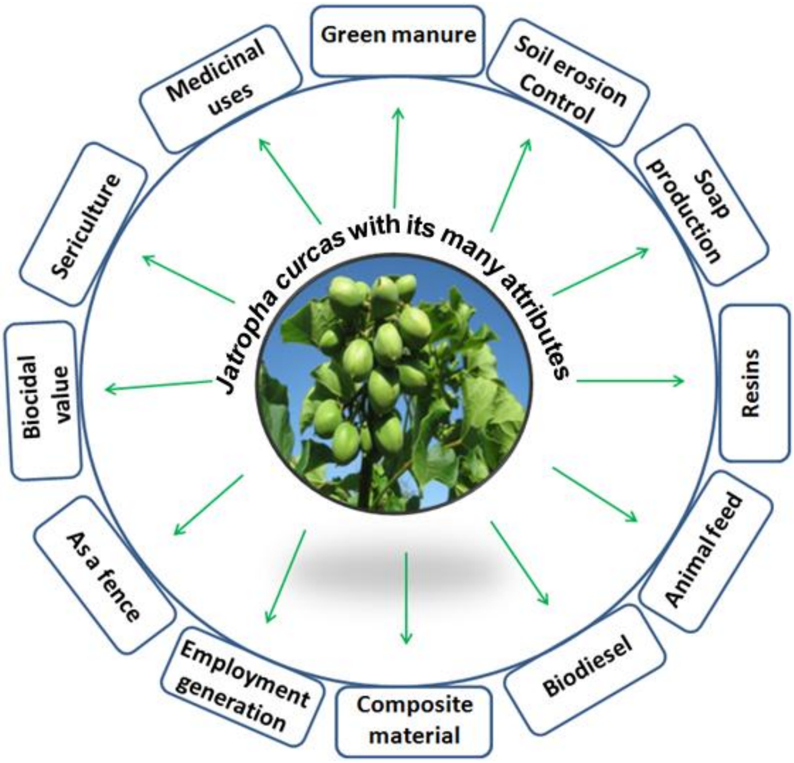
Chapter 1

General Introduction

GRAPHICAL ABSTRACT



All birds find shelter during a rain. But Eagles avoid rain by flying above the clouds. Problems are common, but attitude make the difference.

A.P.J. Abdul Kalam

(Former President of India)

1.1 Motivation and research background

Now a days, researchers are trying to source for new alternative materials that can replace the existing petroleum based products. It is a result of the more environmentally aware consumer society, high rate of depletion of petroleum resources, and spiraling rise in prices of nonrenewable stocks.[1-3] Many government interventions and directives have also been launched in support to deal with this problem. Therefore, development of polymers and eco-friendly materials from renewable resources has received a great scientific attention.[4] Interest has been mainly devoted to the utilization of environmentally benign agricultural resources as renewable feedstock for the polymer industries. Renewable resources such as starch, lignin, protein, cellulose, chitosan, shellac, rosin, poly(hydroxyalkanoates), furanone, alginate, wool fibers, vegetable oils, etc. can be used for the production of variety of polymers. The bio-based polymers can find innumerable industrial applications such as plasticizers, biodiesel, lubricants, adhesives, biodegradable packaging materials, printing inks, paints, coatings, etc.[5]

Among the different renewable resources, plant oils have attracted much attention as raw materials for the chemical industry. Vegetable oils have the economic, environmental, and social advantages as they are non-toxic, non-depletable, domestically abundant, non-volatile, biodegradable, and available worldwide.[6,7] Moreover, various chemical modifications can be performed on vegetable oils, yielding functionalized vegetable oils (FVOs) which can be used to obtain diverse products (Fig. 1.1).[8] A large number of vegetable oils have been utilized for the synthesis of various polymeric resins, such as, polyester,[9] epoxy,[10] poly(urethane),[11] and poly(ester amide).[12] Among the vegetable oils, soybean, castor, sunflower, linseed, palm, tall, and rapseed oils are commonly used for the synthesis of different industrial products. The polymers produced from vegetable oils are capable of competing with products derived from petroleum resources and the properties can be tailored for various end user applications.[13,14] Large numbers of vegetable oils are used to produce variety of polymers such as pressure-sensitive adhesives, elastomers, rubbers, packaging materials, composites, etc. Completely bio-based self-healable polymer networks can be obtained from cross-linking of epoxidized soybean oil by an aqueous citric acid solution.[10] However, the choice of the oil plays an important role on the polymer properties. Obviously, it is due to the variety of the fatty acid composition in the triglyceride structure.[15]

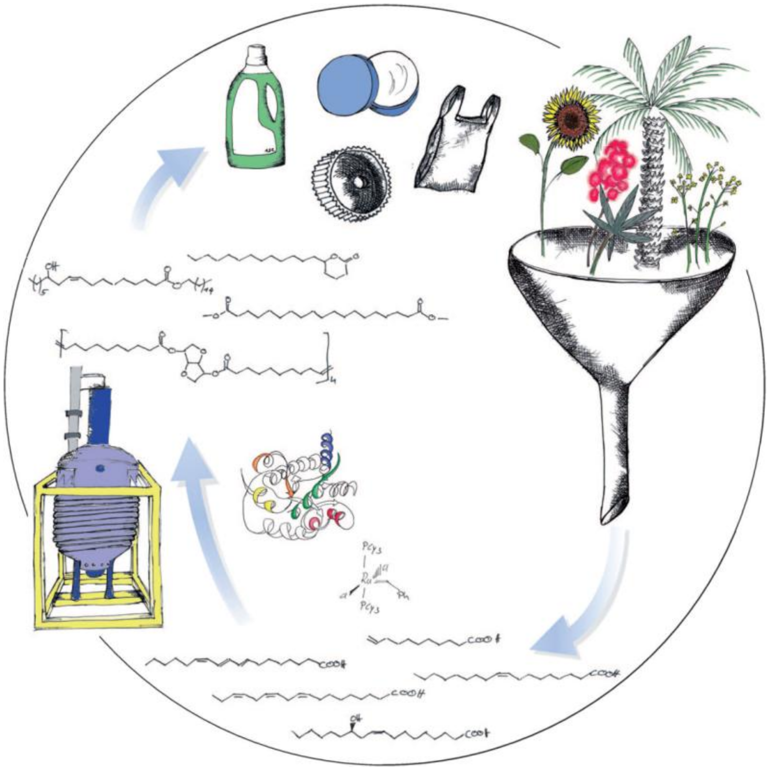


Fig. 1.1: Plant oils as renewable raw materials in chemistry.[7]

Thus, with number of advantages and versatility of vegetable oil derived polymers, the area finds immense potential and significance globally. So far, tremendous geographical and feedstock shift of oleochemical production has taken place from North America and Europe to Southeast Asia from tallow to palm oil. There is growing interest and effort to introduce new oil plants containing fatty acids with interesting and desired properties for chemical utilization, while simultaneously increasing the agricultural biodiversity. At the same time it is also important to cultivate more oil plants to overcome the problem of industrial utilization of food plant oils in the development of the global biodiesel production.[7]

Among the different vegetable oils, *Jatropha curcas* oil has drawn special attention to the scientific community with its various attributes. The crop has considerable potential with multipurpose uses (Fig. 1.2). *Jatropha curcas* is one of the renewable resources that find significant uses not only in bio-energy, but also in medical, food, and non-food application. In addition, the production of oil seeds, percentage of oil content, and the yield per hectare are quite satisfactory (Table 1.1). The seeds of jatropha are good source of oil, which can be used for the production of bio-diesel and value added diverse industrial products. Thus, with the various potentially beneficial products and uses, *Jatropha curcas* can be regarded as a plant of high agro-industrial potential.

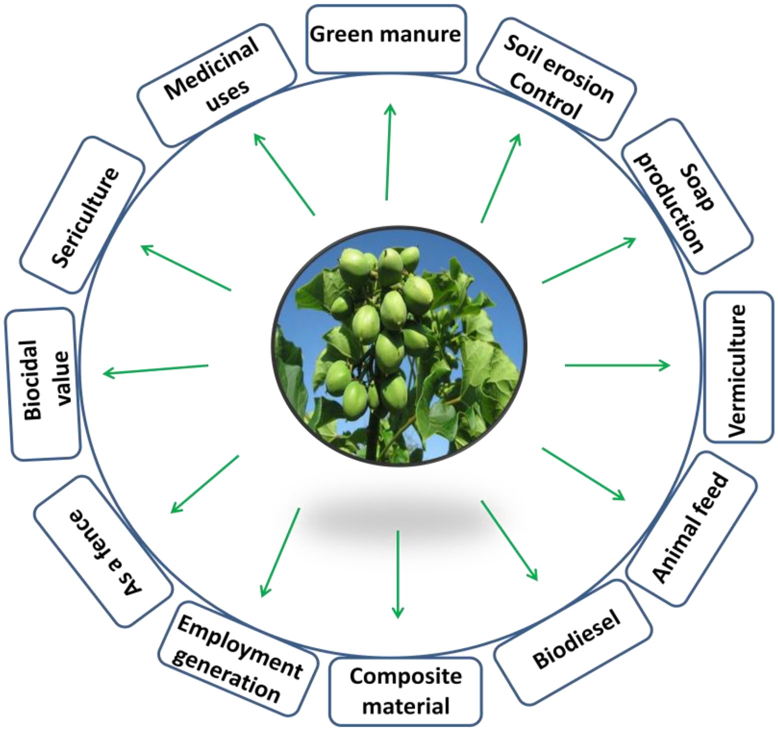


Fig. 1.2: *Jatropha curcas* as multipurpose crop.

Table 1.1: Oil content and production of non-edible oil seeds.[16]

species	oil fraction (%)	seed yield (x 10^5 tones/year)	oil yield (tones/ha/year)
jatropha	50-60	2.0	2.0-3.0
mahua	35-40	2.0	1.0-4.0
pongamia (karanja)	30-40	0.6	2.0-4.0
castor	45-50	2.5	0.5-1.0
linseed	35-45	1.5	0.5-1.0
neem	20-30	1.0	2.0-3.0
others	10-50	5.0	0.5-2.0

The oil can be used for the manufacturing of industrially important products like soap, toothpaste, cosmetics, candle, resins, etc. Besides these, the preparations from all parts of the plant, including seeds, leaves and bark, fresh or as a decoction, are used in traditional medicine and veterinary purposes for a long time.[17,18] For example, the oil has a strong purgative action and is widely used to treat skin diseases and to soothe pain from rheumatism. The seeds are used to treat arthritis, gout and jaundice. The tender twig or stem is used to cure toothache, gum inflammation, gum bleeding, and pyorrhoea. Plant sap and plant extract are used to treat dermatomucosal diseases and allergies, burns, cuts and wounds, inflammation, leprosy, leucoderma, scabies, wound healing, and small pox respectively. Water extract of branches are used to treat HIV and tumor.[19,20] The bark of jatropha contains tannin, which can be used for treating leather. The seed cake (remaining after extraction of the oil) being rich in nitrogen, is an excellent source of plant nutrients. In Nepal, a green manure trial with rice, the use of 10 tonnes of fresh physic nut biomass resulted in increase yield of many crops.[21] It is being used as straight fertilizer and feedstock for biogas production.[22] Moreover, the protein rich jatropha seed cake can be feed for animal if it can be detoxified.[23] With the large number of products and applications of jatropha plant, it has been used for the development of biocomposite material for technical applications. In addition to these, jatropha can be planted to prevent and/or control soil erosion to retrieve land. It can be grown as a live fence for protection of agricultural fields against damage by the farm animals.[24] Thus, the plant serves the purpose of bio fence with respect to cost effectiveness as compared to wire fence. Jatropha plant reduces wind erosion and pressure on timber resources and increases soil moisture retention. Jatropha oil projects can be source of income and organic fertilizer to increase crops yield, as well as a source of ecologically friendly energy to rural farmers.[25] Thus, with the environmental, social, and economic benefits, the non-edible jatropha oil can be a good raw material for the production of polymers without compromising the food industry. Fig. 1.3 presents the exploitation of *Jatropha curcas* components in various applications.

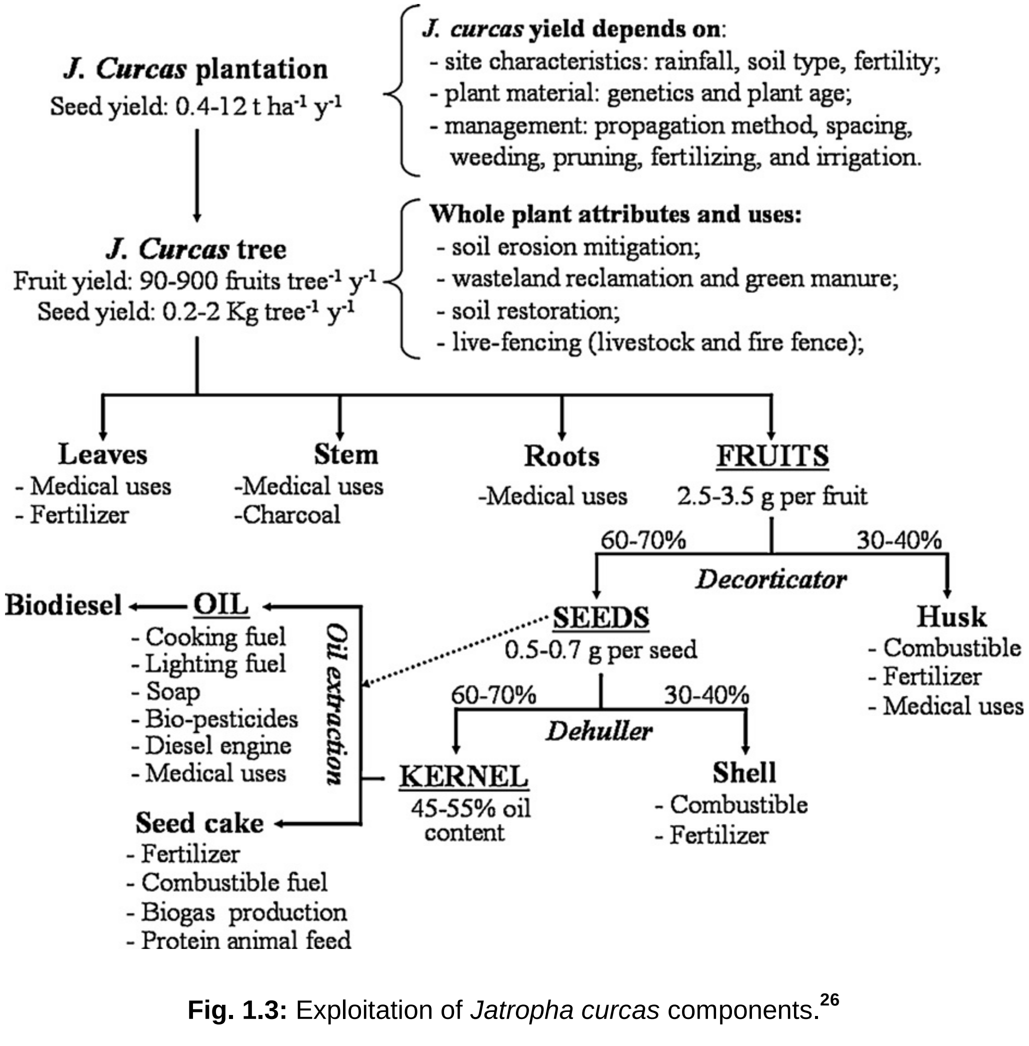


Fig. 1.3: Exploitation of *Jatropha curcas* components.[26]

1.2 The *Jatropha curcas* plant

Jatropha curcas, belonging to the family *Euphorbiaceae,* is a tropical plant that can be grown in low to high rain fall areas. The different parts of the *Jatropha curcas* plant is shown in Fig. 1.4. It is a small tree or large shrub (5-6 m) with smooth pale brown bark and numerous scars due to the fallen leaves. Branches are glabrous, stout, and exude whitish colored watery latex, upon cut.[27] The large green to pale green leaves are smooth and alternate to sub-opposite with three to five lobed spirally phylotaxis, and hypoamphistomatic, with length and width of 6–15 cm, petiole of 5–20 cm long, and paracytic (brachyparacytic) stomata.[28]

Fig. 1.4: Different components of the *Jatropha curcas* plant.

Jatropha curcas flowers throughout the year and pollinated mainly by insects, especially by honey bees.[29] The jatropha fruit contains 2-3 seeds and stay green colored until the seeds are completely developed. After 2-3 months from the fruit formation, the fruits get matured and the color changes from green to yellow, brown, and finally become black.[25] On average each fruit is 2.0–3.5 g weight, 4 cm long, 3 cm diameter, and generally tri-halved. The seeds are black, ellipsoid, triangular-convex, 0.5–0.7 g weight, about 2 cm long and 1 cm thick. Each seed is made up of about 42% husks and 58% kernel. On weight basis, jatropha fruit and seed contain about 17-18% and 34% oil respectively.[30] Jatropha oil has valuable properties like low acidity, good stability as compared to soybean oil, low viscosity as compared to castor oil.

1.2.1 Ecology, distribution, and production of *Jatropha curcas*

Jatropha is a drought-resistant perennial plant and easy to establish, which grows relatively quickly and is hardy in temperate climate. The plant grows almost anywhere except waterlogged lands, even on gravelly, sandy, saline soils, and in the crevices of rocks.[4] Even, jatropha can thrive on the poorest stony soil. Thus, jatropha is a highly adaptable species with versatile properties and applications. However, the strength and productivity of the crop depends on the climate, soil, and growth conditions.

Jatropha curcas grows readily with the following advantages:[31]

- It can be grown in arid zones (20 cm rainfall) as well as in higher rainfall zones and even on land with their soil cover.
- It is a quick yielding species even in adverse land situations, viz., degraded and barren lands under forest and non-forest use, dry and drought prone area, marginal lands even an alkaline soils and also as agro forestry crops.
- It can be a good plant material for eco-restoration in all types of wasteland.
- Jatropha is highly pest and disease resistant.
- It consumes carbon from the atmosphere and stores it in the woody tissues and assists in the buildup of soil carbon.
- During winter, the leaves shed form mulch around the base of the plant and secrete organic matters, which enhance the earthworm activity in the soil and thereby improve the fertility of the soil.

Jatropha was probably distributed by the Portuguese seafarers via the Cape Verde Islands and Guinea Bissau to other countries in Africa and Asia. It is said that the Portuguese brought the physic nut to Asia. The crop well adapted to arid and semi-arid conditions. Nowadays, *Jatropha curcas* is cultivated worldwide, but it has major cultivation area in South Asia, Africa, and Central and South America (Fig. 1.5). Jatropha attracted specific attention of various NGOs addressing rural poverty in Africa and Asia continents from the 1980s due to its versatility, which could contribute to rural poverty alleviation and country's economy development. Around the world 48 African countries, 24 North American counties, 17 Asian countries, and about 14 South American countries have planted jatropha and enjoying its potential benefits.[25] In India, 21 states have planted jatropha in a total land area of 9878 ha. Maharashtra with 1310 ha (13.26% of total land) and Gujarat with 1140 ha (11.54% of total land) land area are the two leading states in India in jatropha plantation.[32]

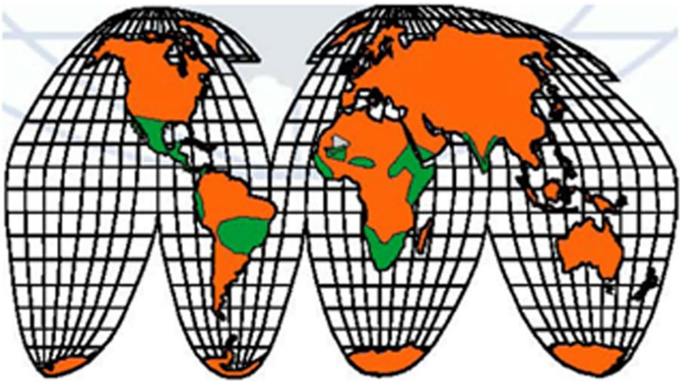


Fig. 1.5: Major distribution areas of *Jatropha curcas* (green) around the world.[4]

India has 60 Mha of waste land including the sides of roads and railway tracks and degraded land that can be used for the cultivation of jatropha plant to check soil erosion and to improve fertility. In addition to this, the oil production can fulfill the future demand for biodiesel in the country. Already in the year 1836, jatropha oil commercially produced on the Cabo Verde Islands and exported to Portugal and France, which was used for street lighting and soap production.[33]

Jatropha plant starts yielding fruit from the second year of planting with limited quantity and the economic yield stabilizes from 4th or 5th year onwards. The plant produces seeds for 50 years with a high oil content of about 37% or more.[31] Depending on agro-climatic zone and agriculture practices, one hectare of plantation gives 1.6 MT oil per year. On average each jatropha plant gives about 2 kg seeds and 0.75-1.0 kg oil.[34] It has been estimated that it requires Rs. 20,000/- per hectare per year inclusive of training overheads, site preparation, plant material, maintenance, planting management, fertilizers, irrigation, deseeding, seed collection, seed processing, etc. In terms of production, the overall cost of jatropha oil is comparatively lower than that of other oils, such as soybean, sunflower, linseed, and rapeseed oil etc.[35]

1.2.2 Extraction, purification, and storage of *Jatropha curcas* oil

Jatropha curcas seeds contain about 30–35% of oil per seed dry mass, which can be relative easily extracted. The production of oil from the seeds require several steps: (1) dehusking process, to separate seeds from husk, (2) dehulling process, to separate kernel from shell, (3) oil extraction process, to produce oil and seed cake as by-product, and (4) oil cleaning process (Fig. 1.6). Dehusking process can be done by hand or through a decorticator machine. Afterwards, the dehulling can be performed manually, by using stone or wooden plank, and then winnowed (26–30 kg h^{-1}), or through a dehuller machine. Prior to oil extraction, the seeds are allowed to dried in an oven (105 °C) or be solar heated for at least 3 weeks.[26]

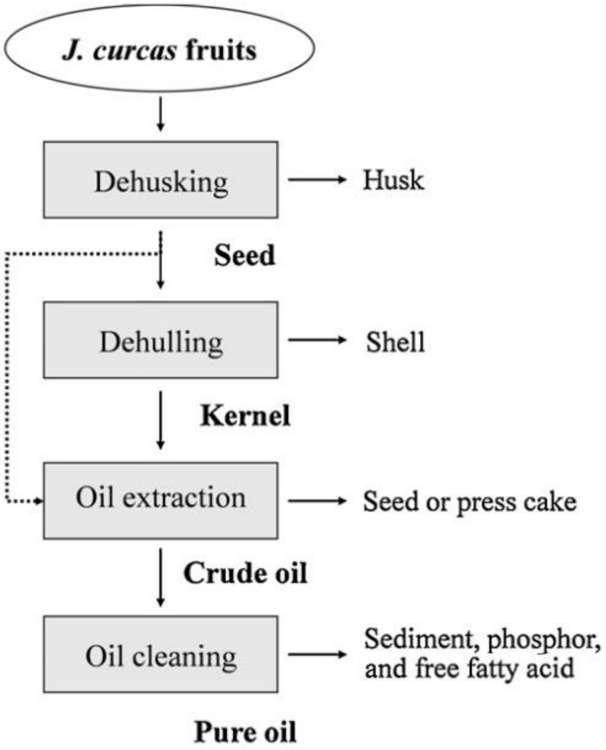


Fig. 1.6: Extraction of *Jatropha curcas* oil.[26]

For the extraction of the oil two popular methods are known; namely, mechanical extraction and chemical extraction. However, the possibilities, procedures, and means are evolving rapidly.[29] The mechanical extraction is performed using presses, such as manual ram press, manual screw press, or engine driver screw press. The mechanical extraction process can be performed on either whole seeds or kernels or mixture of both. In most common practice the whole seeds are used. The chemical extraction process involves the transfer of a soluble fraction from a solid material to a liquid solvent (with or without enzyme). Mainly, n-hexane oil extraction (95% yield), aqueous oil extraction (40% yield), and aqueous enzymatic (hemicellulase, cellulase, or alkaline protease) oil extraction (70–80% yield) methods are used for the extraction of *Jatropha curcas* seed oil.[26] With higher yield and less turbid oil, chemical extraction is advantageous over mechanical extraction. However, the chemical extraction is profitable only at a large-scale production, higher than 50 t of oil per day, and could have a huge negative environmental effect.[36] Additionally, the chemical extraction is performed on kernels only.

The crude jatropha oil contains many impurities, which are solid or dust particles, moisture, free fatty acid, phosphor, color bodies or pigments, and pro-oxidant metals. Removal of these impurities is required to prevent oil deterioration during storage and to get good yield of pure products during conversion. However, the quality requirements are not stringent for lamp fuel or soap-making. The dust and solid particles can be removed by sedimentation, filtration, or centrifuging methods.[37] Sedimentation is the simplest and cheapest way of cleaning by exploiting the earth’s gravity and recommended for small processes. The filtration is carried out in a membrane, in which the particle bigger than its pore size are retained. Degumming is the process of removal of phosphatides, waxes, and impurities in which the oil is treated with water, salt solution or dilute acids. Degumming exploits the affinity of phosphatides for water by converting them to hydrated gums. This allows the gums to coagulate, which is then separated by centrifugation.[38] The free fatty acid (FFA) content of jatropha oil can be reduced with several methods, such as steam distillation, extraction by alcohol, esterification by acid catalysts, and alkali refining.[39] In acid refining process, the oil is mixed with concentrated sulfuric acid and the impurities are allowed to settle down and separated. Afterward, the oil is washed to make it free from mineral acids. In alkali refining process the oil is treated with caustic soda without excessive saponification and emulsification of the oil.[40] The color bodies or pigment from the oil are removed by bleaching process. The oil is bleached by physical or chemical means, but the former is used most commonly. In physical bleaching process, the oil is heated in the absence of oxygen with a bleaching agent, such as bentonite, fuller's earth, activated carbon or amorphous silica, etc.[38]

The quality of jatropha oil can significantly deteriorate if improperly handed and stored. Several chemical reactions, such as hydrolyzes, polymerization, and oxidation can cause the quality degradation.[41] The oil should be stored in a dry and cool place (below 30 °C), avoiding temperature variations and water condensation, exposure to light and air, and potential volatile gaseous substances (like petrol).[26] The oil container should preferably be hermetic and filled up to the maximum (minimum oil surface-to-volume ratio), in order to prevent condensation and thereby water in the oil.[42] Oil can be stored under nitrogen atmosphere to impart better stability of the oil.

1.2.3 Chemical compositions of *Jatropha curcas* oil

Jatropha oil contains approximately 24.60% of crude protein, 47.25% of crude fat, and 5.54% of moisture contents.[43] The general chemical structure of vegetable oil is presented in Fig. 1.7, where R_1, R_2, R_3 represents fatty acid chains which differentiates the vegetable oils from one another. The fatty acid composition of some vegetable oils such as

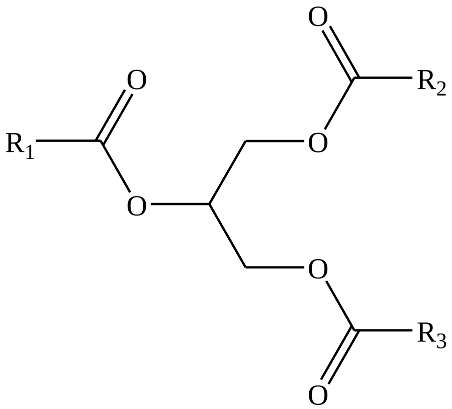


Fig. 1.7: Triglyceride structure of vegetable oils (R_1, R_2, R_3 represents fatty acid chains).

jatropha oil, soybean oil, sunflower oil, palm oil, and pongamia (Karanja oil) summarized in Table 1.2 and the structures are shown in Fig. 1.8 The fatty acid composition may vary depending on growth conditions, climate and soil conditions of the plants. The fatty acids found common in all the oils are oleic, linoleic, palmitic, and stearic acid. Jatropha oil with high percentage of monounsaturated oleic (43.1) and polyunsaturated linoleic acid (34.4) has a semi-drying property (partially hardens when the oil is exposed to air). The large number of unsaturations can be utilized to perform various chemical modifications to obtain diverse value added products.[8,44] However, this semi-drying oil could be an efficient substitute for diesel fuel. The chemical and physical properties such as specific gravity, saponification number, iodine value, hydroxyl value, acid value, calorific value, flash point, and cetane value of jatropha oil are given in Table 1.3. The wide range of the oil characteristics may due to the different oil extraction method and the diverse interaction between plant genotype and environment.[29]

Table 1.2: Fatty acid profile for some common vegetable oils.[4,37]

fatty acid	jatropha oil	soybean oil	sunflower oil	palm oil	pongamia (karanja) oil
lauric acid(C12/0)	-	-	0.5	-	-
myristic acid(C14/0)		0.1	0.2		
palmitic acid(C16/0)	14.2	11.0	4.8	40.3	9.8
palmetoleic acid(16/1)	1.4	0.1	0.8	-	-
stearic acid(C18/0)	6.9	4.0	5.7	3.1	6.2
oleic acid(C18/1)	43.1	23.4	20.6	43.4	72.2
linoleic acid(C18/2)	34.4	53.2	66.2	13.2	11.8
linolenic acid(C18/3)	0.8	7.8	0.8	-	-
saturates (%)	21.1	15.5	11.6	43.4	16.0
unsaturates (%)	78.9	84.5	88.4	56.6	84.0

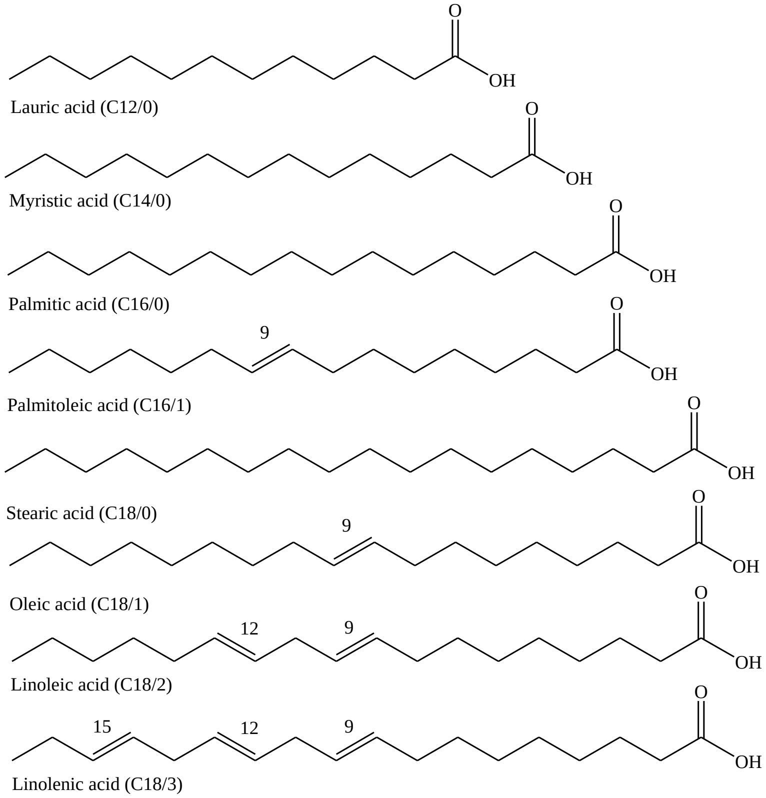


Fig. 1.8: Chemical structure of common fatty acids present in vegetable oil.

Table 1.3: Physicochemical characteristics of *Jatropha curcas* oil.[29,45]

serial no.	characteristics	value
1	specific gravity (25 °C)	0.860–0.933
2	viscosity at 30 °C (cSt)	37.0–54.8
3	free fatty acids % (kg kg^{-1} ×100)	0.18–3.40
4	saponification number (mg/g)	102.9–209.0
5	iodine value (g I_2/100 g)	92.0–112.0
6	hydroxyl value (mg of KOH/g)	2.5-4.0
7	acid value (mg of KOH/g)	0.92-6.16
8	calorific value (MJ/kg)	37.83–42.05
9	flash point (°C)	210–240
10	cetane value	38.0–51.0
11	refractive index (25 °C)	1.468

1.2.4 Products and uses of jatropha seed oil

The oil produced from jatropha seeds has good stability, low viscosity, and low acidity which make it suitable for use as biodiesel. Besides these, jatropha oil has many attributes, due to which it attracted much attention to the scientific community and different chemical industry. The versatility of the oil is reflected in its application and performance in diverse fields. Some of the major areas where jatropha oil plays vital role are discussed below:

Cooking and lighting fuel

Jatropha oil can be used as fuel for cooking and lighting as an alternative of traditional biomass, such as firewood, charcoal, kerosene or petrol. The use jatropha oil has health, economic, and environmental benefits. Use of jatropha oil reduces smoke inhalations and avoids forest cover loss and decreases greenhouse gas emissions.[31] In addition to this, the overall production cost of jatropha oil is low and it is bio-renewable.

Bio-pesticides

Jatropha oil or extract contains insecticidal, molluscicidal, fungicidal, and nematicidal agents due to which it can be used as bio-pesticides.[25] As a natural crop pesticide, it can be a promising alternative to hazardous chemicals in controlling insect pathogens. Additionally, it seems to not affect the population of the beneficial arthropods.[19] However, the potential use of this oil is still need to be commercialized. In a recent study, it was observed that water crude extracts from *Jatropha curcas* shell, branch or leaf possess an herbicidal activity.[46]

Direct use in diesel engine

Jatropha oil can be used directly in some diesel engines as an alternative fuel. For example, the Lister single cylinder engines can sue jatropha oil without any modification other than an appropriate fuel filter. The high viscosity and high FFA content in some vegetable oils make them difficult to use directly into traditional engines. Moreover, in some cases gum formation due to oxidation, polymerization, oil ring sticking, and carbon deposits take place.[41]

Biodiesel

Increasing industrialization and modernization of the world have led to a huge demand for energy, where the major part of that energy is derived from petroleum based resources. But, due to the high rate of depletion of the petroleum resources, many researchers have drawn their attention to look for alternative fuels which can be produced from renewable feedstock. In this regard, jatropha oil can be a promising candidate for the production biodiesel without compromising the food industry. In addition, jatropha seeds have high oil content and the produced biodiesel has comparable properties to that of the petroleum based diesel. The usage of jatropha oil based biodiesel reduces the greenhouse gas emissions. There are four primary methods to produce biodiesel; namely blending, microemulsion, pyrolysis, and transesterification.[37]

Soap

Jatropha oil is used mainly in the manufacturing of high quality soap. The soap helps in treating skin ailments. The produced soap is soft, durable, and well adapted to household or small-scale industrial activity. With easy production technology, soap is one of the most economically attractive products of jatropha oil. Soap is prepared from jatropha oil by cooking it with a solution of sodium hydroxide and allowing the mixture hardening into a mold overnight. It can also be produced from glycerol, which is a by-product in the production of biodiesel.

Glycerol, which can be produced from jatropha oil, is a very important raw material for the production of diverse industrial products like moisturizers, cosmetics, and medicines. It is also extremely effective for washing shearing shed floor and can be used as a degreaser and heavy duty detergent.[25]

Polymers

Although the biggest usage area of jatropha oil is in biodiesel production, in the last decade it has been used in polymer synthesis for many different applications. Some types of polymers prepared from jatropha oil are discussed below.

Polyurethane

Polyurethane resins are formed by the copolymerization reaction of polyols with isocyanates, such as toluenediisocyanate (TDI), methylene-4, 4'-diphenyldiisocyanate (MDI) or others. The polyols can be derived from plant oils and their derivatives. A.S.A. Hazmi et al. reported the preparation of jatropha oil-based polyol (hydroxyl number of 171–179 mg KOH/g) via epoxidation and subsequent ring opening reaction.[47] The prepared polyols were reacted with different isocyanates to prepare polyurethane resins. M.M. Aung et al. reported the synthesis and characterization of polyurethane wood adhesives based on jatropha oil. Shear strength tests of solid wood and plywood showed that the adhesive exhibited better results compared with palm oil-based adhesives. The overall chemical resistance of jatropha oil-based polyurethane adhesives was superior compared to palm oil-based adhesives in response to hot water, acid, and alkali.[35] S. Saalah et al. prepared a series of waterborne polyurethane dispersions from jatropha oil-based polyol with different hydroxyl numbers ranging from 138 to 217 mg KOH/g. The polyurethane films exhibited the stress–strain behavior of an elastomer with a Young’s modulus ranging from 1 to 28 MPa, a tensile strength of 1.8 to 4.0 MPa, and elongation at break ranging from 85 to 325%[48]

Polyesteramide

Polyesteramide resins are amide modified alkyds obtained by esterification reaction between vegetable oil-based amide diol and an acid or anhydride which finds extensive applications in surface coatings industry. They contain repeating ester and amide units in their backbone and possess improved properties like hardness, ease of drying, water vapor resistance, and chemical resistance over alkyd resins.[49] Jatropha oil based urethane modified polyesteramide resins were prepared through a microwave assisted technique and cured at ambient parameters. The resins exhibited good performance under various corrosive media and can be safely used up to 230 °C as a corrosion protective coating material.[50] Kadam, et al. reported the preparation of jatropha oil modified polyesteramide hot melt adhesive using dimer acid and ethylenediamine. It was observed that crystallinity and the inter-molecular forces of attraction played an important role in affecting the mechanical, thermal, rheological, and adhesion properties of the prepared resins.[51]

Polyetheramide

Polyetheramide resins consist of alternating amide and ether moieties in their backbone which are responsible for good adhesion and chemical resistance of their coatings. They are produced form the condensation reaction of an amide diols with a polyol like bisphenol A, resorcinol, etc. Further, polyetheramides can be reacted with different isocyanates, to obtain polyetheramide urethanes. M. Alam and N.M. Alandis have developed a class of urethane-modified polyetheramide resin based on jatropha oil. From the investigation of the physico-chemical and physico-mechanical characteristics of the resins it was found that the resins may find suitable application as an eco-friendly corrosion protective coating. The resins can be safely used up to 200 °C.[52] The drying of the polyetheramides resins occurs at elevated temperature range. Polyetheramide is still new in the world of surface coatings and holds immense scope for exploration and applications.[5]

Epoxy resins

In recent years, epoxy resin formation with epoxidized plant oils and fatty acids are the most frequently studied polymerization involving plant oils and their derivatives. Epoxidation of vegetable oils can be achieved in a straightforward fashion by reaction with, e.g., molecular oxygen, peracids, hydrogen peroxide as well as by chemo-enzymatic reactions.[53] The resulting epoxidized vegetable oils and fatty acid derivatives can be used for obtaining various types of polymers with application possibilities as rubbers, resins or coatings.[54,55] The resins can be cross-linked with suitable curing agents like polyamines, polyamides, polycarboxylic acids, and anhydrides to yield polymers with desirable properties.[15] A. Sammaiah et al., has reported the preparation of epoxidized jatropha oil

(96% yield), which was then used as lubricant for high temperature applications. It exhibited better lubricating property as compared to the soybean oil based resins. The epoxidized oil possesses better oxidative stability as compared to the pure oil.[56] Epoxidized jatropha oil can be used to improve the performance characteristics of alkyd resins. This can be done by blending, which is facilitated by epoxidation of the alkyd resins and cured with an aqueous citric acid solution.[57]

Alkyd resins

Alkyd resins are one of the oldest applications of plant oil renewable resources in polymer science, which belong to the class of polyester resin. For the first time Berzelius reported the preparation of polyester resin from tartaric acid and glycerin, dates back as early as 1847. However, the term ‘alkyd’ was introduced by Kienle in the year 1921 for the oil modified polyester resins. The oil modified alkyd resins exhibited superior properties as compared to the glycerin based polyester resins.[15] A typical structure of alkyd resin is shown in Fig. 1.9.

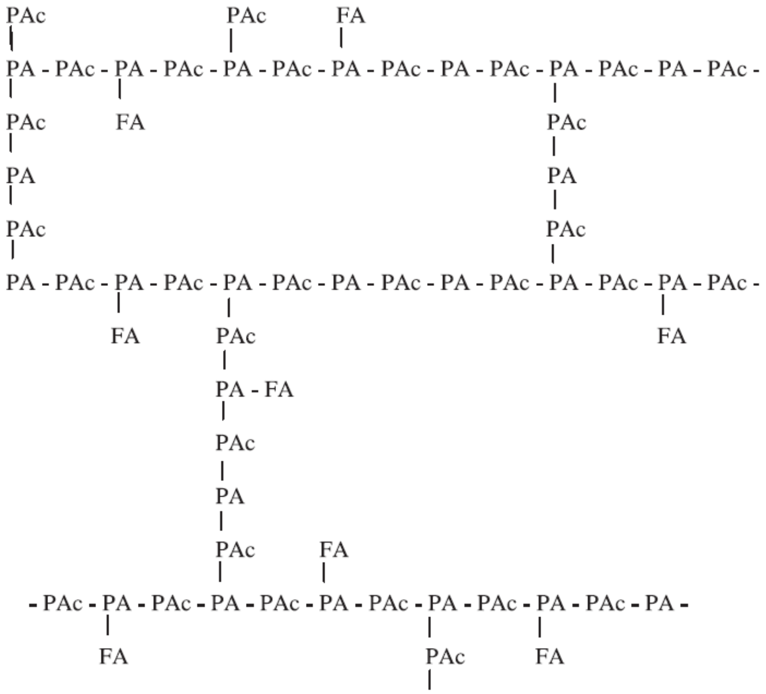


Fig. 1.9: Structure of a typical alkyd resin (PA: polyalcohol, PAc: polyacid, FA: fatty acid).[15]

Jatropha oil based alkyd resins

Patel et al. prepared jatropha oil based alkyd resins and characterized for electrical properties. The resins meet all the requirement of relevant Indian Standard for class ‘‘B’’ baking type insulating varnish. The resins showed dielectric constant of 2.22, dissipation factor of 0.0098, and electric strength 66 kV/mm.[58] Odetoye et al. prepared a series of alkyd resins based on jatropha oil with different oil formulations using a two-stage alcoholysis–polyesterification method. The study revealed that jatropha oil as a potential raw material for the coatings industry. The resins exhibited outstanding color and gloss.[59] Kumar et al. prepared alkyd resins having different amount of jatropha oil (40–80%). The kinetics of polyesterification of jatropha oil, glycerol, and phthalic anhydride leading to the formation of alkyd resins were studied. The initial reaction rate followed the second order kinetics and the rate constant was found to be of the order of 10-5 g (mg KOH)-1 min-1. The extent of reaction and average degree of polymerisation were calculated from the end group analysis. The alkyd resin with 50% oil content has showed the highest degree of polymerisation (2.66).[60] Boruah, et al. prepared jatropha oil based alkyd resins with different proportions of phthalic and maleic anhydride. The resin with 1:3 molar ratio of phthalic and maleic anhydride exhibited optimum properties. The resins possessed remarkable properties like gloss, hardness, adhesion, and chemical resistance.[9]

1.3 Inside the world of alkyd resins

Among the various products of vegetable oils, alkyd resins have attracted the interests of many chemists from both academia and industry. It is directly supported by the huge number of scientific publications and patents covering this field. Several factors are behind the popularity of these resins. For example, alkyd resins are single-pack system and stable for a long time. They are soluble in industrially used low cost solvents. The resins are compatible with many other resins used in surface coating industry. In addition, they possess high order of durability, excellent pigment dispersion, high gloss accompanied by exceptional toughness and adhesion, which make the resins suitable for wide range of applications. The structure and properties can be tailored depending upon the user applications. Moreover, the overall cost of the alkyd resins, including raw materials and processing cost, is very low as compared to the other synthetic resins.[40,61,62] About 60-70% of an alkyd resin comprises of bio-derived or degradable raw materials like fatty acids, glycerol, pentaerythritol which make the resin biodegradable to a greater extent.[63]

1.3.1 Classification

Alkyd resins are classified into the following categories based on the percent weight fraction of oil (oil length) in the resins.[63]

i. short oil alkyd (oil content 30-42% w/w)
ii. medium oil alkyd (oil content 43-54% w/w)
iii. long oil alkyd (oil content 55-68%)
iv. very long oil alkyd (oil content >68%)

Further, depending on the degree of unsaturation of the fatty acid present in the alkyd resins,[61] they are classified as:

i. dying (oxidizing type) and
ii. non-drying (non-oxidizing type)

In the case of the oxidizing type alkyd resins, drying and semi-drying oils like linseed, safflower, soybean, tobacco, dehydrated castor oil with sufficient unsaturation are used to give the resins air drying property.

The non-oxidizing type alkyd resins are obtained mainly from non-drying oils like coconut, castor, hydrogenated castor oil, dhupa oil, where the unsaturation is very low and not able to polymerize in presence air. This type of resins is used with amino resins like urea-formaldehyde and melamine-formaldehyde in stoving finish.[64, 65]

1.3.2 Raw materials

For the manufacturing of alkyd resins, components such as vegetable oils or fatty acids, polyhydric alcohols, and polybasic acids are required. In addition to these, in some cases monobasic acids are used to improve the performance characteristics of the alkyd resins.

Vegetable oils or fatty acids

A large number of vegetable oils (drying, semi-drying, and non-drying type) are used for the manufacturing of alkyd resins. For example, linseed oil,[66] castor oil,[67] tung oil,[68] soybean oil,[69] sunflower oil,[70] safflower oil, mahua oil,[71] tobacco seed oil,[72] rubber seed oil,[73] nahar (*Mesua ferrea* L.) seed oil,[74] yellow oleander (*Thevetiaperuviana*) seed oil,[75] african locustbean seed oil,[76] *Hura-crepitans* L. seed oil,[77] jatropha oil,[9] etc. have been used extensively for the synthesis of alkyd resins. The oil-modified alkyd resins exhibit excellent characteristics like flexibility, adhesion, and gloss. The unsaturation and drying property of the alkyd resins depends on the nature of the oil used. Now a days, in addition to the vegetable oils, different fatty acids have also been used for the synthesis of alkyd resins.[78]

Polyhydric alcohols

Due to the availability and versatility of glycerol, it is the most extensively used polyol component for the production of alkyd resins. Pentaerithritol with its high functionality is the next most widely used polyol, especially for long oil alkyd resins. Trimethylol propane (TMP) can be used as a polyol component for the preparation of alkyd resins. However, due to its sterically hindered structure, the esterification reaction occurs at slower rate. It can be used to prepare hyperbranched alkyd resins.[79] Beside pentaerythritol, dipentaerythritol have also been used to prepare hyperbranched alkyd resins. The resins exhibited excellent adhesion, gloss, and flexibility.[80] In addition to these, a large variety of dihydric alcohols like glycol glycuside, bisphenol-A bis(2-hydroxyethyl) ether, bisphenol-A bis(2-hydroxypropyl) ether, ethylene glycol, propylene glycol, neopentyl glycol, diethylene glycol, 1,3-butylene glycol, etc. can be used as a polyol component for the synthesis of alkyd resins. Recently, Yin et al. reported the use of a sugar alcohol, sorbitol as renewable raw material for the synthesis of alkyd resins.[81]

Polybasic acids

Among the various polybasic components for the synthesis of alkyd resins, phthalic anhydride is used mostly. It is due to its availability at low cost, ease of handling, and stability at the processing temperature. In addition to this, it produces less amount of water during the course of the reaction and thereby reduces the reaction time. After phthalic anhydride, isophthalic acid (IPA) is most widely used dibasic acid. The esters derived from IPA are more resistant to hydrolysis than those of phthalic anhydride in the pH range of 4-8, which is most important range for exterior durability.[82] IPA based coatings are fast drying, tougher, and more chemical resistant. However, the use of IPA requires higher processing temperature for long time, which may lead to greater extent of side reactions. Halogenated polybasic acids like tetrachloro phthalic anhydride and chlorendic anhydride are used to impart fire retardant property to the alkyd resins. In addition, the use of tetrachloro phthalic anhydride makes the alkyd resins more resistant to water and alkali than phthalic anhydride.[61] 2,2-bis-(hydroxymethyl)-propionic acid has been used to prepare hyperbranched alkyd resins.[83] Maleic anhydride, trimellitic anhydride, pyromellitic anhydride, fumaric anhydride, etc. are used in alkyd formulations for water borne alkyd resins.[84] Saturated dibasic acids like adipic acid, sebacic acid, azalic acid, etc. with long hydrocarbon chain confer flexibility to alkyd resins. In addition to these, a large variety of polybasic acid components like citric acid, diglycolic acid, succinic acid, terephthalic acid, glutaric anhydride, tetrabromo phthalic anhydride, succinic anhydride, etc. can be used for the production of alkyd resins depending on the property requirement.

Monobasic acids

In addition to the fatty acids, other monobasic acids like benzoic acid, *p-tert*-butylbenzoic acid, rosin, lauric acid, lactic acid, isooctanoic acid, isodecanoic acid, etc. are used in alkyd resins formulation.[62,85] Alkyd resins with reduced drying time can be obtained by the use of mixture of benzoic acid and *p-tert*-butylbenzoic acid in the resin formulation. Moreover, benzoic acid can be used in short oil alkyd resins to regulate the polymerization at optimum level.[86]

1.3.3 Methods of preparation

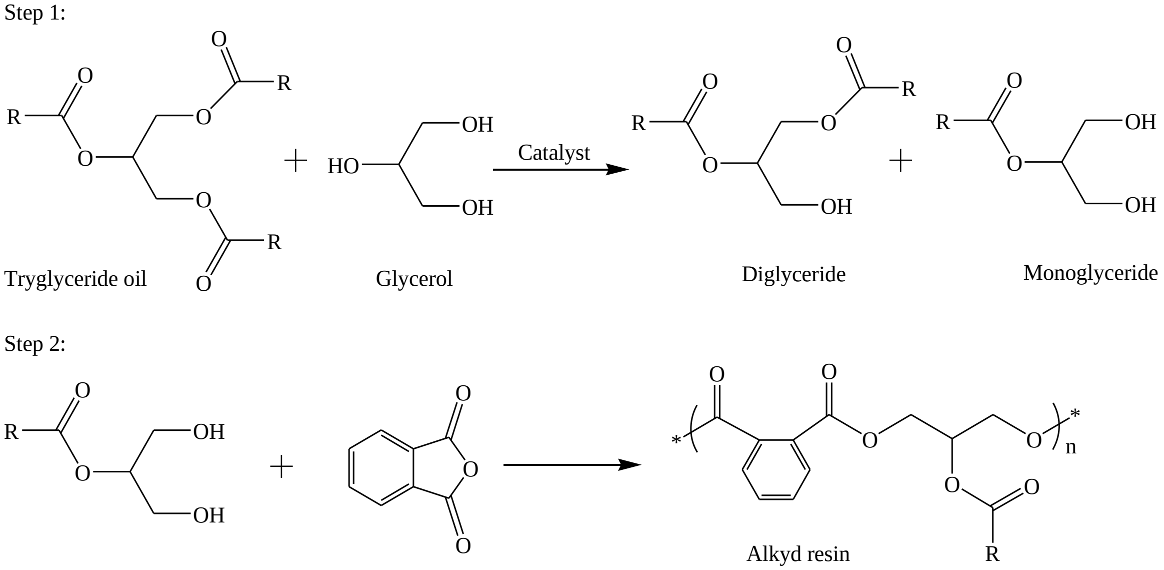
Alkyd resins are typically prepared from the reaction of a polyol, a polyvalent acid or acid anhydride, and fatty acid derivatives. The unsaturated fatty acid derivatives are used to give the resins air drying properties. The two most important methods for the synthesis of alkyds are (i) monoglyceride process, and (ii) fatty acid process.

Monoglyceride process

It is the most commonly used process for the preparation of alkyd resins. The process involves two stages (Scheme 1.1). The first stage is the alcoholysis of the triglyceride oil by a part of the polyols. The progress of the reaction is checked by the methanol solubility of the monoglyceride formed. In reality, the process also leads to the formation of diglyceride to some extent (Scheme 1.1, Step 1).

The second stage of the process involves the esterification of the alcoholysis product with a polyacid (Scheme 1.1, Step 2). The progress of the reaction is monitored by checking the acid value of the reaction mixture.[9] As the reaction proceeds, the acid value of the mixture decreases gradually and reaction is stopped at certain acid values to prevent the gelation.

In this process, the reaction is carried out in the temperature range of 220-250 °C in the presence of a catalyst. A large variety of catalyst including acid and base can be used.[87,88] At high temperature, oxygen seems to hinder the reaction rate and hence the reaction is carried out in inert gas atmosphere of nitrogen or argon. Like oxygen, the byproduct water, formed in the esterification process also reinforces the effect. Therefore, it is necessary to remove water from the reaction mixture to force the reaction towards completion. Two techniques namely fusion and solvent are used to remove the water. In the fusion technique a steam of inert gas removes the water. This technique is often used for the preparation of long oil alkyd resins. In the solvent technique an aromatic solvent (usually xylene), which is immiscible with water is used to form an azeotropic mixture. This technique is mostly useful for short oil alkyd systems.[61,85]



Scheme 1.1: Preparation of alkyd resin.

Fatty acid process

In this method of preparation, the components polyacid, polyalcohol, and fatty acid are added at the same time and subjected to heat. Alkyd resins obtained by this process have high viscosity, good drying, and hardness properties.[15] This process also allows greater freedom in terms of formulation of the resin components.[62] As fatty acid process do not involves any intermediate step, it is advantageous over the monoglyceride process. Moreover, unlike monoglyceride process, this process avoids the use of catalyst and hence reduces the risk of discoloration and oxidation of the resins. The process requires shorten time as compared to the monoglyceride process. However, the process uses more expensive and corrosive fatty acids and requires corrosion resistance equipment for storage. In addition to these, to facilitate handling of the fatty acids in liquid form, preheating equipment is needed.

Besides monoglyceride and fatty acid process, the two less commonly used methods for manufacturing of alkyd resins are (i) acidolysis, and (i) fatty acid-oil. The acidolysis method may be regarded as the reverse of the monoglyceride (alcoholysis) process. In this method, the oil is reacted with the polybasic acid in the first stage and followed by esterification with a polyol in the second stage. Since the process is carried out at high temperature (280-300 °C), side reaction like dimerization of the oil may occur, resulting discoloration of the resins.[61] However, methods have been developed to overcome the problems associated with high process temperature.[89] As the process avoids the use of any catalyst, hence it can be a commercially viable process.

In the fatty acid-oil process, direct reaction of fatty acid, oil, polyols, and the polybasic acid is carried out. The process results high viscosity alkyd resins and has an economic benefit over fatty acid process.[90]

1.3.4 Modification of alkyd resins

To achieve desired level of properties of existing polymers for different industrial applications, modification by physical and/or chemical means is one of the most adaptable techniques. Because, for the development of new polymers it requires new set-up, more time and labor, and ultimately more cost. In the case of alkyd resins, the presence of reactive functionalities like double bonds, hydroxyl groups, carboxyl groups, and ester linkages provide tremendous potential for their modifications. Therefore, alkyd resins with desired properties can be obtained by proper modification with varieties of reactive chemicals and other polymers. The last decade extensive research efforts have been devoted to develop new coating systems based on alkyd resins. These include waterborne coatings, organic-inorganic hybrid and nanocomposite coatings, with superior performance relative to their traditional counterparts.[5]

The short oil alkyd resins with higher proportion of hydroxyl groups can be modified with urea-formaldehyde and melamine-formaldehyde resins to enhance the drying rate, hardness, exterior durability, and alkali resistance. Blends of alkyd resins with chlorinated rubber exhibits better chemical resistance, toughness, and drying time than the virgin one. Reactive silicone intermediates can be used to improve the durability, gloss retention, and heat resistance property of long oil air drying alkyd resins.[62] Unpigmented polymer films can be obtained from silicone acrylate–soya alkyd resins, which exhibits excellent mechanical properties and good exterior durability compared to silicone modified alkyd resin.[91] Dutta et al. reported the preparation of Mesua ferrea L. seed oil modified alkyd-epoxy blends for multipurpose coatings. The blends showed good performance with respect to drying time, hardness, flexibility, gloss, thermal stability, and alkali resistance.[92] Chlorinated rubber seed oil based alkyd resins possess superior drying and flame retardant characteristics relative to their unchlorinated counterparts.[73] Odetoye et al. reported the blending of jatropha oil-based alkyd with acrylic resins. The blended resins dried hard within 5 min, which is comparable with that of the commercial standards. The white gloss paint formulated from the alkyd–acrylic blends (1:3) dried hard within 2 h at an outdoor temperature of 37 ± 2 °C.[93] Soybean oil based water borne alkyd resins for the use of anticorrosive protective coatings can be obtained by the inclusion of s-triazine ring. As compared to the solvent borne coatings these coatings showed good performance in alkaline media.[94] Organosiloxane modified alkyd resins have improved water resistance, wear resistance, thermal stability, and insulating property.[95] Murillo et al. reported the preparation of hyperbranched alkyd resins based on tall oil fatty acids using acid catalysis. The resins exhibited excellent adhesion, flexibility, drying time, gloss and chemical resistance.[83] Saravari et al. reported the synthesis of castor oil/jatropha oil modified urethane alkyd resins. The coating performances of the synthesized resins were comparable with that of the commercial one.[96] Naik, et al. prepared soya fatty acid-based hyperbranched alkyd (HBA) resins. The HBA resins containing unreacted hydroxyl groups were reacted with isophorone diisocyanate to make high solid hyperbranched urethane alkyd (HBUA) resins. The excess -NCO content in the HBUA resins was used to cure with atmospheric moisture, and thus moisture-cured HBUA coatings were formed.[97]

The double bonds in the fatty acid chains of vegetable oil facilitate various modifications to produce alkyd resins with superior properties. For instance the curing time, thermal stability, and tensile strength of jatropha oil based alkyd resins can be improved by epoxidation of the double bonds in alkyd resins and subsequent curing by an aqueous citric acid solution.[57] Odetoye et al. reported the preparation of modified *Jatropha curcas* oil based alkyd resins with improved drying properties. The oil was modified through epoxidation followed by hydroxylation and dehydration in order to increase the degree of unsaturation in the fatty acid chain. Drying performances of white gloss paints formulated from the desaturated oil alkyd, considering a pigment-volume concentration of 20.67% gave improved results.[93] One of the widely studied methods for improving the performance characteristics of alkyd resins is the use of alkyd-acrylic copolymers. The copolymerization brings the specific properties of each component to the resulting polymer. Basically, high gloss, good adhesion, and oxidative drying of the alkyd resins, and rapid drying, good film formation, and favorable chemical resistance of the acrylic latexes are expected. Graft copolymerization of dehydrated castor oil modified alkyd resins with methyl methacrylate and butyl methacrylate significantly improves the drying time and weather resistance property of the resins.[98] Medium oil alkyd resins, based on acrylated *Albizia benth* oil showed superior characteristics in terms of drying time, scratch resistance, impact resistance, adhesion, flexibility, and chemical resistance.[99] Uschanov et al. prepared conjugated and non-conjugated tall oil fatty acid based alkyd resins and further copolymerized with acrylates (methyl methacrylate and butyl acrylate) via miniemulsion polymerization. The steric hindrance of methyl methacrylate influenced the degree of grafting of acrylate and monomer conversion. This work showed that it is possible to prepare stable hybrids, alkyd–acrylate copolymers, with varied chemical composition.[78] Thanamongkollit et al. prepared UV-curable tung oil based alkyd resins by reacting trimethylolpropane trimethacrylate onto the α-eleosterate of tung oil alkyd molecule via a Diels–Alder reaction.[68] Alkyd resins with special rheological properties can be achieved by the incorporation of polyamide (2-10%) at elevated temperature.[100]

However, challenges still remain in terms of properties and performance compared to conventional petroleum based products. The mechanical and thermal properties need to improve for their practical applications. In addition, the resins suffer inferior properties in terms of corrosion resistance, hardness, scratch hardness, anti-microbial activity, barrier property, large volume shrinkage, etc. In this regard, decoration of polymer nanocomposites can offer an effective way to improve the performance characteristics of the conventional polymers. Nanotechnology is found to solve many of the coating related problems with tremendous improvement in the field performance, as compared to the conventional paints and coatings systems.[101] Incorporation of nanoparticles significantly improves the resinous properties of the bio based resins. For instance, incorporation of nanoparticles like silica, silver, and carbon black improves corrosion resistance, anti-microbial activity, and thermal-mechanical properties of the polymers.[102-104]

1.4 Nanocomposite perspective

Research has shown that the development of polymer nanocomposite technology not only expands the performance space traditional polymers but also introduces completely new combinations of properties and thus enables modern technological applications for polymer materials.[105,106] A polymer nanocomposite is a multiphase material which has at least one dimension in the range 1–100 nm or structures that exhibit nanoscale repeat distances between the different phases that make up the material. In particular, attention has been given to those in which nanofillers are dispersed in a polymer matrix.[107] The unique combination of the inherent characteristics of the nanoparticles, such as a high aspect ratio, novel mechanical, electronic, and optical properties, thermal stability, and large number density of particles per particle volume, particle-particle correlation arising at low volume fraction, affects the inherent properties of polymer matrices significantly. It is believed that the interaction between filler and matrix at a nanoscale level is the basis for new and novel properties of the nanocomposites.[107,108] Over the past few years, researchers have extensively used a variety of nano-fillers for the development of advanced nanocomposite materials with balanced properties by exploiting the advantages offer by the nanometer-size fillers. For example, nanoparticles such as clays,[109] carbon nanotubes,[110] graphene oxide,[111] expanded graphite,[2] graphene,[112] metal-oxide,[113] fullerene,[114] polymeric nano-fillers,[115] polyhedral oligomeric silsesquioxanes,[116] metal–non-oxide ceramics[117] have been used extensively for the preparation of nanocomposites with almost all types of polymer matrices. However, clay containing polymer nanocomposites have received intensive attention in today’s materials research as compared to the others.[118] It is due to the fact that incorporation of a small weight percentage of nano clay platelets into a polymer matrix can enhance the mechanical and material properties of the polymer significantly without losing the inherent processability of the polymer. Additionally, clays are naturally abundant, economical, and most importantly, they are benign to the environment and humans.[108] Over the past few decades, a number of methods have been developed for the preparation of clay based polymer nanocomposites (Fig. 1.10). However, the preparative methods are divided into

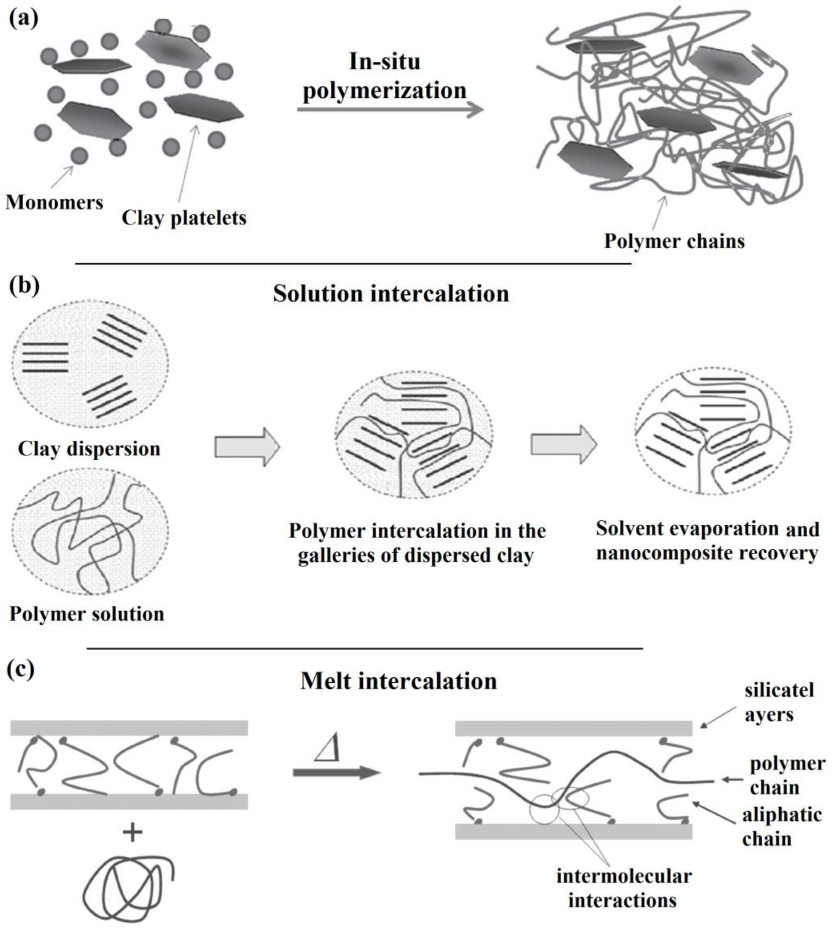


Fig. 1.10: Schematic drawings of three main processing techniques for the preparation of clay-containing polymer nanocomposites: (a) in-situ polymerization, (b) solution intercalation, and (c) melt intercalation.[108]

three main groups. The first one is in-situ polymerization, in which the clay particles are swollen by a liquid monomer or a monomer solution such that polymer formation can occur between the clay layers. The polymerization reaction can be initiated either by heat or radiation, or by a suitable catalyst. The second method is the solution intercalation, in which clay particles are first swollen in a solvent, such as water, chloroform, or toluene and mixed with a polymer solution. The polymer chains intercalate and displace the solvent within the layers of the silicate and the intercalated structure remains upon solvent evaporation. The third technique involves the mixing of a polymer and clay above the softening point of the polymer under shear. This method is known as melt intercalation and has great advantages over both in-situ intercalative polymerization and polymer solution intercalation technique.

In the field of surface coatings, incorporation of nano-fillers imparts special properties to the polymer matrix and it can offer multifunctional coatings. A small concentration of the nano-fillers can reinforce polymer matrix without disturbing the transparency and other properties of the coatings. The most commonly used nano-fillers in this field are TiO_2,[119,120] Fe_2O_3,[101,121] Al_2O_3,[122,123] SiO_2,[124,125] $CaCO_3$,[126,127] ZnO,[128,129] and clay.[130,131] These nano-fillers impart specific properties to the coatings. Dhoke et al. showed that addition of extremely small concentration of nano-ZnO can improve the corrosion resistance, scratch resistance, and abrasion resistance of the alkyd-based waterborne coatings to better extent without disturbing the optical transparency of the coatings. Moreover, it imparts strength to the coatings preventing it from photo-degradation. A small loading level of nano-ZnO in the coating system decreases the curing temperature as compared to the neat coating and thereby it improves the curing and film forming properties.[132] The heat stability and mechanical properties of the silicone-modified alkyd-based waterborne coatings can be improved significantly by the incorporation of very small amount of nano-ZnO. This coating can serve as a good scratch, abrasion, and heat-resistant coating and can find applications in various automotive industries, smoke stacks, stoves, furnaces, heaters, and incinerators and other practical situations where the metal is subjected to high temperature.[133] NiO nanoparticles have remarkable reinforcement on the thermal, mechanical, and flame retardant properties of alkyd-epoxy blends.[3] Nano-Fe_2O_3 modified alkyd based waterborne coatings exhibits effective barrier against corrosive environment.[101] Dhoke and Khanna prepared a nanocomposite coating based on nano-Fe_2O_3 and waterborne alkyd resins. The Fe_2O_3/alkyd nanocomposite coatings showed improved corrosion and UV resistance properties, and better mechanical properties like abrasion and scratch hardness.[121] Graphene oxide significantly improves the thermal and mechanical properties of alkyd-epoxy blends and accelerates the curing rate.[134] Along with the thermal and mechanical properties, the flame retardant property of alkyd-epoxy blends can be enhanced to a greater extent by the incorporation of expanded graphite.[2] Coatings prepared from polyaniline–nano-TiO_2 were found to exhibit excellent corrosion resistance much superior to polyaniline (PANI) in aggressive environments. Apart from corrosion resistance, these coatings have good gloss and shiny surface, which is not easily obtained in conventional coating.[135] Alam et al. reported the preparation of highly corrosion resistant polyaniline/alkyd ecofriendly coatings. These coatings are also quite effective against acid, alkaline as well as saline corrosion even in the absence of top barrier coat.[136] Nano-Al_2O_3 also significantly improves the corrosion resistance of alkyd based waterborne coatings.[122] In addition, incorporation of nano-alumina influences the scratch behavior and mechanical properties of polyurethane coatings.[123] The anticorrosive performance and Young's modulus of the epoxy coatings can be enhanced by the decoration nanocomposites with nano-SiO_2.[137] Addition of a small amount of nano-silica increases the hardness, abrasion resistance, and tensile properties of the polyester-based polyurethane coatings.[125] Bhanvase and Sonawane reported the preparation of a new alkyd based nanocomposite coatings with nano-$CaCO_3$ and water-based polyaniline (PANI). Their study revealed that the nanocomposite coatings are superior in terms of mechanical and anticorrosion performances over neat PANI.[126] Polymer/layered silicate nanocomposite coatings possess excellent gas barrier and anticorrosive properties. However, the anticorrosive performances are strongly influenced by their nano-scale structure and interfacial characteristics.[131]

1.5 Applications

Alkyd resins find a wide range of applications due to their versatile properties such as faster drying time, gratifying gloss, excellent adhesion, and overall low cost. They also possess outstanding flexibility, toughness, and flow behavior with excellent thermal and mechanical properties. Furthermore, the properties of these resins can be tailored by the proper choice of the large variety of components. Thus with these virtue alkyd resins may be regarded as a milestone in the industrial application of coatings.[138] Alkyd resins can be used as both decorative as well as protective purposes like lacquers, textile finishes, top side marine coatings, architectural enamels, metal primers, printing inks, water emulsion paints, etc.

Alkyd based paints are popular in applications that require a high gloss and durable finish. They are most suitable choice for a variety of surfaces, including plaster, wallpaper, aluminum, and wrought iron. Alkyd paints provide a lustrous, heavy duty finish that stands up well to dirt and stains. These paints are widely preferred for high traffic areas in a home such as hallways and play rooms for children. Moreover, these paints are resistant to humidity and moisture and hence they are good choices for kitchens, bathrooms and also cabinets and furniture. In addition to these, the alkyd resins also find extensive applications as varnishes, adhesives, and composite materials.

However, depending on the property requirement different oil length alkyds are used. For instance long oil alkyd are used in exterior trim paints, wall paints, house paints, coach enamels, anticorrosion paints, marine and metal maintenance paints, offset printing inks, silk screen inks, white and pigmental finishes, etc.[40,85] Although, very long oil tall oil fatty acid based alkyd resins find application in outside house paints, trim, and trellis paints, their use is restricted to printing inks industry.[139] Medium oil alkyd resins based on drying oils or fatty acid mixtures are used as binders for air-drying and forced-drying machinery and industrial coatings such as car repair finishes, coatings for trucks, buses and large capacity vehicles, porch and deck paints, equipment finishes, etc. On the other hand, medium oil alkyd resins based on non-drying oils are used for putty and pencil lacquers, external plasticizer for nitrocellulose lacquers, etc. Short oil alkyd resins along with amino resins are used for metal furniture, garage doors, articles made of steel, bicycles, etc. These resins are also used with urea based resins for acid curing wood varnishes.[85,140]

In addition to the conventional uses of alkyd resins, their ease of modification makes them suitable for many advanced applications. For instance, blends of alkyd resins with chlorinated rubber are used in paints for highway markings, swimming pools, concrete floor, etc. Blends of alkyd resins with other resins, such as epoxy, ketonic, and polyamide resins can find application in anticorrosion paints, primers, varnishes, lacquers, etc.[61]

Nano-Fe_2O_3 modified alkyd based waterborne coatings exhibits excellent corrosion resistance property and can be used as protection for steel structure corrosion.[101] Eco-friendly polyaniline/alkyd coatings may find uses in high performance corrosion resistant paints.[136]

Styrenated alkyd resins are used mostly in wall paints, one coat metal finishes, anti-corrosive primers, and solderable zinc powder coatings. Alkyd resins modified with isocyanates can be used as base resin for garage floor paints, parquet varnishes, marine varnishes, etc. However, alkyd resins modified with high amount of isocyanates are suitable for interior matt and satin-finish varnishes, floor paints, and industrial coatings. Alkyd resin based varnishes used for boats are specially modified with isophorone diisocyanate.[141] Long oil alkyd resin, and styrenated alkyd resin based flame retardant paints can be prepared by the incorporation of (i) bis-pyridine bis-tribromophenoxo copper (II) complex, and (ii) polydibromo-phenylene oxide.[142] In rapid drying roller coatings, alkyd resins are modified with methyl methacrylate.[61] Acrylate grafted dehydrated castor oil based alkyd resins have been used in weather work paint for superstructure of ships.[98] Water soluble silicone-modified alkyd resins are excellent in not only weather resistance but also heat resistance. In addition, the so prepared paints possess excellent water resistance and gloss retention property and can be used for outdoor applications such as topcoat for steel petroleum storage tank, barbecue grills, etc.[143] Alkyd resins have been used in gaskets, flexible insulator, printer rolls, and binders for mica. Patel et al. reported that jatropha and rapeseed oil based alkyd resins can be used as electrical insulation material. The electrical properties like break down strength, surface resistivity, dielectric constant, dissipation factor etc. of the alkyd resins are comparable with the commercial standards.[58]

1.6 Scope and objectives

Many things in our daily life consist of coatings, used either for protective, signal, or decorative purposes. Coating enhances aesthetic beauty and durability of a product. However, the increased sustainability of the coatings is required with the increasing demand for coatings. In addition, the coating materials should possess the properties like solvent-free, ease of application, recyclable, and less waste production. In this regard, alkyd resins based on undepletable and renewable resources like vegetable oils can contribute to enhanced sustainability. With the versatile properties, alkyd resins are of low cost and biodegradable, which give them an altitude above the other vegetable oil derivatives. Moreover, a large number of modifications can be performed on alkyd resins to achieve desired level of characteristics for their practical application.

Vegetable oils are environment friendly as they are biodegradable in nature. In addition, they are available worldwide and have many other social and economic advantages. A large variety of vegetable oils have been utilized for the production of different value added industrial products. *Jatropha curcas* seed oil has drawn special attention to the scientific community with its various attributes. So far jatropha oil has been used widely for the production of biodiesels worldwide. However, it is yet a very new candidate in the field of polymer science. Therefore, the versatility of the plant in this area has to be explored.

Inspired from foregoing discussion, the present thesis aims to develop alkyd resins based on *Jatropha curcas* oil and make them suitable for practical applications. In this regard, efforts have been devoted to prepare blends and nanocomposites from these alkyd resins with other suitable components.

Objectives of the present investigation:

- ☞ Synthesis and characterization of *Jatropha curcas* oil modified alkyd resins.
- ☞ Preparation of blends of *Jatropha curcas* oil modified alkyd resins with commercially available suitable resins.
- ☞ To develop *green technology* in order to improve the performance characteristics of the *Jatropha curcas* oil modified alkyd resins.
- ☞ Fabrication of nanocomposites based on *Jatropha curcas* oil modified alkyd resins with different type of nano-fillers.
- ☞ To characterize and evaluate the properties of the prepared nanocomposites.

Plan of the work:

To fulfill the above objectives the following plans of work have been adopted:

- ☞ Collection of jatropha seeds from local areas and oil extraction and purification by conventional method.
- ☞ Synthesis of *Jatropha curcas* oil modified alkyd resins by two stage alcoholysis-polyesterification reactions and their characterization.
- ☞ Preparation of *Jatropha curcas* oil modified alkyd/epoxy resin blends and their properties evaluation.
- ☞ Preparation of blends of epoxidized alkyd resins based on jatropha oil and the epoxidized oil cured with an aqueous citric acid solution.
- ☞ Preparation of alkyd resin based nanocomposites with nano-fillers such as expanded graphite (EG) and graphene oxide (GO) and study of their performance characteristics.
- ☞ Characterization of the nanocomposites by FT-IR, SEM, TEM, UTM, TGA, and DSC analysis.

References

1. Septevani, A.A., et al. *Ind. Crop. Prod.* **66,** 16-26, 2015.
2. Gogoi, P., et al. *Prog. Org. Coat.* **77** (1), 87-93, 2014.
3. Gogoi, P., et al. *J. Appl. Polym. Sci.* DOI: 10.1002/APP.41490, 2015.
4. Abdul Khalil, H.P.S., et al. *Renew. Sus. Energ. Reviews* **22,** 667-685, 2013.
5. Alam, M., et al. *Arabian J. Chem.* **7** (4), 469-479, 2014.
6. Lligadas, G., et al. *Biomacromolecules* **11**(11), 2825-2835, 2010,
7. Biermann, U., et al. *Angew. Chem., Int. Ed.* **50** (17), 3854-3871, 2011.
8. Sun, X.S., & Wool, R.P. *Bio-Based Polymers and Composites,* Academic Press, Elsevier, Amsterdam, 2005.
9. Boruah, M., et al. *Prog. Org. Coat.* **74** (3), 596-602, 2012.
10. Altuna, F.I., et al. *Green Chem.* **15** (12), 3360-3366, 2013.
11. Hablot, E., et al. *Macromol. Mater. Eng.* **293** (11), 922-929, 2008.
12. Ahmed, S., et al. *J. Appl. Polym. Sci.* **82** (8), 1855-1865, 2001.
13. Lu, Y., & Larock, R.C. *Chem. Sus. Chem.* **2** (2), 136-147, 2009.
14. Xia, Y., & Larock, R.C. *Green Chem.* **12** (11), 1893-1909, 2010.
15. Güner, F.S., et al. *Prog. Polym. Sci.* **31** (7), 633-670, 2006.
16. Singh S.P., & Singh D. *Renew. Sust. Energ. Rev.* **14** (1), 200-216, 2010.
17. Dalziel, J.M. *The Useful Plants of West-Tropical Africa,* Crown Agents for Oversea Governments and Administration, London, 1955.
18. Duke, J.A. *CRC Handbook of Medicinal Herbs,* CRC Press, Boca Raton, FL, 1985.
19. Heller, J. *Physic Nut Jatropha curcas L. Promoting the Conservation and use of Underutilized and Neglected Crops.* International Plant Genetic Resources Institute, Rome. 1996.
20. Kaushik, N., & Kumar, S. *Jatropha curcas L. Silviculture and Uses,* Agrobios, Jodhpur, India, 2004.
21. Sherchan, D.P., et al. *Effect of green manure on rice production,* PAC Occasional Paper-2, Pakhribas Agricultural Centre, Dhankuta, Nepal, 1989.
22. Visser, J., & Adriaans, T. *Anaerobic digestion of Jatropha curcas press cake,* Report produced for FACT, Ingenia Consultants & Engineers, Eindhoven, 2007.

23. Martinez-Herrera, J., et al. *Food Chem.* **96** (1), 80-89, 2006.
24. Openshaw, K. *Biomass Bioenerg.* **19** (1), 1-15, 2000.
25. Kumar, A., & Sharma, S. *Ind. Crop. Prod.* **28** (1), 1-10, 2008.
26. Contran, N., et al. *Ind. Crop. Prod.* **42,** 202-215, 2013.
27. Verma, K.C., & Gaur, A.K. *World J. Agr. Sci.* **5** (5), 552-556, 2009.
28. Abdulrahaman, A.A., & Oladele, F.A. *Anatomical basis for optimal use of water for maintenance of some mesophytic plants,* Insight Botony, 2011.
29. Achten, W.J.M., et al. *Biomass Bioenerg.* **32** (12), 1063-1084, 2008.
30. Singh, R.N., et al. *Renew. Energ.* **33,** 1868-1873, 2008.
31. Jain, S., & Sharma, M.P. *Renew. Sust. Energ. Rev.* **14,** 763-771, 2010.
32. Puhan, S., et al. *J. Sci. Ind. Res.* **64,** 890-896, 2008.
33. Jongh, J. (ed.). *The jatropha handbook, from cultivation to application*, FACT Foundation, Eindhoven, 2010.
34. Berchmans, H.J., & Hirata, S. *Bioresour. Technol.* **99** (6), 1716-1721, 2008.
35. Aung, M.M., et al. *Ind. Crop. Prod.* **60,** 177-185, 2014.
36. Adriaans, T. *Suitability of Solvent Extraction for Jatropha curcas*, FACT Foundation 9, Eindhoven, 2006.
37. Koh, M.Y., & Ghazi, G.T.M. *Renew. Sust. Energ. Rev.* **15** (5), 2240-2251, 2011.
38. Carr, R.A. *J. Am. Oil Chem. Soc.* **55** (11), 765-771, 1978.
39. Leung, D.Y.C., et al. *Appl. Energ.* **87,** 1083-1095, 2010.
40. Oil and Color Chemist's Association of Australia, *Surface Coatings,* Chapman & Hall, London, 1981.
41. Parawira, W. *Sci. Res. Essays* **5,** 1796-1808, 2010.
42. Kheira, A.A.A, & Atta, N.M.M. *Biomass Bioenerg.* **33** (10), 1343-1350, 2009.
43. Akintayo, E.T. *Bioresour. Technol.* **92** (3), 307-310, 2004.
44. Zhang, C., et al. *Green Chem.* **15** (6), 1477-1484, 2013.
45. Gübitz G.M., et al. *Biores. Technol.* **67** (1), 73-82, 1999.
46. Li, Y.C., et al. *J. Plant Res. Environ.* **18** (4), 72-78, 2009.
47. Hazmi, A.S.A., et al. *Ind. Crop. Prod.* **50,** 563-567, 2013.
48. Saalah, S., et al. *Ind. Crop. Prod.* **64,** 194-200, 2015.

49. Meshram, P.D., et al. *Prog. Org. Coat.* **76** (9), 1144-1150, 2013.
50. Alam, M., & Alandis, N.M. *J. Polym. Environ.* **19** (3), 784-792, 2011,
51. Kadam, P.G., et al. *J. Adhes. Sci. Technol.* **28** (7), 675-689, 2014.
52. Alam, M., & Alandis, N. M. *High Perf. Polym.* **24,** 538-545, 2012.
53. Meier, M.A.R. et al., *Chem. Soc. Rev.* **36,** 1788-1802, 2007.
54. Xu, J., et al. *J. Am. Oil Chem. Soc.* **79,** 593-596, 2002.
55. Xu, J., et al. *J. Am. Oil Chem. Soc.* **81,** 813-816, 2004.
56. Sammaiah, A., et al. *J. Oleo Sci.* **63** (6), 637-643, 2014.
57. Gogoi, P., et al. *ACS Sustainable Chem. Eng.* **3** (2), 261-268, 2015.
58. Patel, V.C., et al. *J. Appl. Polym. Sci.* **107** (3), 1724-1729, 2008.
59. Odetoye, T.E., et al. *Ind. Crop. Prod.* **32** (3), 225-230, 2010.
60. Kumar, M.N.S., et al. *J. Polym. Environ.* **18** (4), 539-544, 2010.
61. Malshe, V.C., & Sikchi, M. *Basics of paint technology,* UICT, Mumbai, 2004.
62. Paul, S. *Surface coatings science & technology,* John Wiley & Sons, New York, 1997.
63. Hofland, A., *Prog. Org. Coat.* **73** (4), 274-282, 2012.
64. Narkhede, M.N. *J. Col. Soc.* **30,** 2-10, 1991.
65. Dutta, N., et al. *Prog. Org. Coat.* **58** (1), 40-45, 2007.
66. Makarewicz, E. *Prog. Org. Coat.* **28** (2), 125-132, 1996.
67. Onukwli, O.D., & Igbokwe, P.K. *J. Eng. Appl. Sci.* **3** (2), 161-165, 2008.
68. Thanamongkollit, N., et al. *Prog. Org. Coat.* **73** (4), 425-434, 2012.
69. Wang, C., & Jones, F.N. *J. Appl. Polym. Sci.* **78** (9), 1698-1706, 2000.
70. Dullius, J., et al. *Prog. Org. Coat.* **57** (2), 123-127, 2006.
71. Tiwari, S., et al. *J. Sci. Ind. Res.* **61** (2), 110-116, 2002.
72. Ogunniyi, D.S., & Odetoye, T.E. *Biores. Technol.* **99** (5), 1300-1304, 2008.
73. Ikhuoria, E.U., et al. *Prog. Org. Coat.* **59** (2), 134-137, 2007.
74. Dutta, N., et al. *Prog. Org. Coat.* **49** (2), 146-152, 2004.
75. Bora, M.M., et al. *Ind. Crop. Prod.* **52,** 721-728, 2014.
76. Aigbodion, A.I., & Okieimen, F.E. *Ind. Crop. Prod.* **13** (1), 29-34, 2001.
77. Ezeh, I.E., et al. *Ind. Crop. Prod.* **36** (1), 94-99. 2012,
78. Uschanov, P., et al. *Prog. Org. Coat.* **63** (1), 92-99, 2008.

79. Manczyk, K., & Szewczyk, P. *Prog. Org. Coat.* **44** (2), 99-109, 2002.
80. Bat, E. et al. *Prog. Org. Coat.* **55** (4), 330-336, 2006.
81. Yin, X., et al. *Prog. Org. Coat.* **77** (3) 674-678, 2014.
82. Wicks, Z.W., et al. *Organic Coatings Science and Technology,* John Wiley & Sons, New Jersy, 1999.
83. Murillo, E.A., et al. *Prog. Org. Coat.* **69** (3), 235-240, 2010.
84. Angiolini, L., et al. *Ind. Paint Powder* **80** (10), 27-30, 2004.
85. Stoye, D., & Freitag, W. *Resins for Coatings Chemistry*, Hanser Publishers, New York, 1996.
86. Phate, B.W., & Gogte, B.B. *Paintindia* **LV** (3), 71-76, 2005.
87. Gryglewicz, S. *Appl. Catal., A* **192** (1), 23-28, 2000.
88. Goff, M.J., et al. *J. Am. Oil Chem. Soc.* **81** (4), 415-420, 2004.
89. Carlston, E.F. *J. Am. Oil Chem. Soc.* **37** (7), 366-371, 1960.
90. Mark, H.F., et al. *Encyclopedia of Polymer Science and Engineering,* Wiley Interscience, New York, 1985.
91. Kanai, T., et al. *Prog. Org. Coat.* **58** (4), 259-264, 2007.
92. Dutta, N., et al. *J. Appl. Polym. Sci.* **100** (1), 516-521, 2006.
93. Odetoye, T.E., et al. *Prog. Org. Coat.* **73** (4), 374-381, 2012.
94. Pathan, S., & Ahmad, S. *ACS Sustainable Chem. Eng.* **1** (10), 1246-1257, 2013.
95. Palmer, C.S. *Composition for protective coatings*, **US Patent No. 1395451,** November 01, 1921.
96. Saravari, O., & Praditvatanakit, S. *Prog. Org. Coat.* **76** (4), 698-704, 2013.
97. Naik, R.B., et al. *J. Coat. Technol. Res.* **11** (4), 575-586, 2014.
98. Majumdar, S., et al. *J. Coat. Technol.* **70** (879), 27-33, 1998.
99. Akintayo, C.O., & Adebowale K.O. *Prog. Org. Coat.* **50** (4) 207-212, 2004.
100. Winkler, W.B. *Ester modified polyamide resins,* **US Patent No. 2663649,** December 22, 1953.
101. Dhoke, S.K., & Khanna, A.S. *Mater. Chem. Phys.* **117** (2), 550-556, 2009.
102. Zhang, W., et al. *Corros. Sci.* **49** (2), 654-661, 2007.
103. Dolatzadeh, F., et al. *Corros. Sci.* **53** (12), 4248-4257, 2011.

104. Dinh, D.A., et al. *Appl. Surf. Sci.* **298,** 62-67, 2014.

105. Ray, S.S. *Clay-Containing Polymer Nanocomposites: From Fundamental to Real Applications*, Elsevier, Amsterdam, 2013.

106. Ray, S.S. *Environmentally Friendly Polymer Nanocomposites: Types, Processing and Properties*, Woodhead Publishing, London, UK, 2013.

107. Ray, S.S. *Acc. Chem. Res.* **45** (10), 1710-1720, 2012.

108. Ray, S.S. *Macromol. Chem. Phys.* **215** (12), 1162-1179, 2014.

109. Zhu, J., et al. *Chem. Mater.* **13** (10), 3774-3780, 2001.

110. Moniruzzaman, M., & Winey, K.I. *Macromolecules* **39** (16), 5194-5205, 2006.

111. Yingjuan, H., et al. *Chem. Mater.* **22** (13), 4096-4102, 2010.

112. Yang, X., et al. *Polymer* **51** (15), 3431-3435, 2010.

113. Cioffi, N., et al. *Chem. Mater.* **17** (21), 5255-5262, 2005.

114. Laiho, A., et al. *Appl. Phys. Lett.* **93** (20), 203309(1-3), 2008.

115. Jang, J., et al. *Polymer* **46** (11), 3677-3684, 2005.

116. Fu, B.X., et al. *Polymer* **42** (2), 599-611, 2001.

117. Hauser, R., et al. *J. Mater. Sci.* **43** (12), 4042-4049, 2008.

118. Yao, H.B., et al. *Angew. Chem. Int. Ed.* **49** (52), 10127-10131, 2010.

119. Allen, N.S., et al. *Polym. Degrad. Stab.* **85** (3), 927-946, 2004.

120. Li, F., et al. *Polym. Eng. Sci.* **46** (10), 1402-1410, 2006.

121. Dhoke, S.K., & Khanna, A.S. *Corros. Sci.* **51** (1), 6-20, 2009.

122. Dhoke, S.K., & Khanna, A.S. *Prog. Org. Coat.* **74** (1), 92-99, 2012.

123. Sung, L.P., et al. *J. Coat. Technol. Res.* **5** (4), 419-430, 2008.

124. Zhou, S., et al. *Prog. Org. Coat.* **45** (1), 33-42, 2002.

125. Zhou, S.X., et al. *J. Appl. Polym. Sci.* **88** (1), 189-193, 2003.

126. Bhanvase, B.A., & Sonawane, S.H. *Chem. Eng. J.* **156** (1), 177-183, 2010.

127. Yu, H.J., et al. *Prog. Org. Coat.* **55** (3), 296-300, 2006.

128. Xu, T., & Xie, C.S. *Prog. Org. Coat.* **46** (4), 297-301, 2003.

129. Yang, L.H., et al. *Prog. Org. Coat.* **53** (2), 91-98, 2005.

130. Yeh, J.M., et al. *Eur. Polym. J.* **44** (10), 3046-3056, 2008.

131. Yeh, J.M., & Chang, K.C., *J. Ind. Eng. Chem.* **14** (3), 275-291, 2008.

132. Dhoke, S.K., *Prog. Org. Coat.* **64** (4), 371-382, 2009.

133. Dhoke, S.K., et al. *Prog. Org. Coat.* **64** (1), 39-46, 2009.

134. Gogoi, P., et al. *Prog. Org. Coat.* DOI: 10.1016/j.porgcoat.2014.09.022, 2014.

135. Radhakrishnan, S., et al. *Electrochim. Acta* **54** (4), 1249-1254, 2009.

136. Alam, J., et al. *Curr. Appl. Phys.* **9** (1), 80-86, 2009.

137. Shi, X., et al. *Surf. Coat. Technol.* **204** (3), 237-245, 2009.

138. Bruning, H.H. *Ind. Crop. Prod.* **1** (2-4), 89-99, 1992.

139. Myers, R.R., & Perez, R.J. *Film Forming Compositions: Treatise on Coatings,* Marcel Decker, New York, 1972.

140. Sarma, B., et al. *J. Sci. Ind. Res.* **60** (2), 153-158, 2001.

141. Oldring, P.K.T. *Resins for Surface Coatings*, John Wiley & Sons, New York, 2000.

142. Gündüz, G., et al. *Polym. Degrad. Stab.* **64** (3), 501-504, 1999.

143. Mikami, R. & Hanada, T. *Process for preparation of water-soluble, silicone modified alkyd resins*, **US Patent No. 4069178,** January 17, 1978.