK, Sankaranarayanan Y, Sen Gupta SC (1963) *Chemistry of lac*. Indian Lac Research Institute, Ranchi, India
44. Hicks E (1961) *Shellac*. Chemical Publishing, New York
45. Herman Mark (1988) vol 14, 2nd edn. *Encyclopaedia of polymer science and engineering* Wiley, New York, p 451
46. Maiti S, Rahman MDS (1986) *J Macromol Sci Rev Macromol Chem Phys* C26:441
47. Christie WW, Gunstone FD, Prentice HG, Sen Gupta SC (1964) *J Chem Soc*, suppl1:5833
48. Ray D, Sengupta SP (2006) *Indus Eng Chem Res* 45(8):2722–2727
49. Ruiz-Herrera J (1978) The distribution and quantitative importance of chitin in fungi. In: Muzzarelli RAA, Pariser ER (eds) *Proceedings of the first international conference of chitin/chitosan*. MIT Sea Grant Report MITSG 78–87, Boston, 11–21
50. Goosen MFA (1997) *Applications of chitin and chitosan*. Technomic Publishers, NY
51. Wood WA, Kellogg ST (eds) (1988) *Biomass part B, lignin, pectin and chitin*. Academic, San Diego
52. Min BG, Kim CW (2002) *J Appl Polym Sci* 84:13
53. Shin MS, Kim SI, Kim IY (2002) *J Appl Polym Sci* 84:13
54. Chen RH, Liu CS (2002) *J Appl Polym Sci* 84:193
55. Fernandes SCM, Gandini A, Pascoat N, Unpublished results
56. Li Z, Liu X, Zhuang X, Guan Y, Yao K (2002) *J Appl Polym Sci* 84:2049
57. Lehninger AL (1982) *Principles of biochemistry*. Worth Publishers, New York, p 127
58. Philips J, Bluestein BR (1965) (to Witco Chemical corporation). US Patent 2,504:400, 14 Sept 1965
59. Merrifield RB (1963) *J Am Chem Soc* 85:2149
60. Freifelder D (1978) *Recombinant DNA*. Freeman WH, San Francisco
61. Brydson JA (1999) *Plastic materials*, 7th edn. Butterworth, London
62. Pillai CKS, Manjula S (1987) *Polym News* 12:359
63. Bernfeld P (ed) (1963) *Biogenesis of natural compounds*. Pergamon, New York
64. Mac Gregor EA, Greenwood CT (1988) *Polymers in nature*. Wiley, New York
65. Carlson KD, Sohns VE, Perkins RB, Huffman EL (1977) *Ind Eng Chem Prod Res Dev* 16:95
66. Pranger L, Tannenbaum R (2008) *Macromolecules* 41:8682–8687
67. Rudolph H, Ger Offen, 3002762 (1981) *Chem Abstr* 95:151439n
68. Trindade WG, Hoareau W, Megiatto JD, Razera AT, Castellan A, Frollini E (2005) *Biomacromolecules* 6:2485–2496

69. Klein J, Kulicke WE (1981) Polymer pre-prints, ACS Symposium Series. ACS, Washington, DC
70. Lipinski ES (1981) *Science* 212:1465
71. Sinclair RG (1977) US Patents 4,045,418 and 4,057,537
72. Anonymous (2007) Biofuels Bioprod Bioref 1:8. <http://www.uhde-inventa-fisher.com>
73. Tsuji H (1995) *Polymer* 36:2709
74. Kasperceji JE (1995) *Macromolecules* 28:3937
75. Plackett D, Andersen TL, Pedersen WB, Nielsen L (2003) Biodegradable composites based on L-poly lactide and jute fibres. *Compos Sci Technol* 63(9):1287–1296
76. Sébastien F, Stéphane G, Copinet A, Coma V (2006) Novel biodegradable films made from chitosan and poly(lactic acid) with antifungal properties against mycotoxinogen strains. *Carbohydr Polym* 65(2):185–193
77. Mathew AP, Oksman K, Sain M (2006) The effect of morphology and chemical characteristics of cellulose reinforcements on the crystallinity of polylactic acid. *J Appl Polym Sci* 101:300–310
78. Oksman K, Skrifvars M SJ-F (2003) Natural fibres as reinforcement in polylactic acid (PLA) composites. *Compos Sci Technol* 63:1317–1324
79. Shanks KA, Hodzic A, Ridderhof D (2006) Composites of poly(lactic acid) with flax fibers modified by interstitial polymerization. *J Appl Polym Sci* 101:3620–3629
80. Lee S-H, Wang S (2006) Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. *Composites A* 37:80–91
81. Ohkita T, Lee S-H (2006) Thermal degradation and biodegradability of poly (lactic acid)/corn starch biocomposites. *J Appl Polym Sci* 100(4):3009–3017
82. Thyman JHP (1979) *Chem Soc Rev* 8:499
83. Wilson RJ (1975) The market for cashew kernel and cashew shell liquids. Report no G91, Topical products Institute, London
84. Pillai CKS (1993) *Prop Plast, Nov Issue*
85. Knop W, Scheib A (1979) Chemistry and applications of phenolic resins-polymer properties and applications. Springer, Berlin
86. Santha Kumar SV, Dawson CR (1954) *J Am Chem Soc* 76:5070
87. Thyman JHP, Mathews AJ (1977) *Chem Ind (London)*:740
88. Thyman JHP (1975) *J Chromatogr* 111:285
89. Iwahashi S (1957) Japanese Patent 6142
90. Ohashi K (1959) US Patent 29197
91. Menon ARR, Sudha JD, Pillai CKS, Masthew AG (1985) *J Sci Ind Res* 44:324
92. Ghatge ND, Malder NN (1981) *Rubber Rep* 6:139
93. Thyman JHP, Tychopoulos V (1988) *J Planar Chromatogr* 1:227
94. Gedam PH, Sampathkumaran PS, Sivasamban MA (1972) *Indian J Chem* 10:338
95. Paul VJ, Yeddappalli LM (1956) *J Am Chem Soc* 78:5675
96. Murthy BGK, Sivasamban MA (1979) *Cashew Causerie* 1:8
97. Murthy BGK, Aggarwal JS (1972) *J Colour Sci* 11:2
98. Anand LC (1978) *Prop Plast, June*
99. Orazio A, Franco SZ, Franco P, Alexandro S (1970) *Chem Ind Milan* 61:718
100. Aggarwal JS (1976) *J Colour Sci* 15:14
101. Sudha JD, Pavithran C, Pillai CKS (1989) *Res Ind* 34:139