DEVELOPMENT OF POLYESTER RESINS FROM *MESUA FERREA* L. SEED OIL

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Dedicated to my

Ma and Baba

Development of Polyester Resins from *Mesua ferrea* L. Seed Oil

ABSTRACT

The depletion of world oil pool, rising price of petroleum crude oil and stringent environment rules and regulations are pressurizing the polymer scientists to utilize renewable resources as feedstocks for development of polymers. These feedstocks are well accepted by industries due to economical and environmental reasons. In this regard, vegetable oils have a number of advantages as feedstocks for development of many industrial polymers in addition to many other applications. The advantages of vegetable oils are (i) renewable resource, (ii) environment friendly, (iii) biodegradable, (iv) cost effective, (v) available in sufficient quantity, (vi) physically and chemically stable, (vii) easy chemical modification, (viii) possibility of recycling, etc. Vegetable oils play an important role not only for edible purposes but also for non-food applications such as surface coatings including paint, varnishes, etc., printing inks, soaps, shampoos, shoe polishes, cosmetics, pharmaceuticals, lubricants, emulsifiers, plasticizers, multipurpose additives, bio-diesels, etc.

Vast varieties of plants are available in India. The seeds of many such plants contain a large amount of oils. The traditional seeds like linseed, soybean, safflower, coconut, castor oil, etc. have been successfully used commercially for the production of different kinds of resins like polyester (alkyd), polyurethane, polyesteramide, etc. The seeds like natural rubber, karanja, *annona squmosa,* neem, etc. are also under the process of development for production of above resins. These resins are largely used in different industrial applications such as paints, inks, binder for composites, etc. A major portion of these vegetable oils is used in the preparation of polyester (alkyd) resins. Oil modified polyester resins are regarded as workhorse of coating industry. These are of low cost than most of the others resins and give coatings that exhibit fewer film defects during application. However, they suffer from some major problems such as low alkali resistance, low hardness, moderate adhesion, long drying time at higher temperature especially for non-drying vegetable oil. These properties can be modified by physical or chemical blending with many other resins and reactive functional chemicals such as nitrocellulose, amino resins, silicone resins, epoxy resins, isocyanates, styrene, etc.

Mesua ferrea L. (Nahar) plants are available in different parts of India such as Uttar Pradesh, West-Bengal, Western Ghats and especially in North-Eastern part of the country. Nahar seeds contain exceptionally high amount of (70-75%) non-edible oil. This oil possesses oleic (52.3%) and linoleic (22.3%) acids as unsaturated fatty acids and palmitic (15.9%) and stearic acids (9.5%) as saturated fatty acids. Nahar oil may be utilized for the synthesis polyester resins along with other polymers.

SCOPE AND OBJECTIVES

From the literature it has been found that Nahar seed oil is being utilized in the field of bio-diesel and medicines. To our knowledge, this oil has not been utilized in the field of polymer. In addition to this, the fatty acid composition of this oil also reveals that there is a scope of utilizing this oil in the field of polymers.

Under the above facts, the main objectives of the present investigation are as follows:

i) To extract, purify and characterize the Nahar seed oil and its heat treatment for surface coating applications.

ii) To synthesize and characterize conventional polyester (alkyd) resins from the purified oil.

iii) To improve the performance characteristics of polyester resins by blending with other commercial resins.

iv) To use polyester resin as binder material for production of any industrial coating material.

THE THESIS

Chapter 1 deals with the general introduction of vegetable oils and their utilization for the production of polyester (alkyd) resins. A brief review on polyester resins from vegetable oils has been described with meeting the importance, history, general techniques, characterizations, properties and applications. This chapter also described the scope and objectives along with the plan and methodology of the present investigation.

Chapter 2 includes characterization and properties of the purified Nahar oil along with the heat treated oil. The structural analyses of unheated and heated oils at two different temperature, viz. (250±5) ^{0}C and (315±5) ^{0}C for a specified period of time have been studied by spectroscopic methods such as FT-IR, ^{1}H-NMR and GPC analysis as well as by the determination of physical properties such as acid value, iodine value, saponification value, specific gravity etc. The rheological behavior of heated oils has also been studied by Brookfield viscometer. An attempt has been made to establish the co-relationship between variation of viscosity and time of heating.

The film properties such as pencil hardness, gloss, flexibility, adhesion and chemical resistance of the above heated and unheated oils have been investigated. Oils were cured at 200 ^{0}C for specified period of time after mixing with 30 phr (parts per hundred of resin) styrene, 8 phr MEKP (methyl ethyl ketone peroxide) and 4 phr cobalt octate

Chapter 3 involves the synthesis, characterization and properties evaluation of three different polyester resins from the purified Nahar seed oil. The resins with ~55% oil length were synthesized by alcoholysis process of the oils with glycerol to form monoglyceride at (240±5) ^{0}C in the presence of PbO as the catalyst followed by polycondensation with three different ratios of saturated (phthalic anhydride, PA) and unsaturated acid anhydride (maleic anhydride, MA). The polyester resins have been characterized by measurement of physical properties like acid value, iodine value, volatile matter content, viscosity, etc. and spectroscopic techniques such as FT-IR and ^{1}H-NMR. The polyesters resins were cured by mixing with 30 phr styrene as a reactive diluent, 4 phr methyl-ethyl ketone peroxide as an initiator and 2 phr cobalt octate as an accelerator (on the basis of resin weight) at 175 ^{0}C for 9 h (100% PA), at 150 ^{0}C for 7 h (50/50 PA/ MA) and 6 h (25/75 PA/MA) respectively. The film properties such as pencil hardness, flexibility, gloss, adhesion and chemical resistance in different media of the resins were determined. The polyester resin of 50/50 PA/MA showed the optimum properties.

Chapter 4 reports studies on blending properties of above three polyester resins with commercial bisphenol-A based epoxy resin. The blends of the polyester resins with epoxy resin (Araldite 250, Ciba Geigy) were prepared by the solution blending technique using 50/50 (weight/weight) benzene and petroleum ether solvent mixture at room temperature. Both the resins were diluted to 50% solid content and mixed with hardener (Hardener HY 840, Ciba Geigy, 50% of epoxy resins by weight). The film properties of the blends like drying time, gloss, flexibility, pencil hardness, adhesion, impact resistance and chemical resistance in different media like dilute acid, dilute alkali, water, salt solution, etc. were determined. The morphology and thermostability of the blends were characterized by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). This study showed better performance of the blends with respect to drying time, hardness, flexibility, gloss, impact, thermal stability and chemical resistance, especially the alkali resistance.

Chapter 5 describes the blending properties of a 100% phthalic anhydride based short oil alkyd (polyester ~ 40% oil length) with partially butylated melamine formaldehyde MF) resin. The blends of above polyester and MF resins were prepared by mixing them at different weight ratios (80:20, 70:30, 60:40, 50:50, 20:80 and 0:100) with 0.5% (by weight with respect to the total resin) *p*-toluene sulfonic acid (as 2% weight/volume acetone solution). The blends were cured at 120 ^{0}C for 1 h for all cases. The film properties such as pencil hardness, gloss, flexibility, impact resistance, adhesion and chemical resistance in different media of the blends were studied. The morphology and thermal stability of the blends were investigated by scanning electron microscopy and thermogravimetric analysis. The results showed a significant improvement of blend properties especially hardness, thermostability and chemical resistance.

Chapter 6 reports the use of a polyester resin as binder material for industrial stoving paint. The preparation, characterization and properties of this stoving paint are described in this chapter. The maximum work of this chapter was carried out in a paint industry using their set up to establish the commercial viability of this resin. The results indicate that this resin may be used for a low cost stoving deep color paint.

Chapter 7 includes the concluding remarks, highlights of the findings and future scopes of the present investigation. The major achievements of the present investigation are as follows.

i) The heat treatment of a non-drying vegetable oil (Nahar) at higher temperature can cause a significant change in structural characteristics and rheological behavior. Heat treatment also marginally improved the film properties.

ii) This vegetable oil (Nahar) was successfully utilized for the preparation of polyester resins.

iii) The blending of polyester resin with commercial epoxy and melamine-formaldehyde resins significantly improved the drying time, a few film properties of Nahar oil based polyester resins.

iv) A polyester resin based on Nahar oil has been used for the first time to investigate the viability for commercial utilization as a binder for a stoving paint.

Declaration

I hereby declare that the thesis entitled "**Development of Polyester Resins from *Mesua ferrea* L. Seed oil**", being submitted to the Department of Chemical Sciences, Tezpur University, is a record of original research work carried out by me. All sources of assistance have been assigned due acknowledgment. I also declare that neither this work as a whole nor a part of it has been submitted to any other University or Institute for any other degree, diploma or award.

Date: 22.06.06.
Place: Napaam, Tezpur

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CERTIFICATE

This is to certify that the thesis entitled **"Development of Polyester Resins from *Mesua ferrea* L. Seed Oil"** submitted to Tezpur University in the Department of Chemical Sciences under the School of Science and Technology, in partial fulfillment for the award of the Degree of Doctor of Philosophy in Science, is a record of research work carried out by Nandini Dutta under our supervision and guidance.

All helps received by her from various sources have been duly acknowledged.

No part of this thesis has been reproduced elsewhere for award of any other degree.

Niranjan Karak
Dr. N. Karak
(Principal Investigator)

Prof. S. K. Dolui
(Co-Investigator)

Place: Tezpur University
Date: 22.06.06.

Preface

Depletion of the oil pool, rising cost of petrochemical products and worldwide concern about environmental pollution motivate the scientists to utilize more and more renewable resources as feedstocks for the development of their products. For the polymer scientists, vegetable oil is one of the most useful feedstocks as it has number of advantages. Again, vast varieties of plants are available in India, out of which many plants produce acceptable amount of vegetable oils. These oils are being utilized for production of large varieties of industrial polymers such as polyesters, polyurethanes, polyesteramides, etc.

Mesua ferrea L. (Nahar) plant is available largely in different parts of India especially in north-eastern region. Nahar seeds contain exceptionally high amount of oil. This oil has combinations of saturated and unsaturated fatty acids that can be utilized for the preparation of large verities of polymers.

The main aim of the present thesis is to investigate the possible utilization of this vegetable oil for development of polyester (alkyd) resins. In this study, attempts have been made to prepare, characterize and to evaluate properties of polyester resins based on Nahar seed oil. The heat treated oil has been studied to investigate the possibility of using it as a coating material. The performance characteristics of the prepared polyester resins as coating materials have been improved by blending with commercially available resins. One of these resins has been ultimately utilized to produce an industrial paint.

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List of Abbreviations

cm	centimeter(s)
deg. C/ ^{0}C	degree centigrade
DSC	Differential Scanning Calorimetry
eq	equivalent
FT-IR	Fourier Transform Infrared
g	gram(s)
GPC	Gel Permeation Chromatography
h	hour(s)
k	kilo(s)
L	litre(s)
lb	pound(s)
m	metre(s)
min	minute(s)
mV	millivolt(s)
NMR	Nuclear Magnetic Resonance
ppm	parts per million
Rs	Rupees
TGA	Thermal Gravimetric Analysis
Temp	Temperature
v	volume
w	weight
µm	micrometre

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Chapter 1

General Introduction

1.1 Introduction

Now a days, the use of petroleum-based products in manufacturing different industrial products is declining continuously. This is the result of awareness of people to the environmental issues, such as volatile organic solvent emissions and recycling or waste disposal problems, spiraling rise in prices and high rate of depletion of the stocks[1-5]. This has inspired scientists to use renewable natural materials as a viable alternative resource of raw materials for different industrial applications[6-8]. Vegetable oils can play an important role not only for edible purposes but also for industrial applications[9-17]such as surface coatings including paint, varnishes etc., printing inks, soaps, shampoos, shoe polishes, cosmetics, pharmaceuticals, lubricants, emulsifiers, plasticizers, multipurpose additives, biodiesels, etc. These oils have a number of advantages[18-22] like physical and chemical stability, aptitude to facile chemical modification, reduced toxicity, reduced risk for handling and transport, possibility of recycling, renewable and biodegradable, and at the same time available in large quantities in low and stable prices, and are susceptible to agricultural diversification and environmentally benign in nature.

The vast forest resources and farm lands yield a large variety of oil-bearing seeds. A number of seed oils have been used in the synthesis of various polymeric resins like polyester[23, 24], epoxy[25], polyurethane[26], polyesteramide[27], etc. Some of the major seed oils used traditionally for preparation of such resins are linseed, castor, soybean, sunflower, safflower, tung, coconut, etc. Non traditional oils such as rubber seed oil[28], neem oil[18], karanja oil[29, 30], jatropha seed oil[31], kamala seed oil[32], lesquerella oil[33], melon seed oil[34], apricot oil[35], *Annona squmosa*[36], African mahogany seed oil[37], African locust bean seed oil[38], etc. are also used for the same purpose.

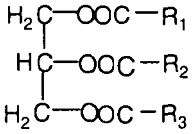
The products based on vegetable oils are developed keeping two criteria in mind. First, the products must meet the same technical and industrial standards as demanded for conventional industrial products, e.g. durability, fastness to exposure, resistance to chemicals, etc. of paints. Secondly, the products must also meet all ecologically relevant standards. For producers of natural paints, ecological compatibility comprises both environmental aspects and human health risk factors[22].

1.2 Vegetable Oils

Many plants produce seeds containing fats. These fats are reserved food for the germinating embryo and worthwhile. They are quite often present in sufficient quantities to make their extraction, in the form of a vegetable oil. Thus vegetable oils are derived from oil-bearing seeds. Many of these vegetable oils are being used in industry and in research and development.

1.2.1 Definition, Classification, Constituents and Importance of Vegetable Oils

The vegetable oils are described as fixed oils. This term separates them from essential oils, the volatile aromatic oils found in the stems and leaves of plants[39]. Vegetable oils are non-volatile but unstable at high temperature[40]. Vegetable oils are mainly triglycerides i.e. glycerine triesters of different fatty acids (Table 1.1) accompanied by mono- and di-glycerides and free fatty acids, but they may also contain phospholipids, free sterols, tocols (tocopherols and tocotrienols), triterpene alcohols, hydrocarbons and fat soluble vitamins[41, 42]. The triglycerides molecule can be expressed as follows



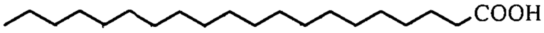
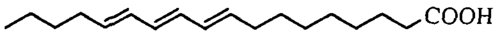
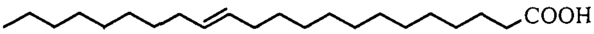
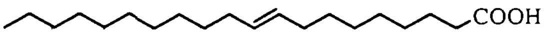
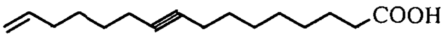
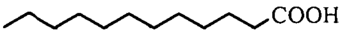
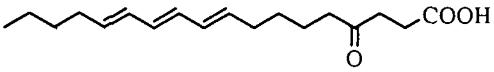
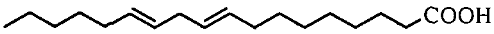
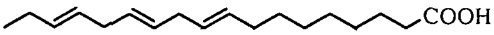
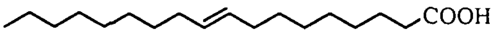
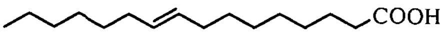
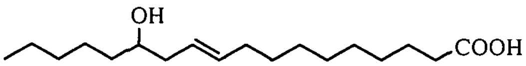
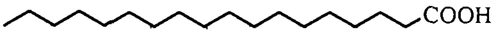
$$\begin{array}{l} H_2C-OOC-R_1 \\ \quad | \\ HC-OOC-R_2 \\ \quad | \\ H_2C-OOC-R_3 \end{array}$$

where R_1, R_2, R_3 represent the hydrocarbon part of different fatty acids.

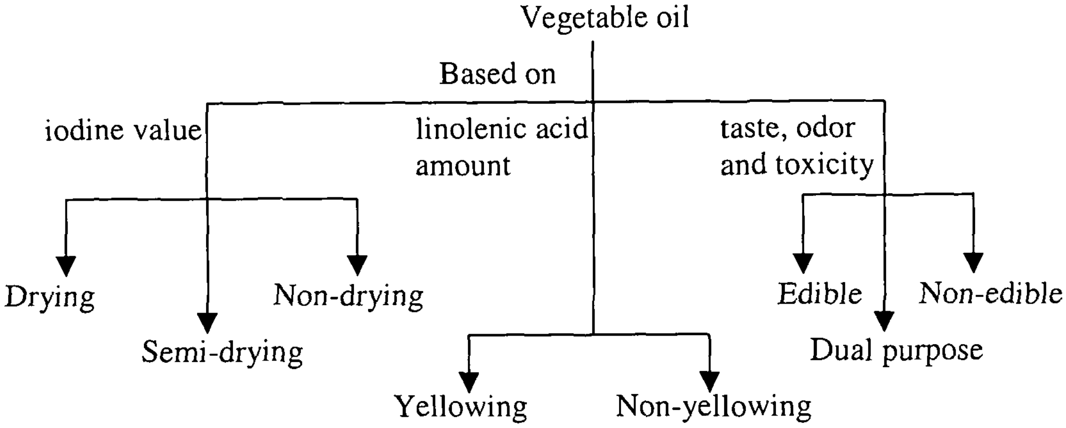
If the fatty acids are of one type, then the triglyceride molecule is called simple triglyceride and if they are of different types, then the triglyceride molecule is termed as mixed triglyceride. Oils are practically almost always mixtures of triglycerides[43] in varying proportions. Oils differ in properties depending upon the nature of fatty acids in the triglyceride molecules[42]. The chemical structures of some fatty acids are given in Table 1.1.

Table 1.1

Chemical structure of some fatty acids

Fatty acid	Structure
Arachidic	
Behenic	
Capric	
Caproic	
Caprylic	
Eleostearic	
Erucic	
Gadoleic	
Isanic	
Lauric	
Licanic	
Linoleic	
Linolenic	
Myristic	
Oleic	
Palmitic	
Palmitoleic	
Ricinoleic	
Stearic	

The general classification of vegetable oils is given in the following scheme (Scheme 1.1)



Scheme 1.1 Classification of vegetable oil

Fatty acids may be saturated or unsaturated. The average value of this unsaturation is normally expressed in terms of iodine value. Drying oils having iodine value over 150, are linseed, perilla, tung, oiticica, walnut, etc. The iodine value of semi-drying oil is in between 120-150 and examples are safflower, sunflower, soybean, water melon, rubber seed, niger seed, and tobacco seed, etc. Whereas non-drying oils having iodine value below 120 includes[39] oils like castor, cotton seed, coconut, rapeseed, olive, karanja, ground nut, sesame, rice bran, etc. However, for non-conjugated oils drying characteristic is related with the average number of methylene groups adjacent to two double bonds per oil molecule (f_n). An oil with f_n value > 2.2 is said to be drying oil, whereas oil with f_n value less than 2.2 is semi-drying. The drying rates are more closely related to f_n than iodine values. This method cannot be used to classify conjugated systems, though this method is superior and more reliable than the conventional iodine value method[44]. Another way of categorizing non-conjugated oils is based on drying index, which is defined as, drying index = % linoleic acid + 2 x (% linolenic acid). Oils are said to be drying when drying[45] index is greater than 70. In addition, oils are classified industrially as yellowing or non-yellowing depending on the linolenic acid amount present in the oil. Generally, the drying oils are yellowing and semi-drying and non-drying oils are non-yellowing. Based on odor, taste and toxicity, vegetable oils may be edible e.g. cotton seed, peanut, olive, master, corn, etc. and industrial e.g. perilla, castor, tung, oiticica, etc. Some are used for dual purpose[39] such as sunflower, safflower, rapeseed, soybean, etc.

The utilization of vegetable oils has gained importance in the context of current scenario of polymer development. The primary advantage of using natural and renewable raw material in the development of industrial polymers is the cost reduction. There are other significances also, like employment of people in cultivation of naturally growing plants, collection of oil seeds and isolation of oil from the seeds. They also include the conservation of the energy required to convert the petrochemicals into the synthetic chemicals and conservation of foreign exchange needed to pay for imported oil, a large proportion of petrochemical source. Above all, the plantation will reduce pollution, which is most important for today's society.

1.2.2 Extraction, Storage and Purification

Seeds are collected from the respective trees and pre-treated in a series of processes involving cleaning, dehulling, size reduction if necessary, cooking and flaking to about 0.3-0.4 mm thickness to rupture the cell. The resulting material is then utilized for extraction[41, 46, 47] of oil by mechanical pressing, solvent extraction, enzymes and high pressure CO_2 extraction processes. The mechanical process is of two types, hydraulic pressing that is the oldest process and screw pressing. In these processes, the pretreated seeds are put through a hydraulic press or screw press to squeeze out the oil and leave protein meal. In solvent extraction process, the oil can be extracted by using a suitable solvent system[48], but in this process there is loss of solvent[41]. In enzymatic process, the pretreated seeds are cooked and ground in water and mixed with the particular enzyme, which digest the solid material from the seed. The oil can then be extracted from the remaining stuff by the use of a liquid-liquid centrifuge method. The enzymes used are cellulase, alpha-amylase, and protease at 1% w/w concentration. Whereas in high pressure CO_2 extraction method, pretreated grounded seeds are mixed under high pressure with CO_2, which dissolve the oil. After the release of pressure, the liquid CO_2 becomes gaseous CO_2 and oil is left behind. The enzymatic and high-pressure CO_2 extraction methods are currently being adopted in commercial scale; as the efficiency of yields are found to be high enough. When the oil contents in seeds are found to be less, in such cases, the size of seeds and moisture contents are adjusted as required and extracted directly with suitable solvent [47, 49].

The improper storage conditions will result in the significant quality degradation. Quality degradation during storage is caused by the presence of moisture, metal soap, oxygen, temperature and equipment design. Moisture is to be avoided due to several reasons, the most important of which is that it leads to hydrolysis of the oil thereby increasing the free fatty acid contents. Oils should be stored at as low temperature as possible. If the oil is pumped out from tanks on the regular basis then the oil is kept at temperature just high enough to prevent graining. This is usually 5 ^{0}C above the temperature to complete melting of the oil. During storage or handling activities, utmost care should be taken to avoid the chances of contamination of oil by oxygen. A typical oil can absorb 2% by volume of oxygen when stored under air, and if any significant portion of this absorbed air reacts with the oil, flavor deterioration will result. When storing oil under air, tanks should be filled completely so that the oil surface-to-volume ratio is minimized and the loss in quality is reduced. Oil may be stored under nitrogen atmosphere to impart better stability to the oil[50].

Of all the unit operations to which vegetable oils are subjected during conversion to pure product, the refining process is the most important. Refining refers to the removal of certain minor constituents from extracted oils. The minor constituents, which are to be removed are dirt, non-fatty materials, color bodies or pigments and in most cases, free fatty acids. Inefficiency in refining is reflected in lower yields of pure products[51].

Dirt can be removed either by settling or by filtration[51]. Degumming is the treatment of extracted oils with water, salt solution or dilute acids such as phosphoric acid to remove phosphatides, waxes and other impurities. Degumming exploits the affinity of phosphatides for water by converting them to hydrated gums. This allows the gums to coagulate, which is separated by a centrifugal separator[50].

The alkali refining process removes free fatty acids without excessive saponification of the oil and without loss of oil by emulsification. The caustic soda solution is used in sufficient quantity to neutralize the free fatty acids. The amount of caustic soda depends on the type of oil, the impurities present and the final color required[39]. In acid refining process, the oil is mixed with concentrated sulfuric acid and the impurities are allowed to settle down and separated and then the oil is washed to make it free from mineral acids[39]. Bleaching is popularly regarded as the partial or complete removal of color[52]. The oil is bleached by physical or chemical means, but the former is most commonly used. In physical bleaching process, the oil is heated in absence of oxygen with a bleaching agent such as bentonite, fuller's earth, activated carbon or amorphous silica, etc. The level of bleaching agent is between 0.2-2.0% of the weight of oil[42, 50].

1.2.3 Mechanism of Film Formation or Drying of Vegetable Oil

The vegetable oils contain triglycerides of saturated and unsaturated fatty acids[42]. When a film of oil containing unsaturated fatty acids is exposed to air it sets gradually and ultimately dries to a tough elastic film[40]. The oxidation of these unsaturated parts of fatty acids by aerial oxygen followed by cross-linking reactions through radical polymerization leads to the film formation or drying of vegetable oils. These reactions are further influenced by use of metal soap as drier. The reaction mechanism is based on the following facts[39, 53].

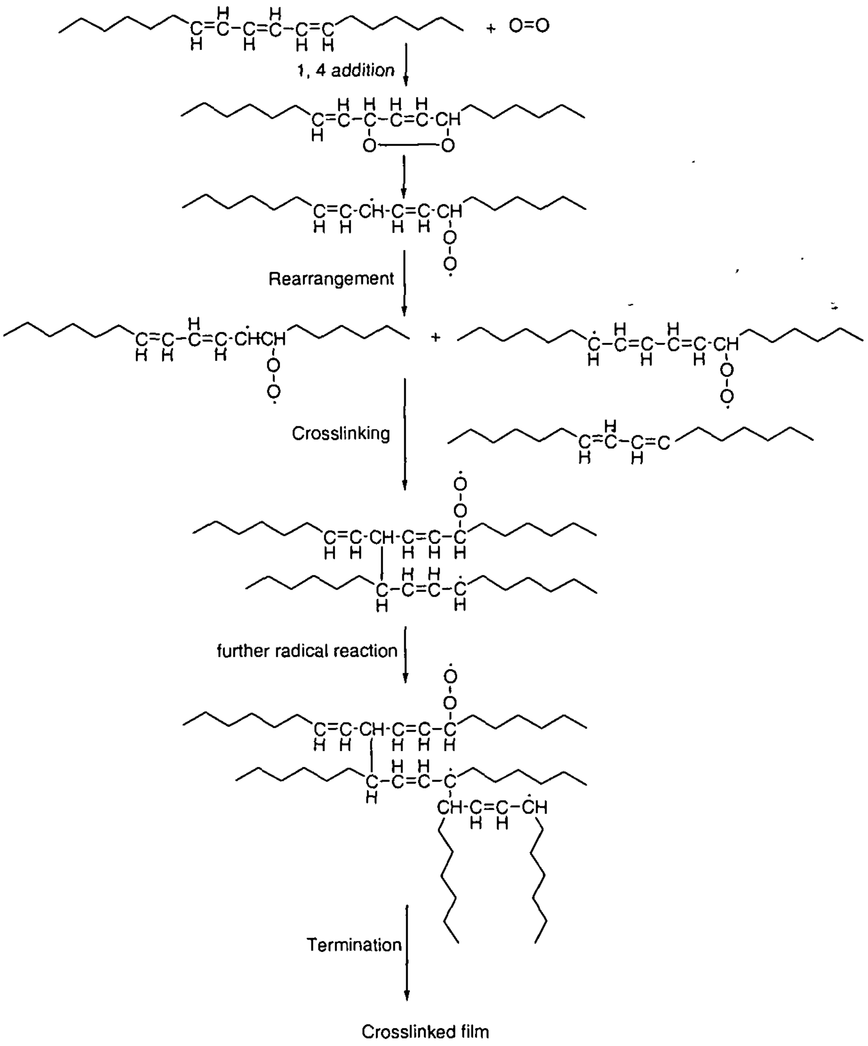
i) During film formation or drying of the oil, considerable absorption of oxygen is observed.

ii) The oils with more conjugated double bonds dry faster than that of less conjugated or non-conjugated systems.

iii) The metal soap driers are further enhancing the rate of drying or film formation.

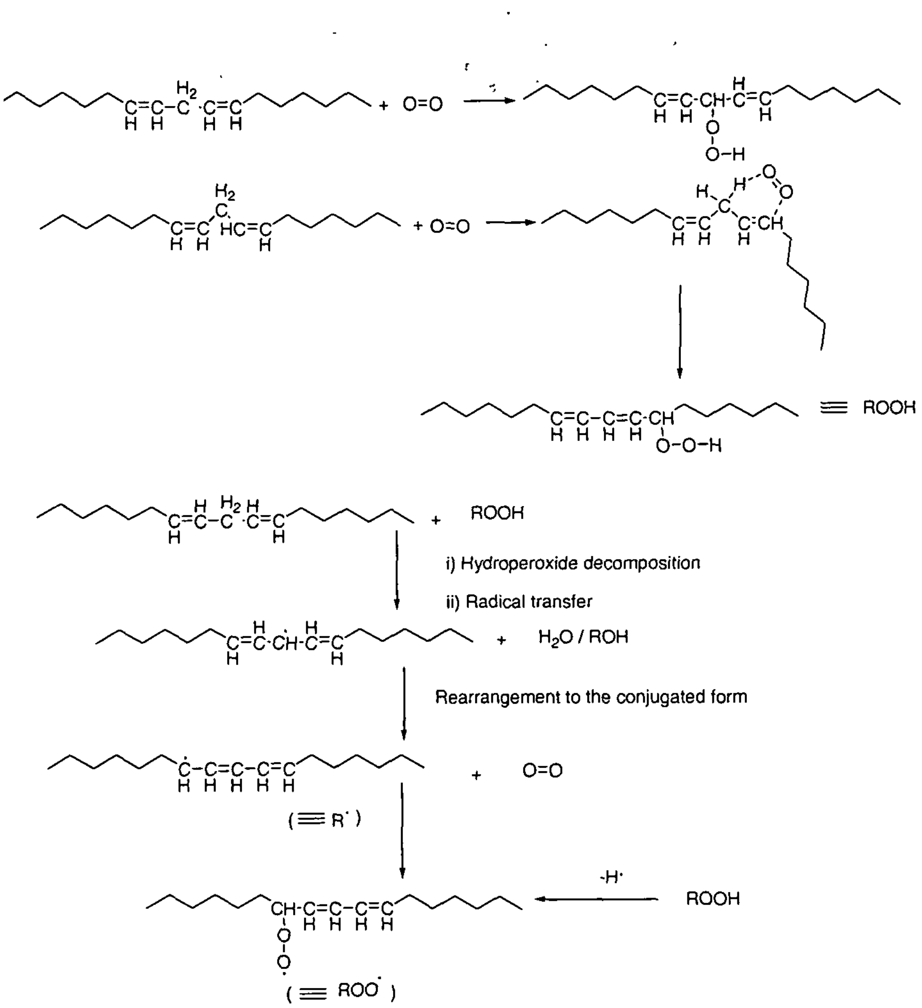
iv) The drying process is markedly influenced by ultraviolet light or by increase of drying temperature.

Thus the drying mechanisms of vegetable oils are different for conjugated (Scheme 1.2) and non-conjugated systems (Scheme 1.3) and these are shown below separately. For conjugated system, oxygen directly attack on the conjugated double bond and form free radicals, which may further undergo rearrangement of the double bonds[53]. The cross-linking reactions occur when the diradicals combine with double bonds in other oil molecules in both the cases.



Scheme 1.2 The film formation mechanism for conjugated oils

For the non-conjugated system, the initial step is relatively slow due to the extensive induction period, where no major changes in chemical or physical state occurred, compared to earlier system. The antioxidants like tocopherols, which are present in the vegetable oil, are also consumed during this induction period[54]. The oxygen attacks the methylene group present in between two consecutive double bonds of the fatty acid. Although in non-conjugated system, the free radicals are formed via hydroperoxide decomposition instead of direct peroxide radical formation as in conjugated system. Also in this case only one radical is formed initially compared to diradical formation in the above case. However, non-conjugated systems are also transforming into conjugated during this film formation reaction [40,53]. The mechanism for this system is as follows.



Scheme 1.3 The film formation mechanism for non-conjugated oils

These $R^{\cdot}$ and $ROO^{\cdot}$ can undergo different types of reactions as shown below:

$$\left.\begin{array}{l} RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet} \\ RH + \dot{O}H \longrightarrow R^{\bullet} + H_2O \end{array}\right\} \text{Transfer of free radical site}$$

$$\left.\begin{array}{l} R^{\bullet} + R^{\bullet} \longrightarrow R\text{-}R \\ RO^{\bullet} + R^{\bullet} \longrightarrow R\text{-}O\text{-}R \\ RO^{\bullet} + RO^{\bullet} \longrightarrow R\text{-}O\text{-}O\text{-}R \end{array}\right\} \text{Crosslinking reactions}$$

Thus, the dry film of vegetable oil may contain different types of linkages such as C-C, C-O-C, C=O, C-O-H, etc. However, the mechanism of film formation or drying of vegetable oil in the presence of metal soap driers is again of different types [42, 53, 55-56].

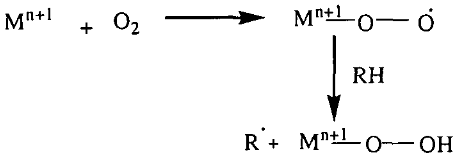
Actually, how the driers catalyze the oxygen uptake, is still not clear, but the decomposition of the hydroperoxide by primary driers occur as follows:

$$M^{n+} + ROOH \longrightarrow M^{n+1} + R\dot{O} + {}^{-}OH$$

$$M^{n+1} + ROOH \longrightarrow M^{n+} + RO\dot{O} + H^{+}$$

(M is the metal like Co, Mn, Pb, etc.)

Driers may also act as oxygen carrier, which may be shown as follows:



$$\begin{tikzcd}[column sep=small] M^{n+1} + O_2 \arrow[r] & M^{n\pm1}\text{—}O\text{—}\dot{O} \arrow[d, "RH"] \\ & R^{\cdot} + M^{n\pm1}\text{—}O\text{—}OH \end{tikzcd}$$

These $R^{\cdot}$ or $RO^{\cdot}$ or $ROO^{\cdot}$ undergo different types of crosslinking reactions as shown earlier.

The mechanism of crosslinking reactions was studied[57-60] for different vegetable oils by using spectroscopy like NMR and IR, liquid chromatographic technique, etc.

1.2.4 Physical and Spectroscopic Characterization

The vegetable oils have been characterized by determination of physical properties[39, 40] like specific gravity, foreign matter, break content, moisture content, unsaponifiable matter, color, color on heating, viscosity, iodine value, acid value, saponification value, hydroxyl value, etc. Vegetable oils have also been characterized spectroscopically[61] to determine their structures.

The chemical composition and structure of the vegetable oils have been determined by using different spectroscopic methods. A brief description of these characterization methods is presented here.

1.2.4.1 Chemical Composition

As the vegetable oils are triglyceride esters of different fatty acids, their composition can be determined by using chromatographic techniques. The analysis of an oil is difficult to carry out due to its complex chemical composition, as it consists of a mixture of triglyceride esters with combination of different free fatty acids. The principal methods used are gas liquid and high performance liquid chromatography for this purpose[62]. Mass spectrometry and NMR spectroscopy are used to identify the individual fatty acids[55]. The identification and determination of various mixed triglycerides of the oil are reported in details in a review paper[63].

1.2.4.2 Chemical Structure

The chemical structure of the vegetable oil can be evaluated by UV, FT-IR, NMR spectroscopies[64-66] and mass spectrometry[67]. The UV spectroscopy is used to detect the different types of conjugation present in the fatty acids[61] of the vegetable oil. The IR spectroscopy is largely used to determine the different functional groups[47] present in the fatty acids of the vegetable oils. Cavallo *et al.* showed[68] that ^{1}H-NMR spectroscopy could readily determine the ratio of the linolenic acid content over all other fatty acids present in the oil and ^{13}C-NMR study could be utilized for rapid determination of linolenic, linoleic and oleic acid present in the same. The use of near infrared spectroscopy is reported for rapid determination of the oxidation level in soybean oil[69]. Mass spectrometry is generally used in connection with chromatography to determine the molecular mass of individual fatty acids present in the vegetable oil. Some studies[57, 58] have been reported about the investigation of oxidation of the unsaturated fatty acids and drying process of vegetable oil to form film by using high performance liquid chromatography, NMR and time-lapse IR spectroscopies. Other instrumental technique such as GPC is used to determine molecular weight[70]and its distribution. DSC is used to study the kinetics[71] of oxidation or film formation.

1.2.5 Heat Treatment of Vegetable Oils

The heat treatment of vegetable oils is an old and commonly used industrial practice[72]. Upon heating, the viscosity of the oil rises due to increase of molecular weight through different types of chemical reactions. Different types of reactions during heat treatment, which include thermal polymerization through[73] Diels-Alder reaction, oxidative polymerization, ester interchange, cyclization, etc. The heated vegetable oils are being used partially as printing ink vehicles. They are also used as surface coating materials.

1.3 Polyester (Alkyd) Resins from Vegetable Oils-A Brief Review

1.3.1 Introduction

Polyester (alkyd) resins are prepared by the condensation of a polyhydric alcohol and a polybasic acid. These polymers can be modified with natural fatty acids or oils and /or synthetic fatty acids[74]. Oil modified polyester resins have been used in surface coating industry for almost 70 years. Today oil modified polyester (alkyd) resins outrank all other synthetic resins in importance and contribute about 50% of the resins for surface coatings[54]. Many factors[39, 54, 75] behind the popularity of these resins are as follows:

i) They are single-pack system i.e. stable in the can for a long time.

ii) The raw materials and processing costs are relatively low compared to other synthetic resins.

iii) They are soluble in low cost industrially used solvents.

iv) They possess high order of durability, excellent pigment dispersion ability, high gloss accompanied by exceptional toughness and adhesion.

v) They are compatible with many other resins used in surface coating industry.

vi) They enjoy wide spectrum of applications such as binder for surface coatings, printing inks, etc.

vii) Their structure and properties can be tailored by varying the selection of raw materials depending upon the cost and availability.

viii) The overall cost of these polymers is very low.

1.3.2 Historical Background

The history of alkyd production dates back to 1847, when accidentally, Barzelius prepared polyglycerol tartrate by the reaction of glycerol with tartaric acid. Barzelius did not persue the matter further and van Bemmelen was the first to study about the above reaction and he synthesized glycerol succinate and citrate in 1856[76, 77]. It was the year 1901, when Watson Smith obtained a hard brittle polymer resulting from the reaction between glycerol and phthalic anhydride, the reaction product was known as glyptal. Between 1910-1915 considerable volume of works was done in General Electric Laboratories regarding the possibilities of commercial uses of glyptals. Glyptals were used as bonding agents for mica flakes and were used for electrical insulating purposes. But the brittleness of glyptals limited their uses as coating binders.

They were therefore modified[75, 78, 79] with fatty acids such as oleic acid and oils. In 1921, these modified resins were termed as alkyds by Kienle. In 1924, Kienle showed that vegetable oils could be introduced into glyptals by alcoholysis technique rather than the fatty acid method. In the year 1925, Kienle and Hovey started a series of investigations on oil-modified polyesters or alkyd resins, which resulted in the issuance of basic US patent 1,893,873 in the year 1933. This achievement is the root-cause of the phenomenal acceptance of alkyd resins as surface coatings. In 1935, when Kienle's patent was declared invalid, then the field of polyester manufacture became accessible to all[74, 76, 80].

1.3.3 Classification

Most common and conventional way of classifying oil modified polyester resin is based on oil length, which refers to the amount of oil present as percent of total non-volatile content. On the basis of oil length they are classified[79] as:

(i) short oil polyester (oil content < 45% w/w)

(ii) medium oil polyester (oil content 45-55% w/w)

(iii) long oil polyester (oil content > 55% w/w)

Polyester resins are further classified depending on the degree of unsaturation of the fatty acid present in the system[54] as:

(i) drying (oxidizing type)

(ii) non-drying (non-oxidizing type)

In oxidizing type of polyesters (alkyds), the oils used are linseed, safflower, dehydrated castor oil, soybean, tobacco i.e. mainly drying and semi-drying oils, where sufficient unsaturation is present to cause the alkyd to polymerize in presence of air at ambient temperature to give acceptable drying to the applied film. These are used in air-drying finishes. Alkyds prepared from the oils with iodine value above 120 show good drying property whereas alkyds prepared from the oils with iodine value between 100-120 take longer period for drying compared to the earlier one[81].

In non-oxidizing type of alkyds, the oils used are coconut, castor oil, hydrogenated castor oil, dhupa oil i.e. mainly non-drying oils, where unsaturation is very low and hence polymerization does not occur in presence of air. These alkyds are used with amino resin like urea-formaldehyde and melamine-formaldehyde resin in stoving finish and they are also used as plasticizers in nitrocellulose laquers[81], etc.

1.3.4 Raw Materials

In order to prepare oil modified polyester (alkyd) resins components such as (i) vegetable oils or fatty acids, (ii) polyhydric alcohols, (iii) polybasic acids and (iv) monobasic acids are required. However, monobasic acid is an optional component among these.

1.3.4.1 Vegetable Oils or Fatty Acids

Oil modified polyester resins are made with drying, semi-drying and non-drying oils or their fatty acids. Sometimes tall oil and fish oils are also used. Chain unsaturation of the resin is derived from the oil or the fatty acid[39]. Now a days, in addition to large number of vegetable oils, different fatty acids are also utilized for the preparation of polyester resins.

A brief description of vegetable oils particularly used for the development of polyester resins is reported here.

Linseed Oil

Linseed oil is a drying oil and it is the most universally used oil[82] in the paint and varnish industry. India is one of the important linseed producing countries, the others being Argentina, North America, Canada and Russia[46, 82]. The oil is obtained from the seed of flax plant. It is one of the most common unsaturated vegetable oils. Linseed oil has good wetting properties[21] for ferrous surfaces. It is the most used single vehicle[21] for primer or soap coats on structural steel. One disadvantage of the use of linseed oil in paints both air-drying and stoving, is its yellowing tendency, which is due to the presence of high proportion of linolenic acid. So the use of this oil and resins made there off is restricted to exterior finishes or interior finishes where color retention is not of importance[39]. Linseed oil satisfies more of the requirements of the protective coating industry than any other single oil.

Castor Oil

Castor oil is obtained from seeds of *Ricinus communis*, which is grown[42] in India, Brazil, South America, Russia, U.S.A., China, Mexico, etc. Castor oil, well known as ricinum oil, is one of the few natural glyceride sources that are almost pure. Castor oil is one of the few natural glyceride sources[83] that are almost pure. Raw castor oil is non-drying oil, which is used as a plasticizer for lacquers, leather-dressing dopes or like formulation[21]. Castor oil is compatible with a large number of natural and synthetic resins, polymers and waxes. The solubility of castor oil in ethyl alcohol distinguishes[82] it from all other vegetable oils, which are practically insoluble in it. The dehydration of raw castor oil changes it from a non-drying oil to a drying oil. Dehydrated castor oil (DCO) has intermediate properties between linseed and tung oil regarding drying time, rate of polymerization, water and alkali resistance. The dried film of DCO is more flexible and elastic than tung oil films, and it does not become brittle on aging[21]. The film of DCO does not dry as hard and yellow as linseed or perilla oil[21]. Properly formulated oil and cooked dehydrated castor oil vehicle films do not wrinkle on exposure to gas fumes. These properties are responsible for dehydrated castor oil becoming a favorite for the production of alkyd resin and varnish in which after tack[21] is overcome. Castor oil gives excellent stoving finishes when used as castor or dehydrated castor alkyd with amino resin. It also finds application in nitrocellulose and spirit soluble compositions as plasticiser.

Tung Oil

The tung oil is obtained from the nuts of two species[82] of trees, *Aleurites fordii* and *Aleurites montana.* The oil was originally available from China hence it is also known as China wood oil. It is cultivated[40, 42] in U.S.A., Argentina, China and North-East provinces of India. It is characterized by the presence of α-eleostearic acid. Tung oil is more viscous than other common vegetable oils. The characteristics properties, which have made this oil so valuable in modern varnish manufacture, are its unique speed of drying and its excellent water resistance. It has also good alkali and chemical resistance. The use of raw tung oil in paints is limited by the fact that it wrinkles on drying. It is therefore, advisable to partly replace tung oil with other oils such as linseed, soybean, perilla, and dehydrated castor oil. Tung oil has great compatibility[21, 42] with natural and synthetic resins.

Soybean Oil

The soybean oil is originated from China. Soybean oil is one of the world's most important vegetable oils in terms of quantity produced[39]. It is an edible and semi-drying oil. Its main attraction is its non-yellowing property due to low percentage of linolenic acid[82]. It is used in the manufacture of alkyd resin. Soybean oils in the proper form may be blended with linseed, perilla, oiticica, dehydrated castor oil and tung oil in the manufacture of house paints, varnish, baking finishes for automobiles and various drying synthetic finishes[21]. Soybean oil can be used as a limited substitute for linseed oil[84].

Sunflower Oil

Sunflower oil is originally obtained from North America. It is also cultivated in Russia, Argentina, France, followed by India and China[46]. Sunflower oil is similar to safflower oil, because of their constituent acids are practically same, although sunflower oil[82] may contain a higher content of gums. It is semi-drying oil, yellows less than linseed oil, but it dries softer and more slowly[21]. Bodied segregated sunflower oil compares well with linseed stand oil in its uses in different formulations and it has an added advantage[82] of good color retention. It may be blended with linseed oil and perilla oil for use in outside house paints. It makes good alkyd resin solutions and can be used[21, 85] in varnish in combination with drying oils.

Safflower Oil

The main producers[46] of safflower oil are USA, Mexico, India, Australia and Europe. It is semi-drying oil and it dries better than soybean oil. There is no after yellowing in the dried film, even under extreme exposure condition. Safflower oil is used successfully in house paints, especially if blended with tung oil, linseed oil or perilla oil. Raw or bodied safflower oil is best suited for alkyds[21, 42] for non-yellowing paints. Safflower oil can replace[86] soybean oil in polyester resin formulation.

Tobacco Seed Oil

USA is the first largest producer of tobacco seed oil, second being India. Tobacco seed is a by-product of tobacco production. The tobacco seed oil is free from[42, 82] nicotine and other harmful substances. It is a semi-drying oil. Tobacco seed oil polymerizes rapidly and air dries and stoves faster than soybean oil though inferior to linseed oil in this respect. Blown oil and stand oils of tobacco seed oil behave similarly to linseed oil. In its non-yellowing property it is similar or even better than safflower or soybean oil. The oil can be used in non-yellowing[40, 87] alkyd finishes.

Oiticica Oil

Oiticica oil is available[42] mainly from Brazil. It is quite similar in many of its characteristics to tung oil. The desirable properties of oiticica oil are attributed to the high content of keto-conjugated licanic acid. Crude oiticica oil is a semi-liquid paste, which in many cases is not a convenient form to use[39]. But, heating at elevated temperature gives permanently liquid oiticica oil. Raw oiticica oil dries to an opaque wrinkled film similar to tung oil film. Large quantities of oiticica oil are consumed by the protective coating industry where it dries hard and more gas-proof than tung oil but has the disadvantage of darkening on heating. Oleoresinous vehicles containing oiticica oil and alkyds are blended[21] to control a definite wrinkle pattern in wrinkle finishes.

Perilla Oil

In India, Perilla oil is found in Assam and Manipur. It is normally used for edible purpose. Perilla oil possesses the highest iodine number[21] of all the raw non-conjugated drying oils. Its drying property lies between the drying property of tung and linseed oil. It is a sort of concentrated linseed oil. It has a greater tendency to yellow. It possesses lower flash point[82], so to avoid explosion care must be taken when it is heated. Perilla oil is blended with other drying or semi-drying oils to improve their properties. The oil has been used to produce alkyd resins and used in the manufacture[21] of undercoat and enamel vehicles.

Coconut Oil

Coconut oil is obtained from copra, the white meat[47, 88] of the fruit of the coconut palm. It is an edible and non-drying oil. Coconut trees grow[41] in Indonesia, Philippines, India, Sri Lanka, Malaysia, Thailand, Africa, America and the Pacific region. Coconut oil is non-drying. The alkyd from coconut oil is blended with urea-formaldehyde and melamine-formaldehyde resin, which gives excellent non-yellowing stoving paint[42].

Poppy Seed Oil

Poppy seed oil is mainly grown in India, Europe and in the North of France[46, 82]. The poppy seed oil was used[21] before linseed oil was known. Poppy seed oil might be substituted for soybean oil if it were more plentiful. The oil has good non-yellowing property[82]. Poppy seed oil film dries softer and slowly than linseed oil. It is used in the manufacture of alkyd resin and other water borne coatings.

Rubber Seed Oil

Rubber seed oil is available[28, 42] mainly in Nigeria, Sri Lanka and India. It is a semi-drying oil. Rubber seed oil is used in the formulation of adhesives, anticorrosive coatings and alkyd resin coatings. Studies on the practical utilization of rubber seed oil revealed that it possesses strong potential[13] to be a substitute for linseed oil in case of alkyd resin production. Along with above mentioned vegetable oils many others are also used for polyester resin preparation.

A list of vegetable oils used for polyester resin preparation is given along with source name, composition and some physical properties in Table 1.2.

Besides vegetable oils, tall oil is also used for the preparation of polyester resin. Tall oil is a by-product of the pulp the paper industry, where it is recovered from the black liquor resulting from the Kraft pulping of coniferous wood pulp industry. Tall oil is a mixture of fatty acids, rosin acids and unsaponifiable matter[5, 40]. Another interesting oil resource for alkyd preparation is non-vegetable origin that is fish oil. The oils extracted from pilchard, herring, menhaden, sardine have been utilized in many countries for polyester preparation. In India too, sardine have been used for the preparation of polyester resin. However, because of lack of proper extraction techniques refining process and non-constant quality supply, the fish oils[54, 102] are yet to be exploited commercially.

Table 1.2 Composition and some physical properties of different oils

Common name	Botanical name	Oil content (%)	Composition of different fatty acids (%)						I.V.	S.V.	References
			Palmitic	Stearic	Oleic	Linoleic	Linolenic	Other acids			
African locustbean	*Parkia filicoidea*	15-20	31	7.70	8.8	42.50	--	Palmitoleic (2.7) Arachidic (4.2) Behenic (3.1)	104	176	38
African mehogony	*Afzelia africana*	25.80	--	--	--	--	--	--	104.46	17.74	37
Apricot	*Prunus armeniaca*	40-50	4-7	--	58-74	20-34	--	--	95-110	190	89-91
Castor	*Ricinus communis* L	40-55	1	1	3	3-4	< 0.2	Ricinoleic (89-90) Dihydroxy stearic (1)	82-88	175-187	46, 82
Dehydrated Castor	*Ricinus communis* L	--	--	--	7-10	75-88	3-8	--	130-145	189-195	42
Chia	*Salvia hispanica* L	30	7.4	3.0	6.65	18.80	63.45	--	200	192	40, 92
Coconut	*Cocos nucifera* L	35.3	8	3.8	5	2.5	--	Lauric (48.2) Myristic (16.6) Capric (7.3) Caprylic (7.6)	81.4	250-264	93, 46
Cotton	*Gossypium barbadense* L	40	25	2.8	17.1	52.7	--	Myristic (1)	97-115	189-198	93
Kamala	*Mallotus philipensis*	35	3.2	2.2	6.9	13.6	--	Kamlolenic (72)	183	178.3	94
Karanja	*Pongamia glabra*	33	9.23	4.48	71	14.5	--	Myristic (0.23)	82	158	1

Continued
(1of 3)

Table 1.2 Composition and different properties of different oils

Common name	Botanical name	Oil content (%)	Composition of different fatty acids (%)						I.V.	S.V.	References
			Palmitic	Stearic	Oleic	Linoleic	Linolenic	Other acids			
Linseed	*Linum usitatissimum*	35-45	9-10	7-8	10-21	13-15	50-61	--	170-204	189-196	46
Lesquerella	*Lesquerella fendleri*	23-29	1.3	2.1	18.1	9.3	14.0	Lesquerolic (51.4), gadoleic (1.2)	107	168	95
Mahua	*Madhuka indica*	50	23.7-24.7	19.3-29.9	36.3-43.3	11.6-15.8	--	--	55-70	187-196	94
Melon	*Colocynthis vulgaris*	51	10.1	11.2	7.2	70.6	--	Arachidic (0.6)	116.0	248.0	34, 96
Mbembe	*Vitex doniana*	29.6	--	--	--	--	--	--	114.4	56.0	16
Nicker nut	*Caesapina bunduc*	34	--	--	--	--	--	--	112.52	197.12	17
Niger	*Guizotia abyssinica*	35-40	5.0-8.4	2.0-4.9	31.1-38.9	51.6-54.3	--	Myristic (1.7-3.4)	130-135	190	42, 97
Neem	*Azadirachta indica*	40-45	19.4	18.3	45.7	14.4	--	Arachidic (1.4)	65-80	180-205	94
Oiticica	*Licania rigida*	30	6-8	4-6	5	8-10	--	Licanic (73-76)	140-180	187-193	40, 42, 46
Poppy	*Papaver somniferum*	36-50	9-11	1-2	13-18	69-77	<3.5	Other (0.5)	130-143	188-195	46
Perilla	*Perilla ocymoides*	30-35	7.5	--	8.5	37	46.5	--	193-201	190-205	42, 98
Palm	*Elaies guinensis*	40-45	44	4	40	10	Trace	Other (2)	51.5-57	196-205	41, 47, 99
Physic nut	*Jatropha curcas*	46-58	15.6	9.7	41	32.1	--	Other (1.4)	93-107	188-196	94
Rapeseed	*Brassica napus* L	36	3-4	1-2	9-16	11-16	7-12	Eicosenoic (7-13) Erucic (41-52)	94-120	168-187	46, 100

Continued
(2of 3)

Table 1.2 Composition and different properties of different oils

Common name	Botanical name	Oil content (%)	Composition of different fatty acids (%)						I.V.	S.V.	References
			Palmitic	Stearic	Oleic	Linoleic	Linolenic	Other acids			
Rice bran	Oryza sativa *L.*	10	16	2	42	37	1	Other (2)	95	170	42, 47, 101
Sesame	*Sesamum indicum*	50-55	9	6	38	45	1	Other (1)	104-120	187-195	46, 47
Soybean	*Glycine max*	16-22	10.5	3.2	22.3	54.5	8.3	Eicosanoic (0.9), Arachidic (0.2)	130	189-195	42, 82
Sunflower	*Helianthus annus*	40	6.3	4.2	18.3	69.0	0.4	--	110-143	188-194	85
Safflower	*Carthamus tinctorius*	25-30	6.0	2.0	14.0	75.0	--	Other (1)	135-150	186-198	46, 47
Tobacco	*Nicotiana tabacum*	33-43	7-10	3.1	17-27	66-76	--	--	130-145	186-197	40, 82
Tung	*Aleurites fordii*	50-60	3-5	1-2	4-9	4-10	1-3	Eleostearic (77-88)	166-170	188-197	46
Uda	*Xylopia aethiopica*	11.5	18.0	--	26.5	45.1	--	--	115.5	207.2	16
Undi	*Calophyllum inophyllum* L	70	17.9	6.1-19.2	36.2-53.1	15.8-28.5	--	Erucic (3.3)	82-98	191-202	96
Walnut	*Juglans regia*	60	11	5	28	51	5	--	160	190	72, 101

(3 of 3)

1.3.4.2 Polyhydric Alcohols

The trihydric alcohol, glycerol is the workhorse polyol component of alkyd resins, because it is present in naturally occurring oils from which alkyds are commonly synthesized. The popularity of glycerol is not only due to its availability, but also due to its adaptability to many technical variations involved in the production of resins[54, 103]. The next most widely used polyol is penta-erythritol (PE). The high functionality of PE is especially useful in long oil polyester resins. The higher functionality of PE may be reduced[54, 75, 77] in several ways, such as use of lower functionality polyols (eg. glycol, glycerol), larger proportion of fatty acids, formaldehyde, monobasic acids like benzoic acid, rosin, etc. Trimethylol propane (TMP) is also used in alkyd synthesis. But it leads to slower rate of esterification because of sterically hindered structure[103]. It also has been used for the synthesis of hyperbranched alkyd resin[104]. Dihydric alcohols are used in the preparation of alkyds having linear structure. It has been reported that sorbitol and xylitol can also be used as substitute for glycerol and PE[105]. Mckillip *et al.*[106] showed that glycol glycoside can also be used as a polyhydric alcohol in alkyd synthesis. The use of polystyrene glycol as a partial substitute of glycerol led to the formation of alkyd resin, which possessed better physical and chemical resistance than conventional styrenated alkyds[107]. Aurelian *et al.*[108] used 1,1′-isopropylidine *bis*(4-cyclohexanol) (I), bisphenol-A *bis*(2-hydroxyethyl) ether (II), bisphenol-A *bis*(2-hydroxypropyl) ether (III), and ethylene glycol (IV) separately for the preparation of alkyd resins and observed that alkyd from (I), (II), and (III) had higher viscosities than (IV). Drying time and hardness for coatings from (III) alkyd were comparable to those for (IV) alkyd, but drying time was reduced and hardness increased for (I) and (II) alkyd coatings. The use of poly pentaerythritol in the synthesis of binder for baking primer was reported[109]. A short list of different polyols with their physical properties is shown in Table 1.3.

1.3.4.3 Polybasic Acids

Phthalic anhydride is the dominant dibasic acid in the manufacture of alkyds. Apart from its availability at low price, it is easy to handle, quite stable upto the temperature at which alkyd resins are cooked, stable to UV radiation, reduces the reaction time as the amount of water evolved is less[80, 103]. The next most widely used dibasic acid is isophthalic acid (IPA). The esters of IPA are more resistant to hydrolysis than those of phthalic anhydride in the pH range of 4-8, the most important range for exterior durability[103]. IPA is used when tougher, fast drying, and more chemical resistant coatings are required. Due to the high melting point of IPA, alkyds of IPA are prepared at higher temperature for longer time, which lead to the greater extent of side reactions[112]. Terephthalic acid (TPA) is also used for alkyd preparation. Dimethyl ester of TPA is more preferred than TPA due to its solubility and low melting point[54, 75]. Tetrachloro phthalic anhydride and chlorendic anhydride impart fire retardant property[113] to oil modified polyester resin. Tetrachloro phthalic anhydride gives polyester resins, which are more water and alkali resistant than phthalic anhydride based polyester resin. Tetrahydro and hexahydrophthalic acids have been suggested as components for low viscosity alkyd resin formulation. Maleic anhydride and fumaric acids are used frequently in alkyd formulation in limited amounts with phthalic anhydride. Maleic anhydride and fumaric acids have been utilized for water borne coatings[19, 28, 114]. If flexibility and plasticization properties are required, then dibasic saturated acids with long hydrocarbon chains such as adipic, sebacic and azalic acids are used[77, 79]. Trimellitic anhydride, dimethylol propionic acid and pyromellitic anhydrides are also used for water borne alkyds [54, 115, 116]. Dimethylol propionic acid has been reported[104] to be used for the synthesis of hyperbranched alkyd resin. Glutaric and succinic anhydride have also been reported[117] for the preparation of low viscosity oil modified polyester resin. El-Hai *et al.* reported[118] that the use of 3,3$'$-methylene *bis*(salicylic acid) as a partial replacement of phthalic anhydride in alkyd formulation led to significant improvement in hardness, gloss and alkali resistance. Volozhin *et al.*[119] prepared alkyd coatings using bicyclo[2.2.2]oct-5-ene-2, 3-dicarboxylic acid, the coatings showed high impact strength, flexural strength, heat resistance and resistance to water. The use of benzophenone tetracarboxylic dianhydride for alkyd resin preparation has also been reported[120]. A short list of different polybasic acids with their physical properties is shown in Table 1.4.

Table 1.3 The molecular formula and some physical constants of some commonly used polyols

Polyols	Formula	Liquid (L) or solid (S)	Melting Point (°C)	Boiling Point (°C) 760 mm	Molecular weight	References
Ethylene glycol	$HO(CH_2)_2OH$	L	-13	193-205	62.08	54, 110
Propylene glycol	$CH_3CH(OH)CH_2OH$	L	-59	188.2	76.11	54, 110
Neopentyl glycol	$HOCH_2C(CH_3)_2CH_2OH$	S	120-130	213	104.15	75, 110
1,3-Butylene glycol	$CH_3CH(OH)CH_2CH_2OH$	L	23-27	207.5	90.2	75, 110
Hexylene glycol	$CH_3CH(OH)CH_2C(OH)(CH_3)_2$	L	--	246	118	110
Diethylene glycol	$HO(CH_2)_2O(CH_2)_2OH$	L	-8	245.8	106.14	54, 110
Dipropylene glycol	$CH_3CH(OH)CH_2OCH_2CHOHCH_3$	L	-40	228-236	134.18	75, 110
Triethylene glycol	$HO(CH_2)_2O(CH_2)_2O(CH_2)_2OH$	L	-7.2	278-300	150.17	75, 110
Glycerol	$HOCH_2CH(OH)CH_2OH$	L	18	290	92.1	75, 110
Trimethylol ethane	$CH_3C(CH_2OH)_3$	S	185-195	--	120.15	54, 110
Trimethylol propane	$CH_3CH_2C(CH_2OH)_3$	S	60	295	134.1	54, 110
Pentaerythritol	$C(CH_2OH)_4$	S	250-258	--	136.17	54, 110
Dipentaerythritol	$[(CH_2OH)_3CCH_2]_2O$	S	222	--	254	110
Methyl glucoside	$C_7H_{14}O_6$	S	166-169	--	194.19	110, 111
Sorbitol	$CH_2OH(CHOH)_4CH_2OH$	S	98	--	182.2	110
Mannitol	$CH_2OH(CHOH)_4CH_2OH$	S	166	290-295	182.2	111
Xylitol	$C_5H_{12}O_5$	S	94-96	--	152.1	111

Table 1.4 The molecular formula and some physical constants of some commonly used polybasic acids

Polybasic acid	Formula	Liquid (L) or solid (S)	Melting Point (°C)	Boiling Point (°C) 760mm	Molecular Weight	References
Adipic acid	$HOOC(CH_2)_4COOH$	S	152	--	146	54, 75
Azalic acid	$HOOC(CH_2)_7COOH$	S	106	286.5*	188.2	75, 110
Benzophenon tetracarboxylic dianhydride	$C_{17}H_6O_7$	S	221-225	--	322.2	111
Chlorendic anhydride	$C_7H_2Cl_6(CO)_2O$	S	240	--	370.718	110
Citric acid	$HOC(COOH)(CH_2COOH)_2$	S	153	--	192.1	110, 111
Diglycolic acid	$HOOCCH_2OCH_2COOH$	S	148	--	134	110
Fumaric acid	$HOOCCH{=}CHCOOH$	S	200**	--	116.1	54, 75
Glutaric anhydride	$C_5H_6O_3$	S	51-55	--	114.1	111
Hexahydrophthalic anhydride	$C_6H_{10}(CO)_2O$	S	35	--	154.2	75, 111
Isophthalic acid	$C_6H_4(COOH)_2$	S	345-348	--	166.14	54, 111
Maleic anhydride	$(CHCO)_2O$	S	53	202	98.06	54
Phthalic anhydride	$C_6H_4(CO)_2O$	S	131.2	285	148.12	54
Pyromellitic dianhydride	$O(CO)_2C_6H_2(CO)_2O$	S	286	400	218	75, 111
Sebacic acid	$HOOC(CH_2)_8COOH$	S	133	295*	202	75, 110
Succinic acid	$HOOC(CH_2)_2COOH$	S	185	235	118.1	54, 110
Terephthalic acid	$HOOC(C_6H_4)COOH$	S	300**	--	166.1	75, 111
Tetrabromo phthalic anhydride	$C_6Br_4(CO)_2O$	S	270	--	463.7	75
Tetrachloro phthalic anhydride	$C_6Cl_4(CO)_2O$	S	254-255	--	285.9	75, 111
Tetrahydro phthalic anhydride	$C_6H_8(CO)_2O$	S	99	--	152.1	75, 111
Trimellitic anhydride	$HOOC(C_6H_3)(CO)_2O$	S	165	--	192	110, 111

** Sublimes, * 100 mm pressuere

1.3.4.4 Monobasic Acids

In addition to naturally occurring fatty acids, other monobasic acids [75, 79] used in alkyd resin preparation are benzoic acid, *p-tert*-butylbenzoic acid, rosin (abietic acid), levopimaric acid, etc. In order to get resins having reduced drying times and very good resistance properties mixture of benzoic acid and *p-tert*-butylbenzoic acid is used[121, 122]. In short oil polyester resin benzoic acid is used to regulate the polymerization at optimum level[123]. The use of rosin for water thinnable alkyd emulsions has been reported[124]. Other monobasic acids such as pelargonic acid, perfluoropelargonic acid, lauric acid, lactic acid, iso-octanoic acid, isodecanoic acid, and versatic acid, etc. are also used[79, 125, 126]. Use of cardanoxy acetic acid in linseed oil-phthalic acid -glycerol based polyester resin has been shown to render better hardness, flexibility and chemical resistance in comparison to linseed oil polyester resin[127].

1.3.5 Methodology

Four methods viz. (i) monoglyceride / alcoholysis, (ii) fatty acid, (iii) acidolysis and (iv) fatty acid-oil have been used to manufacture alkyds. Among these fatty acid and monoglyceride processes are the most common. Brief description of all the above processes is presented below.

1.3.5.1 Monoglyceride / Alcoholysis Method

It is the most commonly adopted method for alkyd preparation. When a mixture of glyceride oil (except hydroxylated oil e.g. castor oil), polyol and dibasic acid or anhydride is heated together, then the polyol solely reacts with dibasic acid component and form polyester. This polyester is insoluble in the oil phase and rapidly forms oil unmodified polyester, which gels at a low degree of reaction[77]. This incompatibility is overcome by heating a mixture of oil and glycerol with catalyst at temperature (225-250) ^{0}C. The extent of alcoholysis is usually checked by methanol solubility of the monoglyceride formed. There are others two methods for checking the extent of alcoholysis; one is to observe solubility of phthalic anhydride in the alcoholysis product and the other is to determine the electrical conductivity of the monoglyceride formed[54, 128]. In reality alcoholysis results in an equilibrium consisting of monoglyceride, diglyceride, unchanged triglyceride and free glycerol. In a typical situation, 51% monoglyceride, 40% di-glyceride, 4% triglyceride and 5% glycerine is an acceptable composition[129]. Alkyds formed from alcoholysis mixtures containing higher proportions of monoglyceride always have superior properties[130]. Attempts were made to measure alcoholysis compositions by different methods[128, 131]. More sophisticated methods such as thin layer chromatography, gas chromatography, HPLC are frequently used[132]. Mandik *et al.*[133] used GPC to determine the concentration of different glycerides for linseed oil. Under the influence of heat and catalyst, the polyols undergo inter etherification, which results[134] in loss of available hydroxyl group and the formation of higher functional polyols. Oxygen seems to retard the alcoholysis reaction, as it is found that the reaction time is almost doubled when the alcoholysis is carried out in the absence of a blanket of inert atmosphere[135]. Traces of water present have been shown to decrease the rate and the extent of monoglyceride formation from castor oil[136]. Roy Choudhury performed glycerolysis for a number of oils and it was shown that the yield of monoglyceride is not dependent on the fatty acid composition of the oil but depend on the solubility of glycerol in the oil, which is more or less dependent upon temperature[137]. Alcoholysis of oil was studied[138] and it was observed that the highest monoglyceride content of the final product was 54-55% and lowest diglyceride content was 23-24%. Sathyanarayana *et al.*[139] carried out alcoholysis of linseed oil with glycerol and characterized the partial glyceride formed by thin layer chromatography-flame ionization detector and proton NMR[139]. They found α-monoglyceride as the predominant product, the concentration of which increased with the decrease in oil length. Igwe *et al.*[138] showed that the alcoholysis reactions of rubber seed and linseed oils were found to be similar, same in the case of melon and soybean oils. This similarity indicates that rubber seed oil and melon seed oil can replace linseed and soybean oils in the synthesis of oil modified polyester resins.

After formation of monoglyceride, the polybasic acid and the rest of polyol are added and the polycondensation is carried out until desired acid value is obtained[103].

Catalysts Used in the Monoglyceride Process

Monoglyceride can be prepared without the use of a catalyst, but in that case it is necessary to use temperature of 280 ^{0}C or higher to achieve the reasonable rate of the reaction. The use of such high temperature leads to dark colored, high viscosity product. Hence catalysts are used to reduce the processing temperature[39, 82]. Alcoholysis reaction is catalyzed by both acids and bases; however base catalysts are known to be much more efficient than acid catalysts[140]. A variety of bases such as metal hydroxides, metal oxides, metal salts of weak acids are used. The commercially used alcoholysis catalysts[141] include oxides, alkoxides of lead, lithium, calcium, tin, zinc, etc. Carbonates and alcoholates are most effective catalysts. The sodium and potassium alkoxide of specific alcohols are also preferred in many cases. A comprehensive study on alcoholysis of soybean oil with pentaerythritol at equimolar amount in presence of catalyst showed that lead compounds are the most efficient catalysts followed by napthenates of lanthanum, calcium, cerium and lithium salts[142]. Gupta *et al.*[143] carried out a general study to determine the rate and extent of alcoholysis of refined soybean oil, linseed oil, dehydrated castor oil with polyols eg. neopentyl glycol, glycerine and pentaerythritol in presence of catalyst such as LiOH, $Ca(oct)_2$, PbO, MeONa, DBTO (di-butyl tin oxide) at temperature of (200-240) ^0C and observed that at a constant temperature and at a fixed concentration of the catalyst, the rate of alcoholysis follow the order LiOH>PbO> DBTO> MeONa> $Ca(oct)_2$ and extent of alcoholysis (monoglyceride/triglyceride ratio) follow the order DBTO>$Ca(oct)_2$ >MeONa> PbO>LiOH. In the case of castor oil, both the glycerolysis rate and the equilibrium glyceride content varied in the order LiOH>CaO>PbO. The use of organotin catalyst[144] (e.g., Fascat 4350) for the preparation of oil modified polyester resin reduces the synthesis time, and generates haze free resin with improved color when compared to lithium neodecanoate catalyst. Athawale *et al.*[83] prepared modified castor oil based polyester resins by chemoenzymatically using enzyme catalyst, Lipozyme IM 60 (lipase from the fungus *Mucor miehei* immobilized on microporous anion exchange resin). The chemoenzymatically synthesized polyester resins showed light color, good reverse impact strength, excellent chemical resistance and storage stability compared to the conventional ones. The use of porcine pancreatic lipase[145] in the synthesis of coconut oil based polyester resin was reported, which lead to the synthesis of more controlled alkyd resin structure than the conventional coconut oil based polyester resin.

1.3.5.2 Fatty Acid Method

In this method polyol, dibasic acid and fatty acids are reacted simultaneously at temperature of (220-260) ^0C until desired alkyd specifications are obtained. In this process fatty acids compete with the phthalic anhydride and the phthalate half ester for the available hydroxyl groups[75]. This process allows greater freedom in formulation because any polyhydric alcohol or blend can be used, and the fatty acids not available as glycerides, such as pelargonic acid, 2-ethylhexanoic acid, tall oil fatty acids, etc. can be used[75, 77].

A special modification of the fatty acid process, developed by Kraft is referred to as the high polymer technique[77, 79, 146]. In this case the dibasic acids and the polyalcohols are precondensed with a portion of the fatty acids, after a low acid number is obtained, the remaining portion of fatty acids is added to complete the polycondensation. Polyester cooked by this method is of light color and more viscous than those cooked by the conventional fatty acid method. Several advantages of fatty acid process[54, 103, 146] over the monoglyceride process are found. These are greater freedom of formulation since any polyol or polyol blend can be used, tailor made product can be made, no catalyst is required so the risk of discoloration and oxidation is reduced, processing is more reproducible as the formation of monoglyceride is not yet fully controlled, processing time is shortened, etc. However, some disadvantages[54, 103, 146] of fatty acid process over the monoglyceride process are also observed. These include fatty acids are more expensive than triglyceride oil, more corrosive than oil so they need corrosion resistant equipment for storage, often have higher melting point than oils so require preheating equipment to facilitate handling them as liquids, more susceptible to discoloration during storage, etc.

1.3.5.3 Acidolysis Method

The acidolysis method may be considered as the converse of the alcoholysis process. Here, the oil is reacted with the dibasic acid component in the first stage of the process, and in the second stage the polyol is added. This reaction occurs at high temperature without a catalyst and its use is limited to polybasic acids, such as isophthalic and terephthalic acids, which do not sublime and are quite insoluble in the monoglyceride until considerable esterification has occurred[75, 77, 146]. At the high processing temperature, side reaction like dimerization of the oil is unavoidable, which leads to discoloration of polyester resin[54]. Procedures have been developed to overcome corrosion problems at high processing temperature and produce light colored resins with good drying properties[147]. Carlston studied[148] the acidolysis of vegetable and marine oils with three isomers of phthalic acid and it was found that orthophthalic acid dehydrates to anhydride before any interchange occurs, but isophthalic and terephthalic acids are heat stable and react easily with oils at (280-300) ^{0}C. Isophthalic acid reacts more rapidly than terephthalic acid. Commercial use of the acidolysis reaction in polyester resin manufacture is economically attractive because no catalysts are required.

1.3.5.4 Fatty Acid-Oil Method

This method involves the direct reaction of fatty acid, oil, polyol and dibasic acid[146]. The ratio of fatty acid to oil must be such that a homogeneous reaction mixture results. This process has a cost advantage over fatty acid process and gives high viscosity polyester, if the fatty acid represents 60-65% of the total of fatty acids and oil. Heat polymerized oil gives even higher viscosity polyester resin[75, 77, 149].

1.3.6 Esterification Techniques

During esterification stage of alkyd resin preparation, water is evolved as a byproduct. Since esterification is an equilibrium reaction, the evolved water must be removed to force the reaction towards completion. The fusion and solvent techniques are used in order to remove water.

1.3.6.1 Fusion Technique

In fusion technique, all the reactants (in case of oil after monoglyceride process) are processed together at the reaction temperature, in a stream of inert gas (N_2 or CO_2), which remove water of esterification and prevent air oxidation[54, 77, 79]. At high temperature the volatile reactants may be lost. The quantities lost must be considered when basic components are added[79]. Fusion technique is often acceptable for polyester containing a high percentage of oil. The equipment cost is comparatively low in fusion process and no water condenser is required.

1.3.6.2 Solvent Technique

In solvent technique, the polycondensation is carried out in the presence of aromatic solvent (usually xylene), which is immissicible in water and capable of forming azeotropic mixture with it. Solvent is commonly used in amounts from 3-10% of the batch. Solvent method is generally used for preparation of short oil polyester resin[80, 82]. Advantages of solvent technique[77, 80] are (i) reaction time is short as water formed is removed rapidly, (ii) extent and rate of reaction can be determined easily, (iii) better color and batch-to-batch reproducibility is obtained, (iv) uniform molecular distribution of the product is obtained, (v) losses of phthalic anhydride by sublimation is reduced, (vi) solvent provides protection against attack by atmospheric oxygen, etc.

1.3.7 Modification of Oil Based Polyester Resins

The modification of existing commercial polymers by physical and chemical means is one of the most accepted industrial techniques to improve desirable level of properties for different applications without the need of newly developed polymers, which may require new industrial set-up, more time and labor, and ultimately require more cost. For oil modified polyester also, the properties are improved by proper modification with varieties of reactive chemicals and other polymeric materials[77]. The presence of reactive sites like double bonds, hydroxyl, carboxyl groups, presence of aromatic rings in phthalic anhydride and ester linkages provide tremendous potential[54] for oil modified polyester modification. There are many polymeric materials and reactive functional chemicals by which alkyds are modified to obtain improved properties for different advanced applications. The short oil polyesters having a higher proportion of hydroxyl groups provide compatibility and reactive sites for urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins[75]. The alkyds modified with UF and MF resins show improved hardness, exterior durability, alkali resistance and rate of drying[150]. Short to medium oil polyester resins are often modified with nitrocellulose to upgrade[54, 75] their gloss, durability, cold check resistance, flexibility and adhesion. Blend of alkyd resin with chlorinated rubber[75] show improved toughness, solvent resistance and durability with excellent alkali, acid and water resistance and drying rate. Epoxy resins are considered as polyols, which react with the carboxylic functions of the alkyd resin. Modification of oil modified polyesters with epoxy resins[151] gives products, which exhibit excellent adhesion properties and improved water and chemical resistance. Epoxy modified alkyds are less expensive than epoxy resins. Epoxy modified polyester resins of soybean and tung oil showed excellent drying and chemical resistance properties[152]. Reactive silicone intermediates react with the hydroxyl groups in long oil air drying polyesters and leads to the improvement[75] of durability, gloss retention and heat resistance. Alkyds modified with poly organosiloxane[153] showed enhancement of water resistance, thermal stability, wear resistance and electrical insulating properties. The excellent adhesion to substrate was reported by the modification of alkyds with carboxy-functional nitrile rubber[154]. The excellent structural compatibility of ketonic resin with alkyd resin resulted in improvement of adhesion, hardness, gloss, storage stability, acid resistance and drying time of the blends[155]. Modification of alkyds with phenolic resins[77] has been shown to render excellent gloss retention and durability of alkyds, together with water and alkali resistance.

The unsaturation in the fatty acid groups of alkyds allows interpolymerization with a variety of reactive vinyl monomers[77, 79] such as styrene, α-methyl styrene, vinyl-toluene, methyl methacrylate, butyl methacrylate, ethyl acrylate, acrylonitrile, etc. The modification of polyester resins based on cotton seed oil, linseed oil, fish oil, soybean oil and sunflower oil with vinyl toluene to improve clarity was reported[156]. Whereas Golhar *et al.* reported[157] about the post styrenation (up to 50% styrenation) of linseed oil based polyesters resins to improve drying time, scratch hardness, resistance towards solvents and chemicals. Significant improvements in drying time and weather resistance properties of dehydrated castor oil based polyester resin were obtained by graft copolymerization[158] with methyl methacrylate and butyl methacrylate. Akintayo *et al.* reported[159] the modification of *Albizia benth* medium oil alkyd by acrylation, the study revealed that at optimum level of modification acrylated resin show better drying, flexibility, scratch hardness, impact resistance and chemical resistance properties. The use of N, N-dihydroxyethyl acrylic acid amide as partial replacement of glycerol in the preparation of medium oil polyester resin reduced the need of anticorrosive pigments in primer formulation[160]. Water reducible acrylic–alkyd resin prepared by the esterification of monoglyceride based on palm oil and carboxy functional acrylic copolymer showed[161] excellent water and acid resistance and good alkali resistance. Alkyd resins are frequently modified with isocyanates viz. toluene di-isocyanate, isophorone di-isocyanate, hexamethyl di-isocyanate, etc. to produce modified urethane alkyds with improved film hardness, durability, drying rate and chemical resistance[54]. Polyamide modification of alkyds is widely used to obtain special rheological properties i.e. thixotropic alkyds. Thixotropic behaviour is achieved by incorporating 2-10% polyamide in alkyd at higher temperature[162]. The incorporation of metal alcoholates mainly aluminium alcoholates with alkyd resins lead to enhanced through drying, greater film hardness and improved water, chemical and weather stability[163]. Whereas chlorination of *Albizia benth* medium oil polyester resin was carried out[164] by passing dry chlorine gas through the resin, which resulted in improvement of chemical and mechanical properties.

1.3.8 Characterization

Oil modified polyester resins are being characterized by conventional techniques for determination of different physical properties[39] like iodine value, acid value, saponification value, hydroxyl value, viscosity, volatile matter content, specific gravity, etc. Structural analysis, molecular weight determination and thermal characterization are generally performed by techniques like FTIR/NMR, GPC and TGA/DSC respectively[165-169].

Determination of physical properties like iodine value indicates the degree of unsaturation present in the resin, which implies their drying ability by the conventional drying techniques. Similarly, the results of acid value, saponification value, hydroxyl value and viscosity indicate the level of free –COOH groups, molecular weight (chain length), free –OH groups and processibility respectively. The extent of reaction in the preparation of alkyd resin was monitored by determination of acid value at various time intervals of the resinification reaction[170].

FT-IR technique is largely used[165] to determine the functional groups present in the structure like carboxyl group, ester group, hydroxyl group, unsaturation, aromatic ring, etc. The curing reactions of palm oil alkyd and melamine-formaldehyde resin blends were studied[171] by FT-IR technique. The significant reduction of the absorbance peaks of -O-H and $>N-CH_2OCH_3$ and formation of methylene ether linkages with time at constant temperature was utilized for this purpose. The photoacoustic fourier transform infrared spectroscopy has also been utilized for *in-situ* measurements of the curing processes in alkyd based on soya fatty acids[172]. IR spectroscopy was also utilized for the determination of the oil content in oil modified orthophthalic polyester resins[173]. Even miscibility of chlorinated polypropylene with alkyd resin in the specified mixing ratios was studied by FTIR spectra[174].

^{1}H-NMR can play an important role to understand the actual structures of a range of alkyd paint binders and their precursors, the drying oil, polyol, and aromatic acids being used[175]. In general, ^{1}H-NMR indicates the presence of different types of protons[169] like carboxylic, hydroxyl, ester, carbonyl, hydrocarbons of saturated and unsaturated, aliphatic, aromatic, etc. This spectroscopic technique was also used for fast qualitative and quantitative determination of fatty acids in alkyd resin urethanes[176]. In addition to structural identification of the oil, the ^{1}H-NMR spectra provided quantitative determination of the oil, the phthalic anhydride and polyol components in the alkyd resins[177]. Similarly ^{13}C-NMR technique is utilized[165] to find out the presence of chemically different carbon atoms in aromatic, aliphatic, unsaturated, saturated hydrocarbons, in ester, carboxyl group, etc. It was used[178] to measure the extent of reaction in stoving alkyds as the degree of cure of the alkyds affects the resolution of the spectrum. Spyros reported[179] the application of advanced 1D and 2D ^{1}H- and ^{13}C-NMR techniques for the characterization of various alkyd resins used in the coating industry. 2D NMR allows the spreading of chemical shift information in two dimensions, so much more for alkyds exhibiting complex 1D NMR spectra with broad and/or featureless peaks.

The molecular weight and its distribution of oil modified polyesters are generally determined by GPC technique. The use of GPC analysis for monitoring the formation of di- and mono-glyceride, and di- and mono-trimethylol propane esters has been reported[33].

The thermal characterizations of the resin are generally carried out by TGA and DSC techniques. By TGA technique along with the thermostability of the resins in different environment, the pattern of degradation, kinetics of degradation, char residue, etc. are determined[167, 168]. Whereas DSC technique is most widely used to get the information[167, 168] about the phase change, different chemical changes like degradation, cross-linking, etc. The kinetic of cross-linking reactions is also determined by DSC technique. The nature of curing reaction of an alkyd based on dehydrated castor oil fatty acid and melamine-formaldehyde resin mixture was studied[180] by DSC methods. The use of DSC was also reported for the determination of optimum curing temperature for mixture of alkyd and melamine-formaldehyde resins[181] and for measurement of peroxides formed in order to monitor drying extent of alkyd resins[182].

In addition to the above, the technique scanning electron microscopy (SEM) is utilized to study the morphology of the blends of alkyds with other resins and compounded alkyds (paints), which indicate the dispersibility, compatibility of different components present in the system[183]. Aurelia *et al.* reported[184] the study of morphology of alkyd and melamine-formaldehyde resins and their mixtures with clay by using transmission electron microscopy (TEM). Atomic force microscopy (AFM) is used to study the alkyd surface structure[185].

1.3.9 Structure and Property

Oil modified polyester resins possess wide varieties of structural compositions, as they can be prepared from a large variety of vegetable oils. These vegetable oils possess different fatty acid compositions and structures[39]. As the structure of a material determines its properties and behavior, so these resins exhibit a wide range of properties, which are useful for their different applications. Even though the main structural linkage is ester but they also have functional groups like unsaturation, hydroxyl, epoxy, aromatic ring, etc. along with saturated aliphatic hydrocarbon chain, which influence the ultimate properties of the resins. The diversity in properties of polyester resins is mainly due to the presence of ester linkage, which influence the properties in the following ways[186].

i) Chemically it is a weak linkage being susceptible to hydrolysis, aminolysis and ester interchange. The first two reactions lead to chain scission, which detoriate the properties of the resins.

ii) As it is a polar group, it can affect the high frequency electrical insulation properties of the resins.

iii) These polar ester groups may also act as proton acceptors allowing interactions with other groups, which increases inter-chain attraction and in terms of the affects on melting point and rigidity of the resin.

iv) This linkage appears to influence the chain flexibility along with the polymethylenic chain. Thus this affect of ester linkage cancels the previous effect.

v) Chemical properties of a polymer are influenced by the presence of different chemical linkages, rigidity and compactness.

This structure and property relationship is very useful to understand the expected properties of the resins. A brief overview of different properties of oil modified polyester resins are presented here. The physical properties like solubility, density, crystallinity, optical properties, etc. are mainly influenced by the nature of the vegetable oils, polybasic acids and polyols.

Solubility of polyester resins varies with oil length of resins[80, 187]. Long oil polyester resins are soluble in aliphatic hydrocarbon solvents. As the oil length decreases, mixtures of aliphatic and aromatic solvents are required[188], and the resins possessing oil length below 50 require aromatic solvents[103]. The non-polar side chain would increase solubility in hydrocarbons. In order to optimize the solid content of the alkyd resin solution, with a view to lower volatile organic compound emission, extensive studies have been carried out on solubility parameter and solution viscosity of alkyd resin[189-191]. Alkyds with high acid number, which are neutralized with amines, are soluble in water due to salt formation[192].

The ability of a polymeric material to crystallize is determined by its molecular structure. A regular structure has potential to exhibit crystallinity while an irregular structure will tend to be amorphous in nature. The general structure of the alkyd resin is very complex in nature as they are obtained from a mixture of fatty acids with different structures and compositions. Further in resinification reaction, no stereo-specific catalyst is used so the product obtained is random in nature. Thus the crystallinity of alkyd resin is rare to obtain rather they are amorphous and highly flexible[54].

The specific gravity is a function of the weight of the individual molecule and the way they pack. The hydrocarbon chain with no heavy atom and amorphous nature of the alkyd resins make them of lower specific gravity[28, 193].

The correct mechanical and rheological properties of the resins are very much essential for their utilization in various fields. These properties are mainly influenced by the presence of chain entanglement, coiling, different inter- and intra-molecular attraction forces, crosslinking density, rigidity, and their molecular weight and its distribution. Higher the molecular weight, higher will be the entanglement and coiling. The larger the influence of these factors, the higher will be the mechanical properties and viscosity. The flexibility of the condensation product increases[194] with the increase of molecular weight of the oil or fatty acid. As alkyd resins possess flexible hydrocarbon chain in their structure and amorphous in nature, so generally they exhibit good impact strength[39, 54]. However, they do not have excellent mechanical strength. Although the major part of the structure of alkyd resins are non-polar hydrocarbon but due to the presence of polar ester group, free hydroxyl and carboxyl groups, the adhesion characteristics of this resin is sufficienly high for their different applications. The rheological behavior that is the flow behavior of the alkyd resins is generally complex in nature. This type of fluid exhibits more non-Newtonian flow at moderate to higher shear rates but nearly Newtonian at low shear rate. Rheological characteristics such as flow behavior improves and sagging increases with increase in fatty acid content[77]. The rate of viscosity increase is much greater for short oil polyesters than for the long oil type[110]. The higher the degree of unsaturation the higher the viscosity due to the greater extent of dimerization[103]. Fatty acids with conjugated double bonds dimerize more rapidly than those with non- conjugated bonds. Alkyds of the same solution concentration and same acid number will increase in viscosity in the order soybean < linseed < tung[103]. The use of thixotropic alkyd resins is the best way of obtaining reproducible flow properties[79].

The optical properties like refractive index, clarity, color, transmittance, reflectance, etc. are important properties for polymeric material. As alkyd resins are amorphous in nature, so if they are free from other impurities or additives then they may exhibit transparency, unless they have some chemical moieties, which absorb visible light. One of the most important performance properties of alkyd resin in coating material is gloss. Gloss refers to the specular reflection or the light reflected at the same angle of incidence. In general alkyd resins show semi to high gloss. The lower the oil content of the resin, the better the color stability and gloss retention[79]. However, the high levels of unsaturation remaining in the cured films cause loss of gloss on exterior exposure[103]. Higher functionality alcohols allow an increase in the fatty acid content, which results in better gloss retention[116].

The electrical properties of a polymer like dielectric constant, dielectric strength, resistivity, etc. are the parameters for their electrical applications. Alkyd resins exhibit generally moderate insulating characteristic with lower resistivity and higher dielectric constant and power factor due to the polar nature of ester group[186]. But these characteristics are influenced by the condition of application.

Thermal properties of a polymer are extremely important for their end applications. The important features of a polymer like bond strength, inter- and intra-molecular forces, resonance stability, crystallinity, imperfections in structures, molecular weight, etc. are responsible for its thermal behaviour. Long oil polyester resin and styrenated alkyd resin were made flame retardant by incorporation of *bis*-pyridine *bis*-tribromophenoxo copper complex and polydibromo phenylene oxide[195].

The chemical resistance of a polymeric material depends on many factors such as solubility, chemical linkages, cross-linking, permeability and the chemical environment under which that was tested. The ester linkage of alkyd resin is highly susceptible to hydrolysis and aminolysis that resulted reduction in molecular weight and hence detoriation of properties[186]. However the presence of aromatic ring adjuscent to this group may offer some protection against this unstability. Modification of alkyds with styrene, isocyanate, phenol, etc. offers good resistance[79, 80] to water and alkali. Steric factors also offer greater resistance to hydrolysis[79].

1.3.10 Applications

The oil modified polyester resins find wide range of applications mainly because of their many outstanding properties such as flexibility, adhesion, gloss, toughness, dispersibility with pigments, drying time, flow behavior along with overall low cost [54, 196]. Further their properties can be tailored by proper choice of the feed stock as a large variety of raw materials with different structures and compositions are available for the preparation of these resins. Thus due to this versatility, they may be regarded as a milestone in the industrial application of coatings[2]. Alkyd resins are widely used[80] for both decorative as well as protective purposes such as architectural enamels, lacquers, top side marine coatings, textile finishes, metal primers, printing inks, caulking compounds and water emulsion paints, etc.

Depending on the oil length of the resins, their uses are generally different. Long oil polyesters are used in exterior trim paints, house paints, wall paints, anticorrosion paints, coach enamels, marine and metal maintenance paints, offset printing inks, silk screen inks, binder for metal printing enamels, white and pigmental finishes, etc.[39, 79]. Whereas the application of very long oil alkyds is mainly restricted to printing ink industry for different types of products[39] such as heat set inks, quickset inks, metal decorating inks, etc. Though very long oil polyesters based on tall oil fatty acids find utility in outside house paints, trim and trellis paints[197]. The medium oil polyesters resins based on drying oils or fatty acid mixtures are used as binders for air-drying and forced-drying machinery coatings and industrial coatings. They are also used[77, 79, 192] in car repair finishes, original equipment manufacturing finishes, top coats and coatings for trucks, buses and large capacity vehicles, porch and deck paints etc. The non-drying types are used [198] for putty and pencil lacquers, external plasticizers for nitrocellulose lacquers, etc. The short oil polyesters are used in combination with amino resins for industrial stoving enamels (metal furniture, bicycles, garage doors, radiators, every articles made of steel). Short oil polyesters are also combined with urea resin for acid curing wood varnishes and mixed with nitrocellulose for inexpensive, easily applied furniture lacquers and refinishes [79, 192, 199].

Polyesters with variable oil lengths are modified with variety of polymers as well as grafted with different reactive chemicals for their advance applications. Blends of chlorinated rubber with alkyds are used[54, 116] as paints for highway markings, swimming pools, concrete floor, etc. Silicone modified alkyd paints are used[188] for protection in moderately high heat environments, such as fireplace mantel coatings and barbecue grills. They are also used for outdoor applications[54] such as topcoat for steel petroleum storage tank. Alkyd resins modified with epoxy resins are used[152] in anticorrosion paints, can coatings, primers. The alkyd-ketonic blend may find a wide applications[155] in formulation of inks, paints, varnishes and lacquers. Alkyds modified with polyamide resins are generally used[54] in air-drying non-drip paints. Alkyd resin based coating containing carboxy functional nitrile rubber can be applied as protective coatings on metal surfaces for railway transport, construction and equipments[154].

Vinylated very long oil alkyds are used in lithographic paints[39]. Styrenated alkyd resins are widely used[151] for flat wall paints, one coat metal finishes, solderable zinc powder paints, and anti-corrosive primers. Alkyds modified with methyl methacrylate are used in roller coatings where rapid drying is required[54]. Acrylate grafted dehydrated castor oil polyesters are used[158] in weather work paint for superstructure of ships. Funakoshi *et al.*[200] reported the use of composition containing acid anhydride modified chlorinated polyolefins and acrylic modified alkyd resin as primer for polyolefin substrates. Alkyds modified with isocyanates are used[151] as the base resins for parquet varnishes, garage floor paints, marine varnishes and many types of primers. When the modification is done with higher amount of isocyanates, the resins are used for the preparation of interior matt and satin-finish varnishes, floor paints, and industrial coatings. Especially, in case of varnishes used for boats, isophorone diisocyanate modified alkyd resins are used[151].

Wang *et al.*[201] reported the possible application of water borne alkyds for railroad cars. Other applications include the use of alkyds in gaskets, printers rolls, flexible insulation, and as binders for mica[80]. Alkyd resin putty was applied on hardened white cement filled tiles to ensure the toughness and smoothness[202]. Alkyd resin containing niobium carbide nanoparticles have been used[203] for production of radio wave absorbing materials. These materials can be used as protective screen, mantle or coating material masking equipment from radio detection. These are also used for protection of personnel from radio emission, and as a radio wave absorbing label for security papers and documents.

1.4 Scope and Objectives of the Present Investigation

From the main features of the foregoing discussion, it has been found that many vegetable oils are widely used in place of petroleum based products as the raw materials in the production of many important industrial products like surface coatings including paints, varnishes etc., printing inks, soaps, cosmetics, pharmaceuticals, lubricants, emulsifiers, multipurpose additives, biodiesel, plasticizers, etc. Again vegetable oils are environment friendly as they are biodegradable and obtained from nature. Vast varieties of widely grown plants and herbs are available in India. Seeds of many plants contain oils, those are viable alternatives of petroleum resources for many applications. *Mesua ferrea* L. (Nahar) is a plant that produces high oil content seeds. In India, it is available[94, 204] in North-East region, Karnataka, Kerala, Tamilnadu, West-Bengal and Uttar Pradesh, etc. The oil content of Nahar seeds is exceptionally high (70-75%) and it possesses both saturated and unsaturated fatty acids. Also there is a few reports on the utilization of this oil in the fields of medicine and biodiesel[204, 205]. However, there is no report on the utilization of this oil in the field of polymer, to our knowledge. So, it appears that there is a lack of systematic and comprehensive study on the utilization of this oil in the field of polymer. Hence, the following questions may arise in this area.

i) Whether this oil can be used as a coating material after heat treatment?
ii) Whether this oil can be utilized for the preparation of any polymer?
iii) Whether this polymer can be used as a coating material?
iv) Whether the performance characteristics of this polymer can be improved by any physical or chemical means?

Under this background the main objectives of the present investigation are as follows:

i) To study the physical and spectroscopic characteristics of the unheated and the heated *Mesua ferrea* L. seed oil.
ii) To synthesize, characterize and properties evaluation of *Mesua ferrea* L. seed oil modified polyester resins.
iii) To improve the performance characteristics of *Mesua ferrea* L. seed oil modified polyester resins by blending with commercially available resins.

iv) To use a *Mesua ferrea* L. seed oil modified polyester resin for the preparation of an industrial paint.

1.5 Plan of Work

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

i) A state of art literature survey will be conducted in the area of utilization of vegetable oils in the field of polymer.

ii) Seeds will be collected from local areas and utilized for isolation of oil.

iii) The isolated oil will be purified by the conventional method.

iv) The purified oil will be characterized physically and spectroscopically before and after heat treatment.

v) The purified oil will be utilized for preparation of polyester resins.

vi) The polyester resins will be blended with other commercial resins for surface coating application.

vii) The polyester resin will be utilized for the preparation of an industrial paint.

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Chapter 2

Mesua ferrea L. Seed Oil and Its Heat Treatment

2.1 Introduction

A large variety of vegetable oils are used as raw materials in the coating industry. Out of these, many traditional oils such as linseed, castor, soybean, safflower, sunflower, etc. are largely used for preparation of many industrial products. But because of growing prices and limited supply of these oils, the scientists have started exploring for non-traditional oils available in abundance[1]. Out of various non-traditional vegetable oils, kamala, karanja, karinotta, neem, undi, gokharu, etc. are some of the important oils that may be mentioned.

The drying oils have been in use for surface coatings applications for a pretty long time. But as they could not satisfy the standard requirements for film properties like chemical resistance, abrasion resistance, etc., so latter on heat treatment of the vegetable oils and polyester production were evolved[2-3]. Thus heat treatment of vegetable oils is an old and commonly used industrial practice[4]. In this process, certain degree of polymerization is achieved by heating the oil at high temperature. Thermal polymerization leads to the improvement of oil characteristics[5]. Upon heating, the viscosity rises in a characteristic manner, which is due to molecular growth[6]. The thermal polymerization is monitored by checking viscosity with time of heating[1]. The nature of the reaction during heat treatment has been quite extensively investigated[5, 7-10]. It has been found that different types of reactions are taking place during heating. These reactions[5, 7-10] are thermal polymerization through Diels-Alder reaction, oxidative polymerization, ester interchange, cyclization, hydrolysis, etc. Currently, heated vegetable oils are being used as printing ink vehicles compared to petroleum based products[2].

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As it has already been described in the scope of the present investigation that *Mesua ferrea* L. (Nahar) seed oil is an important non-traditional vegetable oil, which may be employed for heat treatment studies in order to impart characteristic properties for use as coating material.

In this chapter, therefore, heat treatment imparted to Nahar seed oil was discussed and the properties of heated oils were evaluated along with the properties of unheated oil.

2.2 Experimental

2.2.1 Materials

Mesua ferrea L. (Nahar) seeds were obtained from the plant (Fig. 2.1), which is large, beautiful and evergreen tree of 3-15 m height with a conical crown. It is commonly found in different parts of India[11, 12] such as in North-East region, West Bengal, Karnataka, Kerala, etc. The oil is brown in color, pungent and slightly viscous liquid. The tree bears flowers between April and July, and fruits between October and November. The average yield of seeds (Fig. 2.2) per tree is around 10-15 kg. The oil content is about 70-75%. According to a survey done in 1983, the availability of Nahar seeds in India per year is 5,690 tonnes[13]. The Nahar seeds used for the work of this chapter were collected from Barpeta, Assam, India. The oil was extracted from the dried seeds by pressing method using screw press. The oil was purified by degumming with water followed by refining with 0.01% aqueous NaOH solution, and then washed with distilled water and dried under vacuum[14]. Previous workers reported that Nahar seed oil possesses oleic (52.3%) and linoleic (22.3%) acids as unsaturated fatty acids and palmitic (15.9%) and stearic acids (9.5%) as saturated fatty acids[15].

Methyl-ethyl ketone peroxide (MEKP) and cobalt octate were obtained from Kumud enterprise, Kharagpur. MEKP is a clear liquid with density of 1.053 g/mL and cobalt octate is 2% solution of cobalt octate in cyclohexanone.

Styrene was obtained from Merck, Germany of density 0.906 g/ml, assay $\geq$ 99%. It contained tertiary butyl catecol as inhibitor. Styrene was used after removal of the inhibitor by washing with 4% alkali solution followed by washing with distilled water and then drying.

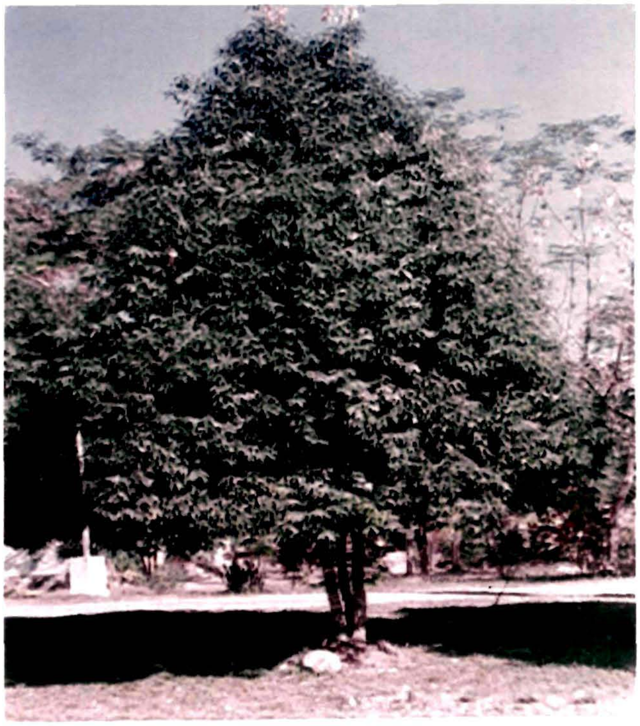

Fig. 2.1 Photograph of *Mesua ferrea* L. (Nahar) tree

Fig. 2.2 Photograph of *Mesua ferrea* L. (Nahar) seeds

2.2.2 Instruments and Methods

FT-IR spectra of unheated and heated oils were recorded in FT-IR spectrophotometer (Impact-410, Nicolet, USA) using KBr pellet. ^{1}H-NMR spectra of the unheated and heated oils were recorded in NMR spectrometer 200 MHz (ACF-200, Brucker) using $CDCl_3$ as the solvent and TMS as an internal standard. The molecular weights of unheated and heated oils were determined by GPC analysis (Waters, USA, Model 515) using THF as the solvent. The viscosities of both unheated and heated oils were measured using Brookfield viscometer (Model LVT, Serial number 201543, USA). The relationship between viscosity and time of heating of the oil was established by using least square fitting method with the help of a computer.

The physical properties of unheated and heated oils such as acid value[16], iodine value[17], saponification value[18], and specific gravity[3] were determined by the standard methods.

The film thickness of cured films was determined by Pentest, coating thickness gauge (Sheen Instrument Ltd., Model 1117, UK). The pencil hardness of the cured films was measured using pencils of different grades ranging from 6B to 6H. The coated mild steel plate is placed on a horizontal surface. The pencil is held firmly against the film at an angle of 45^0 and pushed away from the operator in a 6.5 mm stroke. The process is started with the hardest pencil and continued down the scale of hardness, the pencil that will not cut into the film will give pencil hardness (ASTM D 3363-00)[19]. The gloss characteristics of the cured films were found out[20] using glossmeter (AIMIL, Ajmer), over resin coated mild steel plate at an angle of incidence of 45^0. The adhesion performance of the coated films on mild steel plate was tested by using the commercial cello tape as per the cross-cut tape test method (ASTM D 3359-97)[21]. This test is performed to establish whether the adhesion of a coating to a substrate is at an adequate level. Flexibility test was performed using flexibility apparatus (PEI, Kolkata). It is an empirical test for assessing the resistance of coating to damage, detachment and/or cracking from a metal substrate when subjected to bending around a cylindrical mandrel. The films of both unheated and heated oils over tin plate were bent over a 6.25 mm diameter mandrel through 180^0 and examined for any damage, detachment or cracking of the film as per the standard procedure[22]. The film is said to be flexible, if it does not show any damage, detachment or cracking. The chemical resistance of the cured films was performed in different chemical environments. Glass plates coated with films of heated and unheated oils were kept in 250 mL beakers containing 150 mL of different chemicals for 4 days and then observed for any change on films.

Heating of Nahar oil

Measured amount of oil was poured into a 3 necked round bottomed flask fitted with a mechanical stirrer and a thermometer. One neck of the flask was kept open to facilitate the removal of volatiles produced during heating and to expose the oil to open air. The oil was heated at two different temperatures i.e., at (250±5) ^{0}C and at (315±5) ^{0}C with constant stirring up to 6 h separately. The bulk viscosity of heated oil was measured at every 1 h interval of heating for both temperatures.

Preparation of Films and Curing

Unheated and heated oils were mixed separately with 30 phr (parts per hundred) of styrene, 8 phr of MEKP and 4 phr of cobalt octate by hand stirring at room temperature for 5-6 min. Then mixtures were uniformly spread on mild steel plates (150 mm X 50 mm X 1.60 mm), tin plates (150 mm X 50 mm X 0.40 mm.) and glass plates (75 mm X 25 mm X 1.75 mm) and then allowed for curing at 200 ^{0}C.

2.3 Results and Discussion

2.3.1 Structural Analysis

On heating the oil at (250±5) ^{0}C and (315±5) ^{0}C for 6 h, some significant changes in the oil composition were observed by spectroscopic such as FT-IR, ^{1}H-NMR and also by GPC technique. Evaluation of acid, iodine and saponification values, and also specific gravity data have established the changes that occurred in composition of the oil after heating.

Various physical properties like acid value, iodine value, saponification value and specific gravity value of unheated oil (S-1), oil heated at (250 ± 5) ^{0}C for 6 h (S-2) and oil heated at (315±5) ^{0}C for 6 h (S-3) are given in Table 2.1. From this table, it has been observed that the acid value increases from S-1 to S-3 (Table 2.1). Heating accelerates the oxidative rancidity and frying at high temperature that initiates thermal degradation with the formation of decomposition products[23-25] such as ketones, aldehydes, free acids, hydroxylic compounds, esters, etc. Building up of free acids leads to the increase of acid value[26]. Saponification value increases from S-1 to S-3 and the overall molecular weight of the products increased, as supported by GPC analysis (Table 2.1). Again the specific gravity range from 0.921 to 0.936 indicates that there is no heavy element present in the oil. The little increase of specific gravity is due to the formation of polymeric product[5]. The decrease of iodine value from S-1 to S-3 indicates progressive polymerization and reduction of polyunsaturated fatty acids in heated oil[8, 24], which is further supported by ^{1}H-NMR spectroscopic studies (Figs. 2.3, 2.4, and 2.5). Melnick suggested the change in iodine value as a simple control index of the development of thermal polymers since failure to find a drop in iodine value would indicate freedom from polymer formation[27]. Reduction of polyunsaturated fatty acids is further observed from ^{1}H-NMR spectra, where the decrease in methine proton at around $\delta = 5.30$ ppm took place in S-2 and S-3 (Figs. 2.4 and 2.5), which is also supported by other report[28]. The other important ^{1}H-NMR peaks[29-32] are assigned for S-1, S–2, S-3 and shown in Table 2.2.

Table 2.1

Different physical properties of unheated oil (S-1), oil heated at (250±5) ^{0}C for 6 h (S-2) and oil heated at (315±5) ^{0}C for 6 h (S-3)

Properties	S-1	S-2	S-3
Acid value (mg KOH/g)	28	42.68	55.19
Saponification value (mg KOH/g)	190	233.75	239.24
Iodine value (g I_2/100 g)	82	68.36	55.55
Specific gravity (31 ^{0}C)	0.921	0.930	0.936
Weight average molecular weight (M_w)	1623	1810	2607
Polydispersity	1.09	1.85	2.38

Table 2.2

The ^{1}H-NMR peaks and the corresponding protons of S-1, S-2 and S-3

Chemical Shift (δ ppm)	Protons
0.84-0.90	Protons of methyl terminal groups
1.15-1.30	Protons for all the internal $-CH_2-$ groups
1.5-1.6	Protons for $-CH_2-$ group attached next to the terminal methyl group
1.9-2.0	Allylic CH_2
2.2-2.3	α-protons of ester groups
2.7	Double allylic CH_2
4.0-4.3	Protons of glyceride moiety
5.2-5.4	Protons of the $-CH=CH-$ moiety

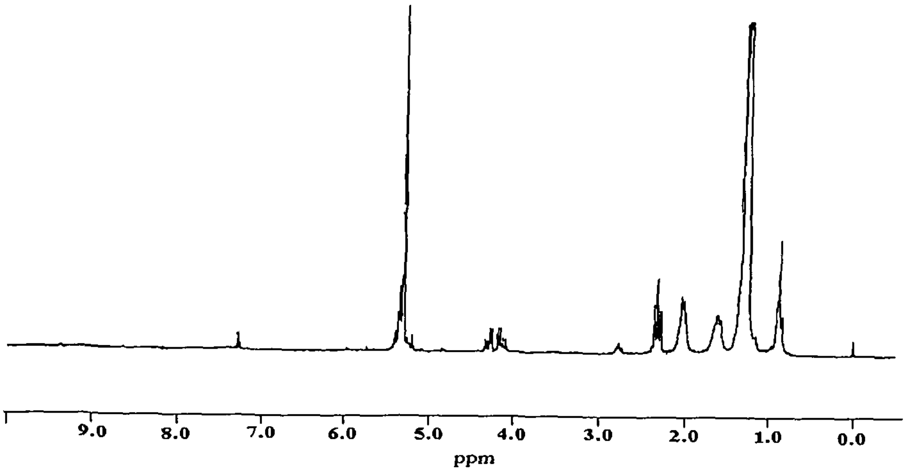

Fig. 2.3 ^{1}H-NMR spectrum of S-1

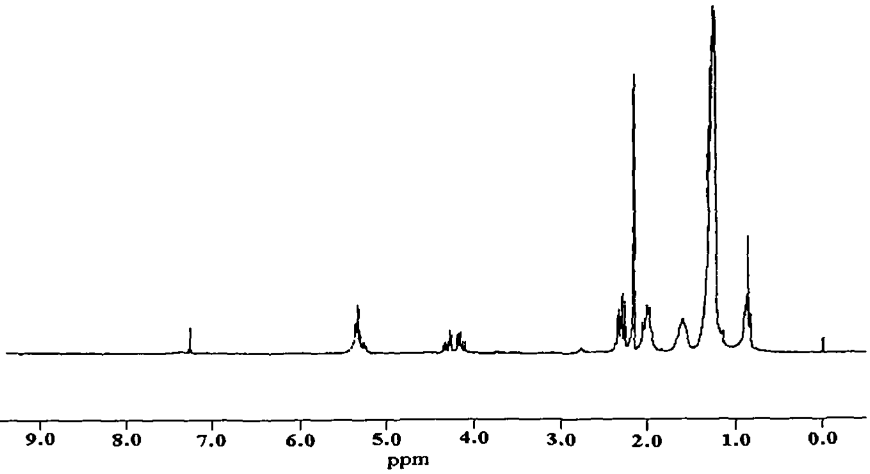

Fig. 2.4 ^{1}H-NMR spectrum of S-2

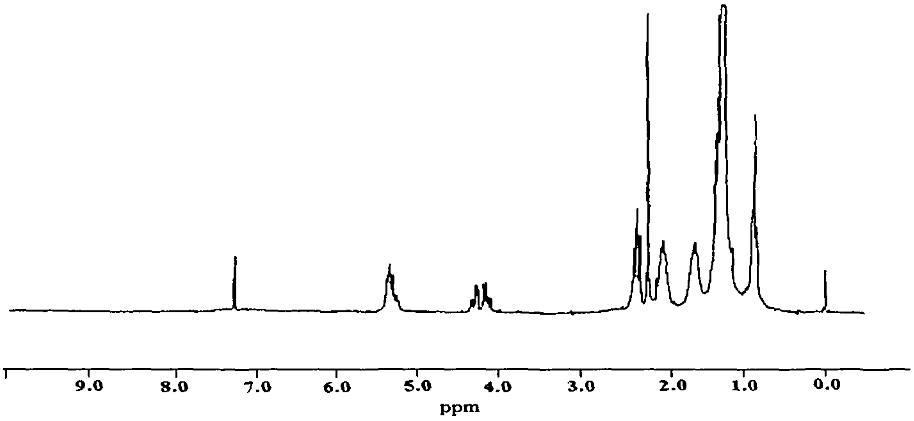

Fig. 2.5 ^{1}H-NMR spectrum of S-3

The important FT-IR peaks[29, 30, 33] for S-1, S-2 and S-3 are assigned in Table 2.3. FT-IR spectra were recorded for the oil heated at two different temperatures (250±5) ^{0}C and (315±5) ^{0}C after every 1 h interval upto 6 h. In case of the oil, which was heated at (250±5) ^{0}C (Fig. 2.6), the intensity of hydroxyl group absorption increases after 3 h of heating due to the increase of hydroxyl compounds, but when the oil is heated at (315±5) ^{0}C then after a certain period, intensity of hydroxyl group absorption decreases (Fig. 2.7). This may be due to some esterification or etherification reactions. The oil having strong absorbance at about 1744-1747 cm^{-1} due to stretching vibration of carbonyl group of the triglyceride esters (Figs. 2.6 and 2.7). On heating at (315$\pm$5) ^{0}C, a new carbonyl absorbance was observed at 1708-1711 cm^{-1} (Fig. 2.7), which is due to the formation of aldehydic or ketonic functionalities. The peak intensity is found to increase with the time of heating, this finding is supported by Moreno *et al.*[34], where intense heating led to the formation of carbonyl compounds, which resulted broadening of the band at 1743 cm^{-1} to lower wave number. Again, on heating at this high temperature, the absorbance maximum at 1614-1617 cm^{-1} continuously decreases with the increase of heating temperature and time (Fig. 2.7). This is again due to the decrease in concentration of unsaturation in the oil. Actually, heating promotes polymerization of the oil via conjugation of unconjugated double bonds[35]. Inter- and intra-molecularly crosslinked polymers are also formed by virtue of cyclization[9] and reaction involving conjugated double bonds of one fatty acyl moiety and a point of unsaturation on another moiety. This is also observed in ^{1}H-NMR spectra as discussed earlier.

Table 2.3

The main FT-IR peaks and the corresponding functional groups of S-1, S-2 and S-3

Bands (cm^{-1})	Assignment
3467-3471	O-H stretching vibration
2852 - 2924	Aliphatic C-H stretching vibration
1744-1747	C=O stretching vibration of triglyceride ester
1614-1617	C=C stretching vibration
1462-1464	C-H bending vibration
1162-1165	C-O-C stretching vibration of ester
722-723	Methylene rocking vibration

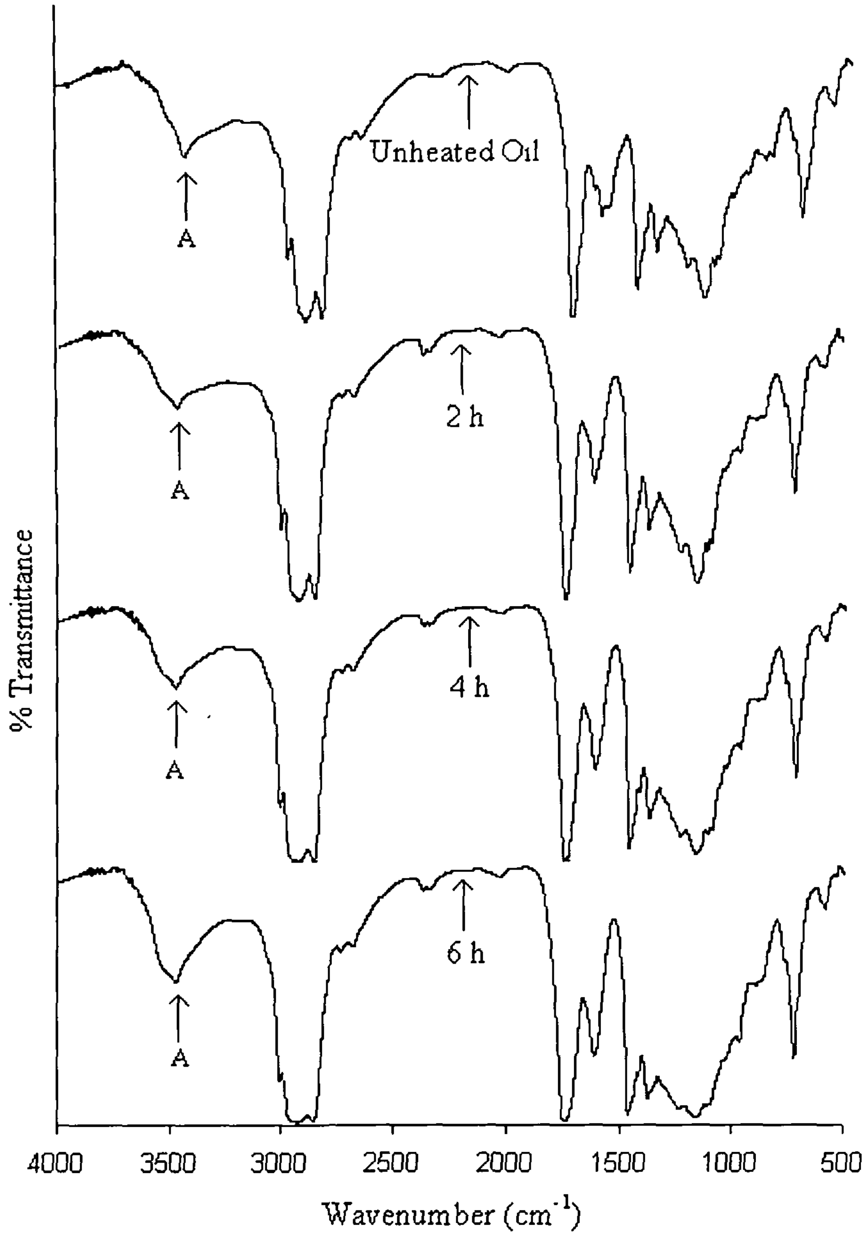

Fig. 2.6 FT-IR spectra of unheated oil; oil heated at (250±5) ^{0}C for 2 h, 4 h and 6 h (A= peak for O-H functional groups)

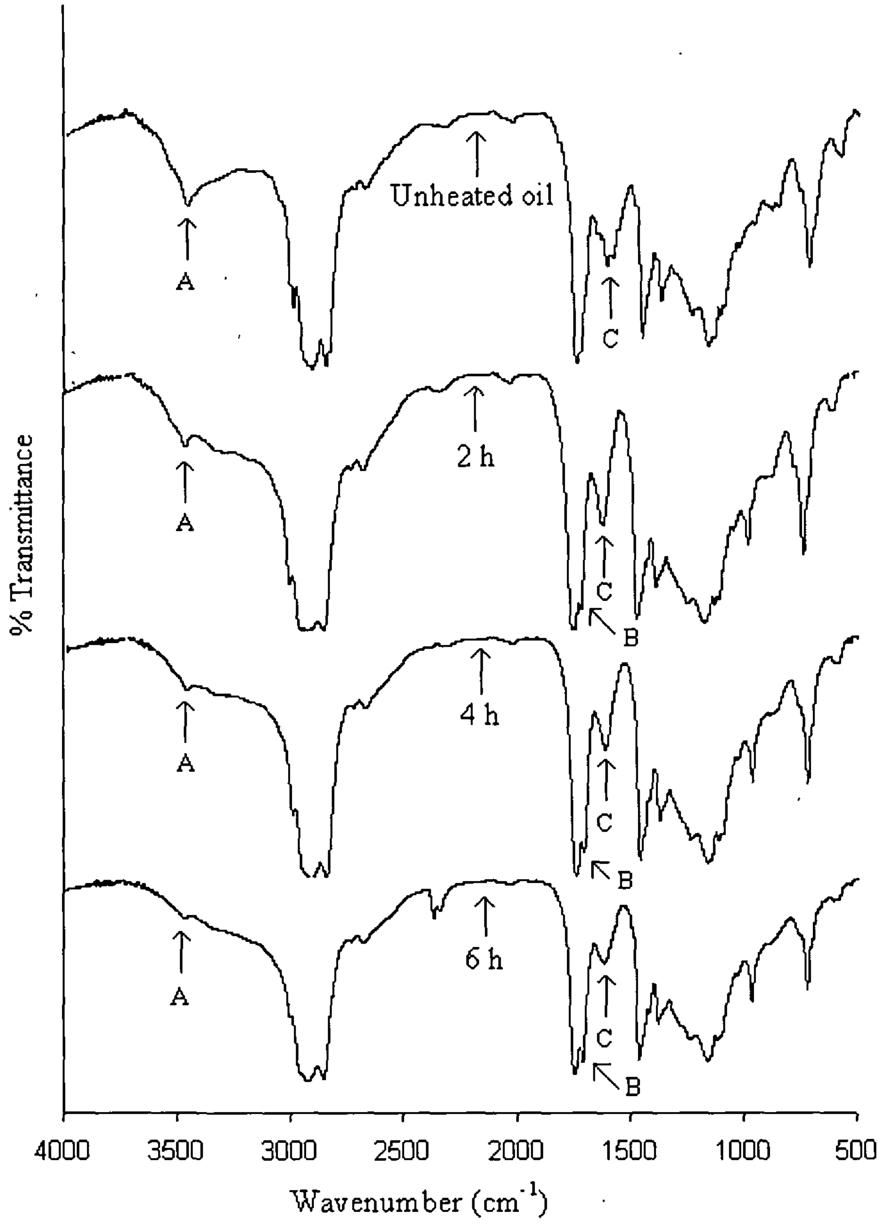

Fig. 2.7 FT-IR spectra of oil; oil heated at (315±5) ^{0}C for 2 h, 4 h and 6 h
(A= peak for O-H functional groups, B= peak for new >C=O absorbance, C= peak for C=C stretching vibration)

The GPC chromatograms of S-1, S-2 and S-3 are shown in Figs. 2.8, 2.9 and 2.10, whereas the weight average molecular weight (M_w) of samples are given in Table 2.1. In all chromatograms, there is one major peak with a small shoulder on the right side, i.e., one major peak and one minor peak, which indicates the presence of two types of molecules in the oil. The main peak may be the mixture of triglycerides and oligomeric glycerides, and the minor peak may be the mixture of free fatty acids with lower glycerides. During heating of the oil, the weight average molecular weight increases[36] (Table 2.1), due to the continuous polymerization of the oil[24] but at the same time there is also formation of more free fatty acids, as indicated by the increase of the minor peak in both temperatures, even though at higher temperature it is more predominant. The increase of free fatty acids is also supported by acid value determination, whereas the higher molecular weight was further supported by viscosity measurement. It has also been found that on heating at higher temperature, polydispersity index (Table 2.1) increases, which may be due to the formation of high as well as low molecular weight products[2].

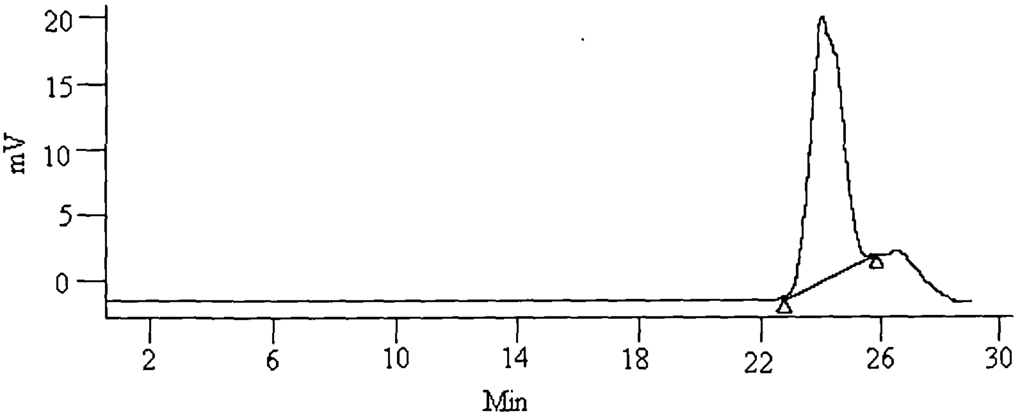

Fig. 2.8 GPC chromatogram of S-1

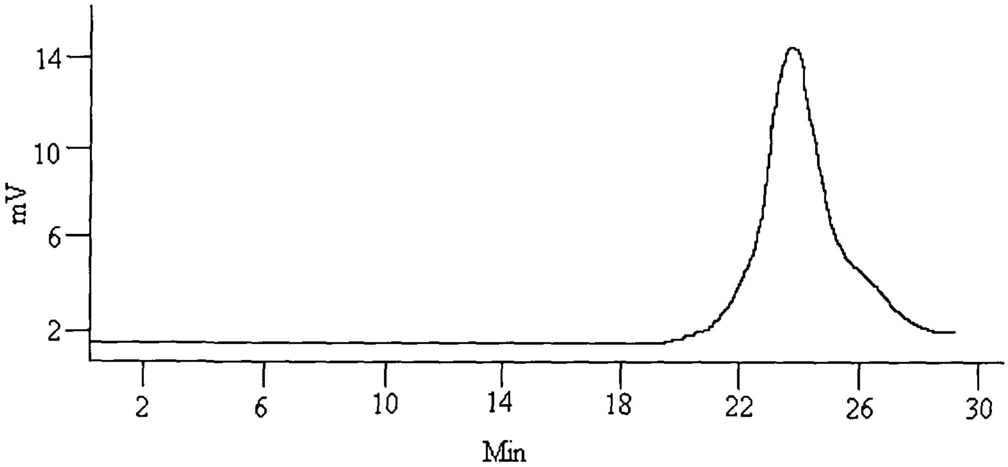

Fig. 2.9 GPC chromatogram of S-2

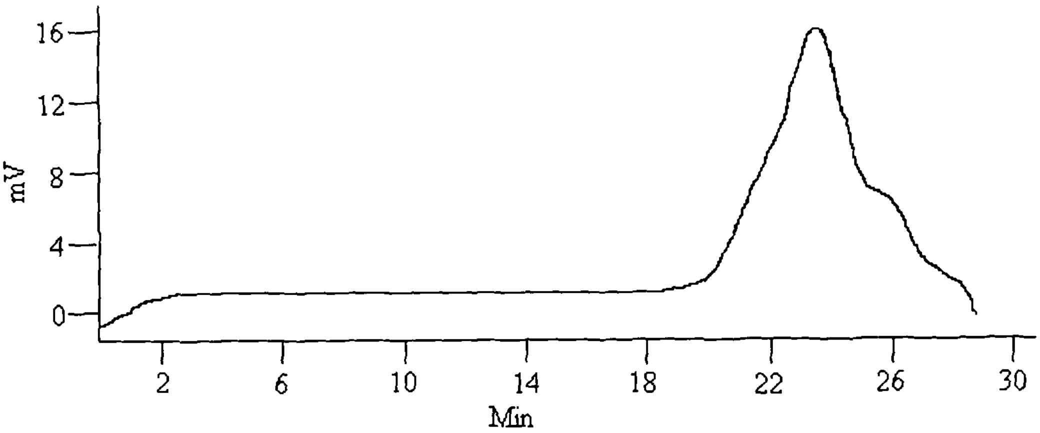

Fig. 2.10 GPC chromatogram of S-3

2.3.2 Rheological Behavior

The change in viscosity of S-2 and S-3 are shown in Figs. 2.11 and 2.12. At (250 ±5) °C, the slower rate of increase of viscosity at the initial stage of heating may be due to inhibition action of natural antioxidant[37, 38] such as mesuol[39], an aromatic phenolic type compound[40] present in the Nahar seed oil, which prolongs the induction period[41]. As this antioxidant retards the oxidative thermal degradation, so the rate is slow in the early stage of heating. It has been supposed that during the early stage of heating of vegetable oils, the triglyceride ester molecules undergo different kinds of reactions such as the isomerization of unconjugated systems into conjugated systems and decomposition into lower molecular weight products like hydroxyl, carboxyl, carbonyl compounds[1] and esters, which have a greater tendency to recombine to form new products[42]. This retardation period is followed by the rapid interaction of the decomposition products to form new ones including cyclic products[9] with propensity to increase the bulk viscosity[43]. Thus during the heating period of the oil at higher temperatures in the presence of air, there is thermal polymerization through Diels-Alder reaction[44], oxidative polymerization[10], ester-exchange reaction[5], cyclization reaction[9], etc., which increased the viscosity of the oil at both temperatures. The formation of polar groups such as carbonyl, hydroxyl, ester, etc. is supported by FT-IR studies. The increase in molecular weight in both cases is confirmed by GPC analysis (Table 2.1). For better understanding of the variation of viscosity during the heating of Nahar seed oil, the viscosity data obtained by Brookfield viscometer were utilized by fitting into a

3rd order polynomial equation like $\eta = at^3 + bt^2 + ct + d$, where η is the viscosity in poise, t is the time of heating (h), a, b, c, d are polynomial co-efficients. The values of a, b, c and d are constants and determined by data fitting using least square method. Values of a, b, c, d are as follows:

$a = -0.0014$, $b = 0.0471$, $c = 0.214$, $d = 0.6712$ for S-2

$a = 0.0319$, $b = -0.2281$, $c = 0.895$, $d = 0.6793$ for S-3

From the graphical representations of theoretical and experimental values (Figs. 2.11 and 2.12), it is clearly understood that there is a very little difference between theoretical and experimental values, which is on average within 5% error. Thus the change of viscosity during heating of the oil is not linear. Further the variation of viscosity with time in this case is also not exponential like semi-drying oil[2, 10], rather it is more complex polynomial in nature.

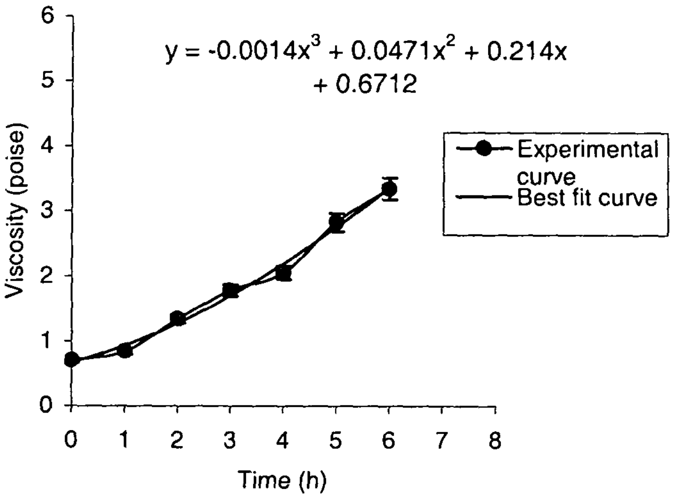

Fig. 2.11 Variation of viscosity with time for S-2

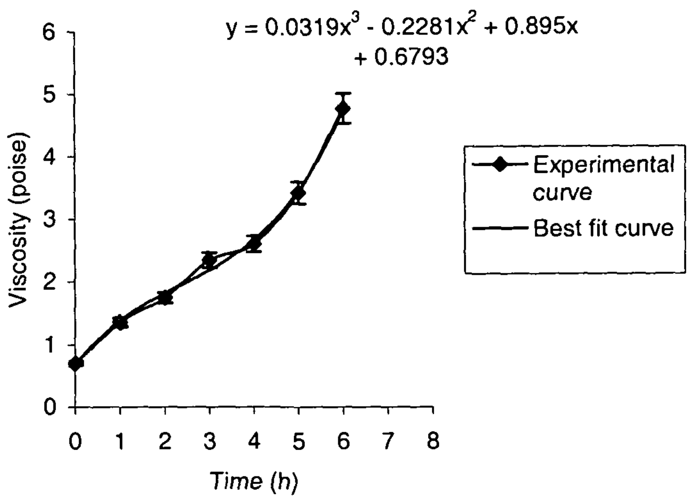

Fig. 2.12 Variation of viscosity with time for S-3

2.3.3 Curing Study of Films

From the curing study of films it has been observed that the film of S-3 dried faster than S-2 followed by S-1 (Table 2.4). This may be due to the fact that heating at higher temperature causes isomerization of double bond from non-conjugated to conjugated system along with formation of high molecular weight products (Table 2.1). As in the process of drying, the coated films are converted from the liquid to the solid state by the process of crosslinking reactions. These are mainly radical reactions by peroxide or aerial oxidation by absorbing oxygen from atmosphere at high temperature of double bonds of the oil. Also a free radical chain reaction may be initiated as hydroperoxides decompose and the subsequent chain growth polymerization reaction gives higher molecular weight, crosslinked products. Further the rate of oxidative polymerization increases with the extent of conjugation and unsaturation of the oil. Thus these types of oxidative radical reactions are faster for conjugated systems than non-conjugated systems and also drying will be faster for higher molecular weight films compared to lower one, so the above trend of drying process was observed.

2.3.4 Coating Performance

The performance of coated films of thickness 25-30 μm was tested by determination of pencil hardness, gloss, flexibility and adhesion, as shown in Table 2.4.

From the table, it has been found that the film of S-3 shows the highest pencil hardness which may be due to the fact that at high temperature relatively high amount of rigid cyclic products are formed through Diels-Alder reaction and cyclization process. All other properties of the unheated and heated oils are more or less remain the same.

Table 2.4

Performance characteristics of S-1, S-2 and S-3

Code	Drying time*(h)	Pencil Hardness	Gloss (45^0)	Flexibility	Adhesion
S-1	6	B pass HB fail	61	Pass	5B
S-2	5.5	B pass HB fail	62	Pass	5B
S-3	4.5	HB Pass F fail	62	Pass	5B

*temperature used for drying is 200 ^{0}C

2.3.5 Chemical Resistance

The chemical resistance data of the films (Table 2.5) of heated oil (S-2 and S-3) as well as unheated oil (S-1) showed high resistance to salt solution and distilled water, but relatively poor resistance to alkali. Even though the alkali resistance of the unheated oil (S-1) is marginally good, but for the other films, the alkali resistance is poor may be due to the presence of significant amount of alkali hydrolyzable ester groups in the polymer chains. The films from heated oil (S-2 and S-3) showed better resistance to aqueous HCl compared to the film from unheated oil because of the presence of higher degree of unsaturation in unheated oil compared to heated oil. This unsaturation may undergo addition reaction with HCl thereby affecting the film.

Table 2.5

Chemical resistance of S-1, S-2 and S-3

Type of media	S-1	S-2	S-3
Alkali (0.5%)	Fair	Poor	Poor
HCl (10%)	Fair	Excellent	Excellent
NaCl (10%)	Excellent	Excellent	Excellent
Distilled water	Excellent	Excellent	Excellent

2.4 Conclusions

Thus from this study, it can be concluded that there is a significant change in structural characteristics of the Nahar seed oil by heat treatment at high temperature. The FT-IR, ^{1}H-NMR spectroscopic studies and GPC analysis provide very useful information on the chemical nature of the heated and unheated oils. The rheological behavior of the heated oil is non-linear in nature and influence greatly at high temperature when heated for long period. From curing study, it has been seen that heating enhances the drying ability of the non-drying oil. However, films from heated oil did not able to show significant improvement of coating performance, except the marginal improvement of hardness and acid resistance compared to unheated oil.

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Chapter 3

Mesua ferrea L. Seed Oil Modified Polyester Resins

3.1 Introduction

The classical definition of oil modified polyester (alkyd) resin[1-4] is "the resinous product of polyhydric alcohol, polybasic acid and vegetable oil and/or fatty acids". The inclusion of oil in polyester resin differentiates it from oil free polyester resin[5]. The incorporation of oil in the resin increases the oleophilic character of the resin, thereby improving the solubility in hydrocarbon solvents. It also improves the flexibility of the resin as it acts as an internal plasticizer[6]. Oil modified polyester resins form the largest group of synthetic resins available to the coating industry and its consumption[7] is greater than that of any other resins. Low cost and versatility of properties are the main factors[8] responsible for their wide uses. The use of oil for preparation of polyester resins reduces the consumption of petroleum-based products[9]. Hence it minimizes the environmental pollution. It also possesses many advantages such as renewability, biodegradability in a short time, availability in large quantity and environmental friendliness, etc.

A number of both traditional and non-traditional vegetable oils are being utilized for polyester preparation[10-12]. There are reports on exploitation of *Mesua ferrea* L. (Nahar) seed oil in the fields of medicine and bio-diesel preparation. But, to our knowledge this oil has not been used for the preparation of any industrial resin. Further, it has already been observed that only heating of this oil does not lead to a useful product for surface coating application. As polyester resins have many advantages over other industrially used resins for different applications as described in chapter 1, section 1.3.1. So *objectives of the present investigation are to utilize this oil* for preparation of polyester resins, to characterize and evaluate their properties.

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3.2 Experimental

3.2.1 Materials

The Nahar seeds used in the present investigation were collected from Jorhat, Assam, India. The oil was obtained from the dried seeds by pressing method using screw press and purified as mentioned in chapter 2, section 2.2.1.

Phthalic anhydride (PA) obtained from S. D. Fine Chem. Ltd., Boisar with melting point 131-133 ^{0}C, sulphated ash 0.005%, minimum assay 99.5% and it was used as received.

Maleic anhydride (MA) obtained from Loba Chemie, Mumbai with melting point 50-53 ^{0}C, maximum sulphated ash 0.05% and minimum assay 99.5%. It was used without further purification.

Glycerol obtained from Merck, Mumbai with density 1.26 g/mL, maximum sulphated ash 0.005%, minimum assay 99%. It was used as received.

Lead mono-oxide obtained from Loba Chemie, Mumbai with minimum assay 99%, maximum limit of impurities chloride 0.02%, cupper 0.005%, iron 0.01%. It was used as received.

Styrene obtained from Merck, Germany and the specifications have already been discussed in chapter 2, section 2.2.1.

Methyl-ethyl ketone peroxide (MEKP) and cobalt octate were obtained from Kumud enterprise, Kharagpur. The specifications of these have already been mentioned in chapter 2, section 2.2.1.

3.2.2 Instruments and Methods

FT-IR spectra of resins were recorded in FT-IR spectrophotometer (Impact 410, Nicolet, USA) using KBr pellet. ^{1}H-NMR spectra of resins were recorded in NMR spectrometer (90 MHz, EM-390, Varian, USA) using $CDCl_3$ as the solvent and TMS as an internal standard. The thermogravimetric analysis of the cured resins was performed using TGA analyzer (Mattler Toledo, SDTA 821^e) under the nitrogen atmosphere with heating rate of 20 ^{0}C/min. The viscosity of resins was measured at (28$\pm$2) ^{0}C using Brookfield viscometer (Model LVT, Serial number 201543, USA).

Different properties of resins such as acid value, iodine value, and saponification value were determined by the standard methods as mentioned in experimental part of chapter 2, section 2.2.2. The volatile matter content of resins was determined according to the IS standard[13] by heating the sample at (105±2) ^{0}C for 3 h.

The film thickness of cured films was determined by Pentest, coating thickness gauge (Sheen Instrument Ltd., Model 1117, UK). The coating performance of the cured films was evaluated by determining pencil hardness using pencils of different grades ranging from 6B to 6H, gloss using glossmeter (AIMIL, Ajmer), flexibility using flexibility apparatus (PEI, Kolkata), adhesion using and commercial cello tape respectively. All the methods of these tests and chemical test are same as described in the experimental chapter 2, section 2.2.2.

Resinification Reaction

A three-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer and a nitrogen gas inlet was charged with 34.92 g (0.04 mole) of Nahar oil, 7.36 g (0.08 mole) of glycerol and 0.05 weight percentage (with respect to the oil) of lead mono-oxide with continuous stirring. Then the mixture was heated continuously upto (240±5) ^{0}C for 30-40 min until it formed monoglyceride, confirmed by solubility in methanol (resin: methanol=1:3 v/v) at ambient temperature. Then the reaction mixture was cooled to (125±5) ^{0}C and 0.12 mole of acid anhydride in the form of fine powder with 1.98 g of excess glycerol (27%) was added. Then the reaction temperature was increased up to (220±5) ^{0}C until it reached acid value of ~ 20-30.

Resins of different compositions were prepared by changing amount of PA and MA as shown in Table 3.1.

Table 3.1

Composition of different resins

Code	Percentage of anhydride
Resin A	100% PA
Resin B	50% PA + 50% MA
Resin C	75% MA + 25% PA

Curing of Resins

A homogenous mixture of each resin with 30 phr (parts per hundred gram of resin) of styrene as the reactive diluent, 4 phr of MEKP as the initiator and 2 phr of cobalt octate as the accelerator was prepared in a glass beaker at room temperature by hand stirring for 5 min. Then mixtures were uniformly spread on mild steel plates (150 mm X 50 mm X 1.60 mm), tin plates (150 mm X 50 mm X 0.40 mm.) and glass plates (75 mm X 25 mm X 1.75 mm) and then allowed for curing at different temperatures for the specified time period.

3.3 Results and Discussion

3.3.1 Properties of the Oil

The physical properties like acid value, iodine value, saponification value, specific gravity, weight average molecular weight, polydispersity and the chemical structure as obtained from FT-IR and ^{1}H-NMR spectra of the oil have already been discussed in the previous chapter.

3.3.2 Resinification of Oil

The Nahar oil modified polyester resins were prepared by the conventional alcoholysis process using fusion method in the presence of lead mono-oxide as the catalyst (Scheme 3.1). The first step of resinification reaction was performed at (240-245) ^{0}C with two equivalents of glycerol to obtain monoglyceride. This monoglyceride is required to produce polyester in the next step of resinification reaction, where it was esterified with PA and MA at (220-225) ^{0}C. However, the alcoholysis reaction does not go to completion under the used conditions and the reaction mixture may contain[14] α-monoglyceride (I), β-monoglyceride (II), α, α$'$-diglyceride (III), β, β$'$-diglyceride (IV) (Fig. 3.1), unreacted triglyceride (oil) and glycerol. The combination of all these is loosely termed as monoglyceride, where the major component is α-monoglyceride. In a similar type of alcoholysis reaction of linseed oil with glycerol (1:3.3 mole ratio of oil:glycerol), 58-60% α-monoglyceride was reported[15]. This partial glyceride formation and role of catalyst has already been discussed in chapter 1 section 1.3.5.1.

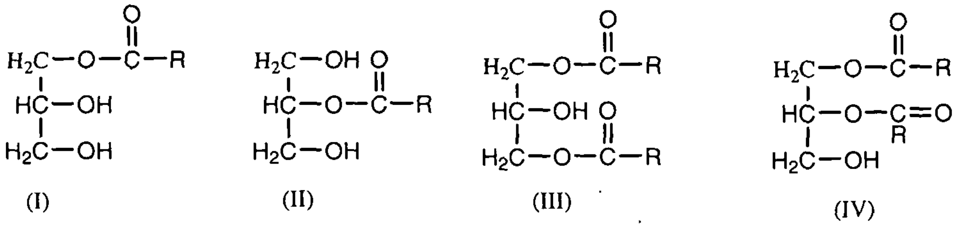
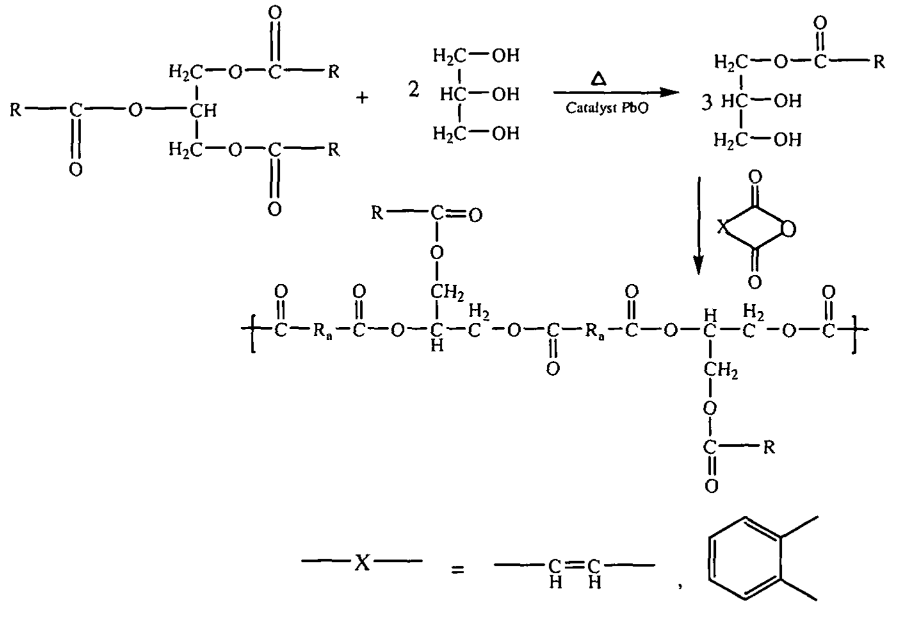


Fig. 3.1 Structure of α-monoglyceride (I), β-monoglyceride (II), α, α′-diglyceride (III), β, β′-diglyceride (IV)

In this resinification reaction no solvent was used to avoid limitations associated with solvent like removal, health hazards, flammability, etc. Further, nitrogen gas was used as the inert blanket, which facilitates the removal of water produced during condensation reaction in the second step. This also avoids the use of Dean-Stark apparatus for azeotropic distillation. The extent of reaction was monitored by measurement of acid values at different intervals of time and the reaction was stopped at the desired level of acid value (Table 3.2). The yield of resins was found to be above 90%.



R is mixture of hydrocarbon parts of fatty acids of the oil

Scheme 3.1 Alcoholysis followed by polycondensation reaction

3.3.3 Physical Properties of Resins

The physical properties like color, acid value, iodine value, volatile matter content, viscosity, etc. for the resins are given in Table 3.2.

Table 3.2

Physico-chemical properties of resins

Properties	Resin A	Resin B	Resin C
Color	Dark-brown	Dark-brown	Dark-brown
Acid value (mg KOH/g)	18.61	23.68	34.00
Iodine value (gI_2/100 g)	56.47	50.72	57.21
Volatile- matter (%)	2.8	3.08	3.38
Viscosity (k poise)	20	50	45
Saponification value (mg KOH/g)	353.53	377.60	295.02

The incorporation of MA increases the acid value as the resinification reaction was deliberately stopped at earlier stage to avoid undesirable gel formation. The moderate acid values of all resins support their moderate reactivity for surface coating applications. This will also help the resins to be used as matrix for fiber reinforced composite preparation, especially for the polar cellulosic fiber such as bamboo fiber[16]. The low volatile matter content[17] makes these resins suitable for non-polluting coatings.

3.3.4 Structural Analysis of Resins

The FT-IR spectral (Figs. 3.2, 3.3 and 3.4) data of resins indicate the presence of important linkages[18-21] such as ester group, olefinic double bond and other characteristic peaks as shown in Table 3.3.

Table 3.3

The main FT-IR peaks and the corresponding functional groups of resins

Peak (cm^{-1})	Functional groups
3463-3499	O-H stretching vibration
3004	Unsaturated C-H stretching vibration
2850-2926	CH_2 assymetric and symmetric vibration
1736-1738	C=O stretching vibration
1580-1645	C-C stretching vibration of C=C aliphatic, C=C aromatic and combination band of both C=C aliphatic and C=C aromatic band
1161 and 1260-1280	C-O-C stretching vibration attached with aliphatic and aromatic moiety
980-987	C-C stretching vibration
731-743	Out of plane aromatic C-H bending vibration

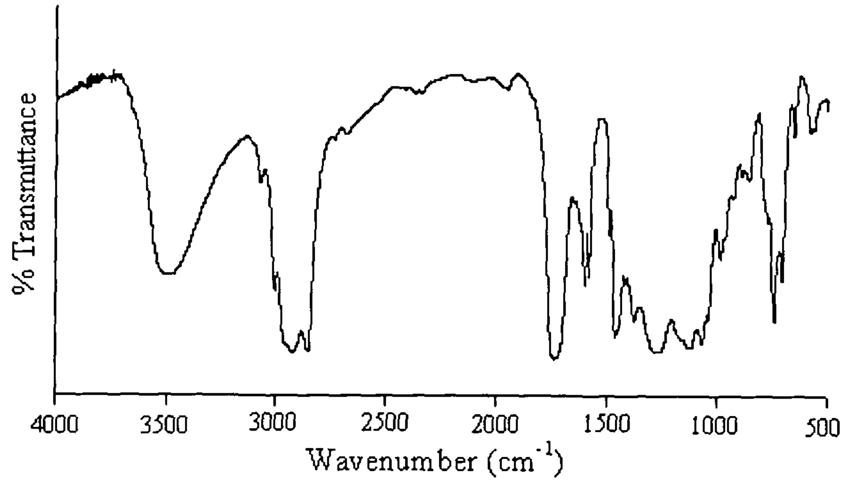


Fig. 3.2 FT-IR spectra of Resin A (100% PA)

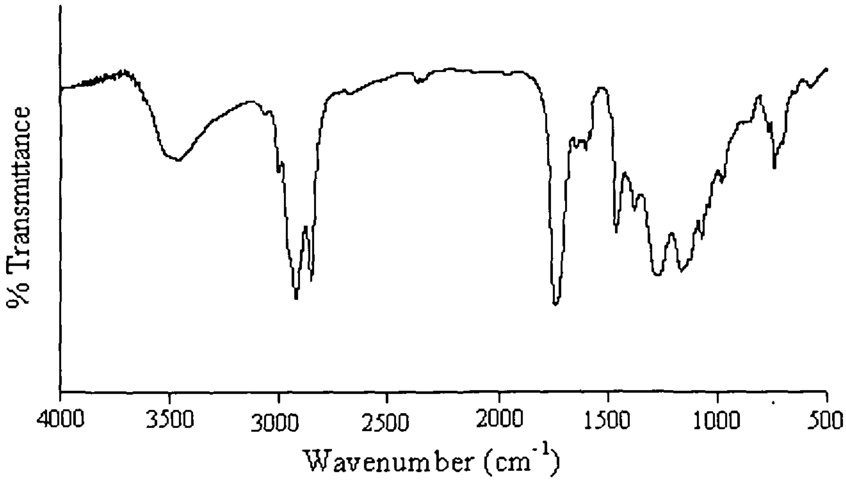


Fig. 3.3 FT-IR spectra of Resin B (50% PA and 50% MA)

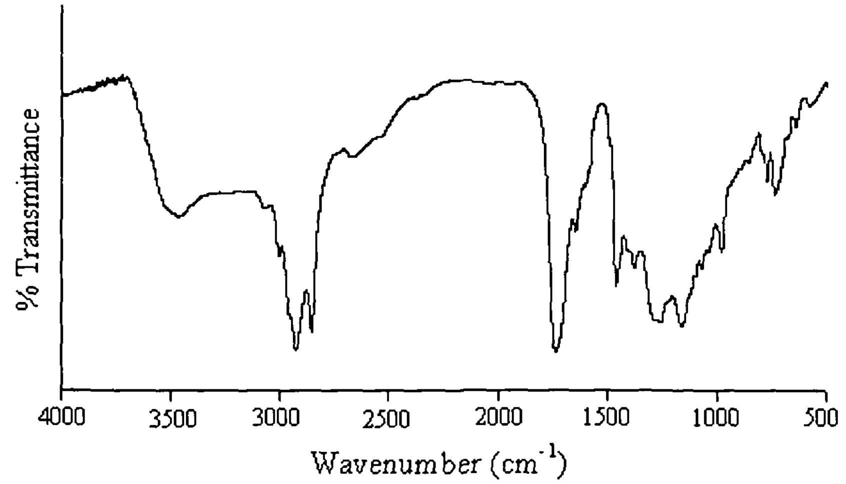


Fig. 3.4 FT-IR spectra of Resin C (75% MA and 25% PA)

Thus polyesterification reaction is confirmed by FT-IR analysis (Table 3.3). It was also noticeable that for pure Nahar oil, the C=O band was at 1747 cm^{-1}, whereas for the resins the C=O band was at 1736-1738 cm^{-1}, indicating some modification[22] around the carbonyl group. Peaks for unsaturation of fatty acid moiety at ~ 1580 cm^{-1}, aromatic PA moiety at ~ 1600 cm^{-1} and MA moiety at ~1645 cm^{-1} were observed in the resins. In Resin A, as there was no MA moiety, so peak at 1645 cm^{-1} was absent (Fig. 3.2). Whereas in Resin B and Resin C, all three peaks appeared in the FT-IR spectra, though the intensity of peaks varied with the relative concentration of components in resins (Figs. 3.3 and 3.4).

From ^{1}H-NMR spectra of resins (Figs. 3.5, 3.6 and 3.7), the presence of following protons[18, 23] is confirmed, which supported the structure as shown in Scheme 3.1. Peaks at δ = 0.85-0.89 ppm are for terminal methyl group of the fatty acid chains, and δ = 1.59-1.60 ppm may be due to protons of -CH_2- group attached next to the above terminal methyl group. Peaks at δ = 1.15-1.30 ppm are for protons of all the internal -CH_2- groups present in the fatty acid chains. Peaks for protons of unsaturated carbons appear at δ = 5.33-5.34 ppm and the methylene protons (-CH_2-) of glycerol moiety are found at δ = 3.59-4.79 ppm, whereas the proton for -CH- of same moiety is observed at very high value of δ = 6.32-6.89 ppm may be due to desheilding effect by the anhydride moiety possessing one unsaturation unit (MA) or aromatic ring (PA). The PA containing resin shows aromatic protons at 7.52-7.73 ppm, whereas protons for MA unit show peaks at δ = 2.00-2.36 ppm.

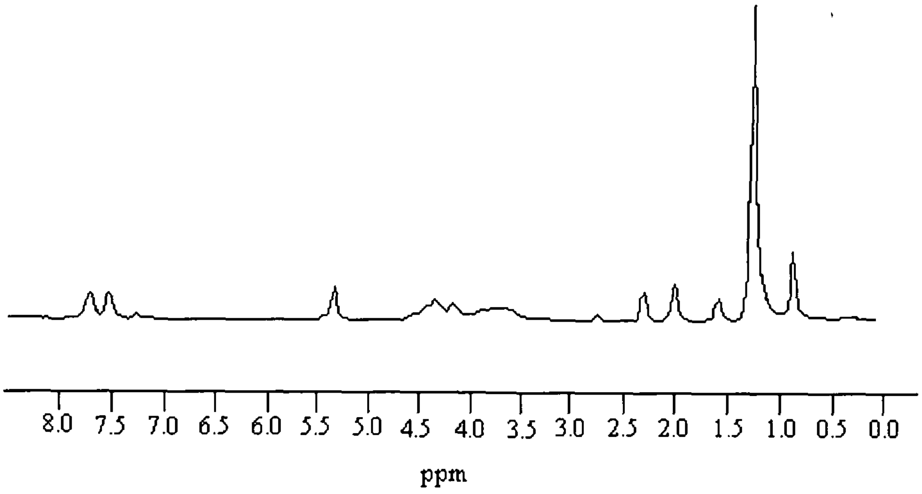


Fig. 3.5 ^{1}H-NMR spectrum for the Resin A (100% PA)

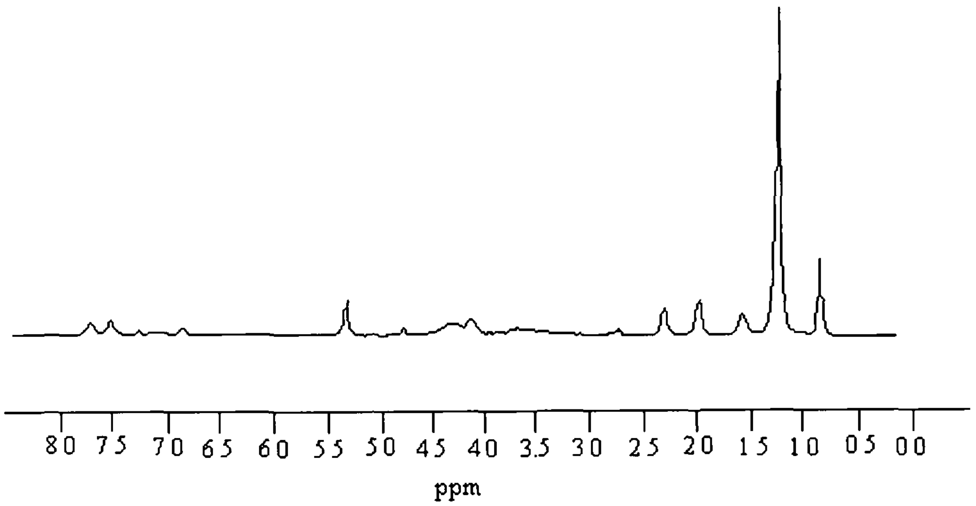


Fig. 3.6 ^{1}H-NMR spectrum for the Resin B (50% PA and 50% MA)

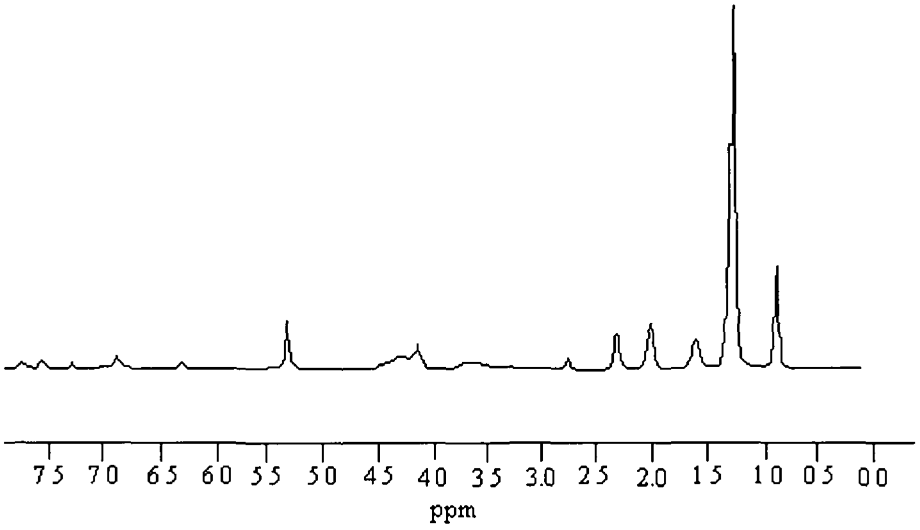


Fig. 3.7 ^{1}H-NMR spectrum for the Resin C (75% MA and 25% PA)

3.3.5 Curing Study of Resins

From the curing time measurement (Table 3.4), it is observed that curing time decreases continuously with the increase of MA content of resins. This may be due to the fact that with the increase of MA content in resin, the degree of unsaturation increases, which decreases the curing time[24], as the unsaturation is the main component for crosslinking reaction by free radical mechanism. However, the overall curing time for all resins is quite long, due to the non-drying nature of the oil.

3.3.6 Coating Performance

The coating properties of films (film thickness 50-55 μm) like pencil hardness, gloss, flexibility, adhesion are given in Table 3.4. From the table, it is observed that the pencil hardness of the cured films increases with the increase of PA content, which may be due to the rigidity of phenyl group, which restricts the rotation of the polymer chain[24]. The gloss decreases with the increase of MA content, may be due to the increase of flexibility as supported by pencil hardness values of the cured resins. Thus, the cured resins with more MA have lesser surface smoothness compared to resin with more PA, thereby exhibiting lower gloss[25]. All films have shown good cross cut adhesion[2] to the substrate due to the presence of polar groups such as -OH, -COOH, -COO-, etc. They also show good flexibility due to the presence of flexible long hydrocarbon chain of fatty acid as well as lesser degree of crosslinking for non-drying nature of the oil[1, 26].

Table 3.4

Curing time and performance characteristics of the resins

Properties	Resin A	Resin B	Resin C
Drying time	9 h at 175 ^{0}C	7 h at 150 ^{0}C	6 h at 150 ^{0}C
Pencil hardness	H	HB	2B
Flexibility	Pass	Pass	Pass
Gloss (60^0)	85	81	70
Adhesion (%)	5B	5B	5B

3.3.7 Thermal Property

The thermostability of the cured resins has been studied by thermogravimetric (TG) analysis under N_2 atmosphere. The TG traces of cured resins are shown in Fig. 3.8. The initial 1-2% weight loss is due to the loss of moisture. This has been confirmed from the isothermal heating of the polymers at 150 ^{0}C for 12 h, which indicates a same amount of weight loss without any change in chemical structure confirmed by FT-IR spectroscopy. From the Fig. 3.8, it is found that initial decomposition temperature increases with the increase of PA content in resins. This may be due to the presence of higher amount of aromatic moieties, which enhances the intermolecular attraction among the polymer chains. This type of interaction decreases with the increase of MA content. Thus, with the increase of MA content, the crosslinking density increases thereby increasing the thermostability of the cured resins, as reflected in the subsequent decomposition temperatures of resins (Fig. 3.8). However, the amount of char residue at 600 ^{0}C is very low and almost equivalent for all cases, which may be due to the fact that at that temperature there is no such thermostable moiety present in any of these resins. Thus, Nahar oil modified polyester resins showed very good thermostability under the nitrogen atmosphere.

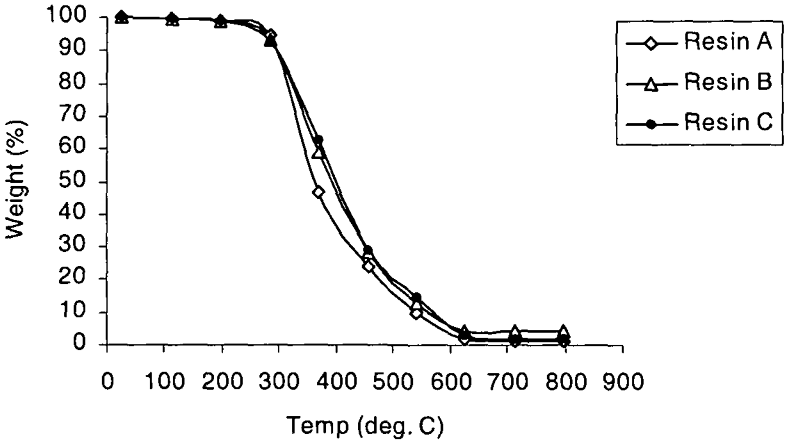


Fig. 3.8 TG traces of Resin A, Resin B and Resin C

3.3.8 Chemical Resistance

The chemical resistance data of resins (Table 3.5) indicate that they are highly resistant to dilute HCl, aqueous NaCl solution and distilled water. The resin based on 100% PA is fairly resistant to alkali, may be due to presence of rigid aromatic moiety, but with the increase of MA content, the alkali resistance decreases[17]. This poor alkali resistance of resins is due to the presence of alkali hydrolyzable ester groups.

Table 3.5

Chemical resistance of Resin A, Resin B and Resin C

Type of media	Resin A	Resin B	Resin C
Alkali (0.5%)	Fair	Poor	Poor
HCl (10%)	Excellent	Excellent	Excellent
NaCl (10%)	Excellent	Excellent	Excellent
Distilled water	Excellent	Excellent	Excellent

3.4 Conclusions

From this study, it can be concluded that the renewable Nahar seed oil has a tremendous potential for preparation of polyester resins. These resins can be utilized for surface coating applications like other vegetable oil based resins. The cured resins have exhibited good coating performance characteristics such as very good gloss, adhesion and flexibility along with high chemical resistance to dilute HCl, aqueous NaCl salt solution and distilled water. The resins have also exhibited high thermostability under the nitrogen atmosphere. Thus, these may be used for non-polluting coating formulations. However, the major drawback of these resins is long curing time, which may limit their many coating applications.

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Chapter 4

Blends of *Mesua ferrea* L. Seed Oil Modified Polyester and Epoxy Resins

4.1 Introduction

Vegetable oil based polyester (alkyd) resins have a wide range of industrial applications[1] such as industrial finishes and maintenance, architectural uses, etc. These resins have a number of advantages in surface coating applications. These include versatility in structure and properties, overall low cost, ease of applications, etc.[2-4] However, they suffer from some major drawbacks such as low alkali resistance[5], low hardness[6], do not dry at ambient condition[7] while prepared from non-drying oil, etc. So to improve those drawbacks of polyester resins, blending with other suitable resins[8-10] such as epoxy resin, amino resin, silicone resin, ketonic resin, etc. can be performed, as polyester resins have good compatibility with a wide variety of other resins. This good compatibility[11] comes from the relatively low viscosity of resin and from the structure of resin that contains a relatively polar and aromatic backbone as well as aliphatic side chains with low polarity. Blending technique may be used effectively to improve the inferior properties of both components. Miscible polymer blends produce a new improved material from the less superior individual components, but well established miscible polymer blends are very rare to get[12, 13]. However, semimiscible blends with highly disperse mixtures are also improving properties to an acceptable range[14].

Since epoxy resin is available commercially for long time and it has number of better properties[5, 15-19] like adhesion, hardness, alkali resistance, thermostability, mechanical properties etc., compared to oil modified polyester resins, so this resin can be used as one of the blend component in this case. It also has large number of epoxy and hydroxyl groups, which may take part in crosslinking reactions[20] with oil modified polyester resin.

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From the previous chapter, it has been found that *Mesua ferrea* L. (Nahar) seed oil based polyester resins have long drying time, low alkali resistance and relatively low hardness, which may limit their uses in various coating applications. So, in this chapter, the main objective is to improve the above drawbacks by blending with commercially available bisphenol-A based epoxy resin using solution blending technique.

4.2 Experimental

4.2.1 Materials

The polyester resins of three different compositions, which are already reported in chapter 3, have been used for blending purpose. Bisphenol-A based epoxy resin, Araldite LY 250 and Polyamido amine based hardener, HY 840 were obtained from Hindustan Ciba Geigy Ltd. and used as received. The specifications of epoxy resin and hardener are given in Table 4.1.

Table 4.1

Specifications of epoxy resin and hardener

Name	Araldite LY 250 (Ciba Geigy)	Hardener HY 840 (Ciba Geigy)
Viscosity at 25 ^{0}C (mPas)	450-650	10000-25000
Epoxy equivalent (g/eq)	182-192	_
Epoxy content (eq/kg)	5.2-5.5	_
Amine value (eq/kg)	_	6.6-7.5
Density at 25 ^{0}C (g/cm^3)	1.15	0.98

4.2.2 Instruments and Methods

FT-IR spectra of the blends were recorded in FT-IR spectrophotometer (Impact 410, Nicolet, USA) using KBr pellet. The morphology of the blends was studied by the scanning electron microscopy (SEM) analysis using JSM 35CF (JEOL) after gold coating. The thermogravimetric analysis of the blends was performed using Mattler Toledo TGA analyzer/SDTA 821^e under the nitrogen atmosphere with heating rate of 10 ^{0}C/min.

The film thickness of the cured films was measured by Pentest, coating thickness gauge (Sheen Instrument Ltd., Model 1117, UK). Coating performance of the cured films was evaluated by determining pencil hardness using pencils of different grades ranging from 6B to 6H, gloss using glossmeter (AIMIL, Ajmer), flexibility using flexibility apparatus (PEI, Kolkata), adhesion using commercial cello tape respectively. All methods of these tests and chemical test are same as described in the chapter 2, section 2.2.2.

Preparation and curing of Blends

Blends of polyester and epoxy resins were prepared by solution blending technique using solvent mixture of 50:50 (w/w) benzene and petroleum ether. The polyester and epoxy resins separately thinned to 50% solid content and then mixed together along with the hardener. The hardener is added in each case by maintaining the ratio of epoxy to hardener 2:1. The compositions of the blends are shown in Table 4.2. Each blend was coated on mild steel plates (150 mm X 50 mm X 1.60 mm), tin plates (150 mm X 50 mm X 0.315 mm) and glass plates (75 mm X 25 mm X 1.75 mm) and then allowed for curing at a particular temperature.

Table 4.2

Recipes of blends

Polymer code	*Polyester resin* (%)*	*Epoxy resin (%)*
P-1	50 (Resin A)	50
P-2	50 (Resin B)	50
P-3	50 (Resin C)	50
P-4	_	100

*Resins were described in chapter 3

4.3 Results and Discussion

4.3.1 FT-IR Study of Resins and Blends

The FT-IR spectra of resins have already been discussed in the earlier chapter. The important peaks[21-23] for epoxy resin are listed in the following table (Table 4.3).

Table 4.3

The main FT-IR peaks and the corresponding functional groups of epoxy resin

Bands (cm^{-1})	Assignment
2871-2965	Aliphatic C-H stretching vibration
3495	O-H stretching vibration
1606	Aromatic C-H stretching vibration
1456	Characteristic of aromatic ring
914	Epoxide group

From the FT-IR spectra (Fig. 4.1) of the cured blends P-1, P-2 and P-3, it has been found that the important peak for C=O of ester which was present in case of resins at 1736-1738 cm^{-1} and got shifted to 1741-1747 cm^{-1} may be due to interaction of epoxy resin and the hardener with alkyd resins. The peak for epoxide group at 914 cm^{-1} which was present in epoxy resin with a significant intensity, decreased in case of all blends including P-4 indicating the reaction between epoxy and curing agent[24]. The slight presence of epoxy group was observed after curing may be explained by steric hindrance, which unable the full reaction between epoxy resin and the curing agent[25]. Further, there is a noticeable increase of intensity of peak for hydroxyl group at 3371-3386 cm^{-1} in the blends compared to the polyester resins, may be due to formation of more hydroxyl groups through interaction of hardener with ester of polyester resins (Scheme 4.1) and these are partly engaged in hydrogen bonding with carbonyl groups.

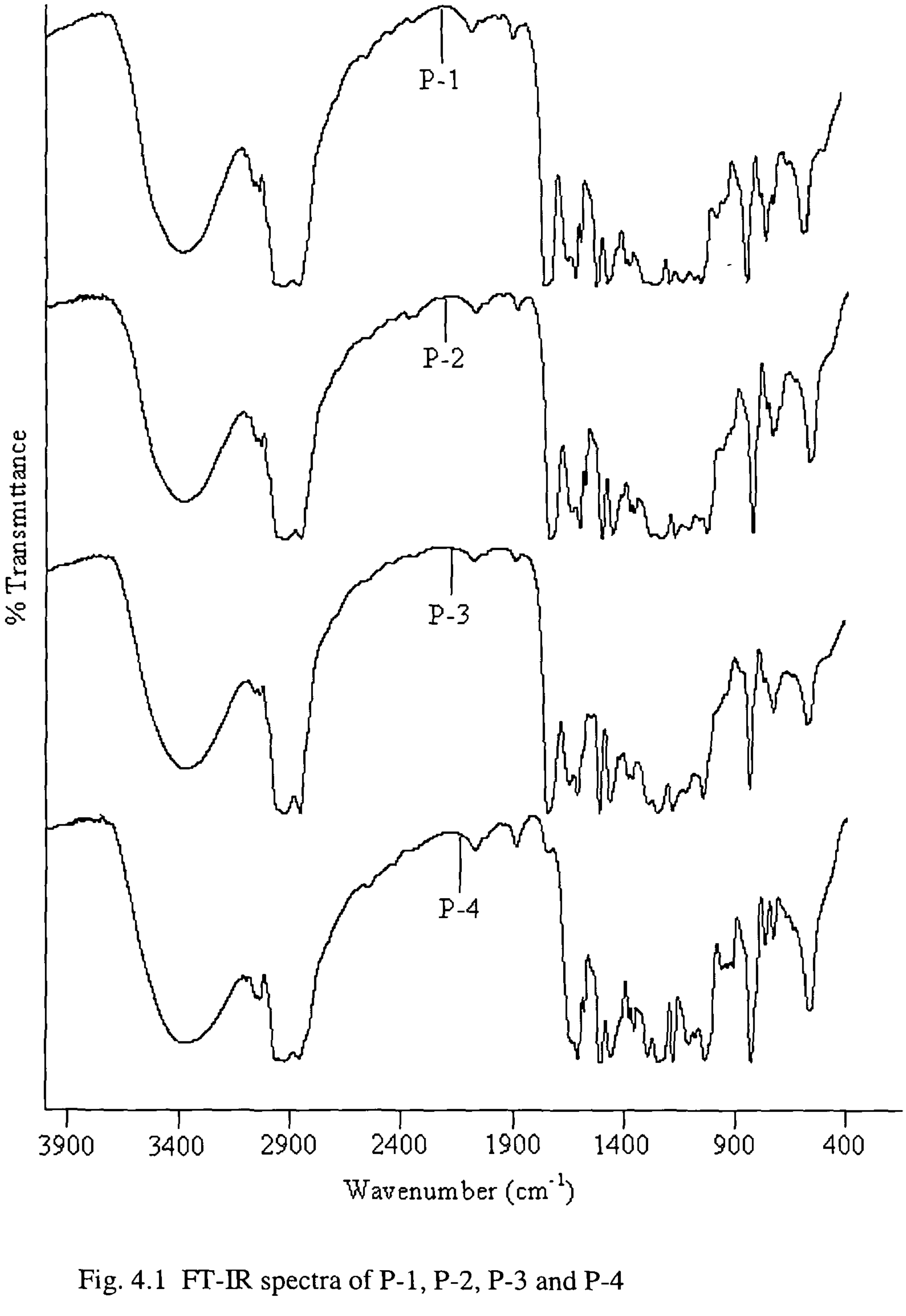
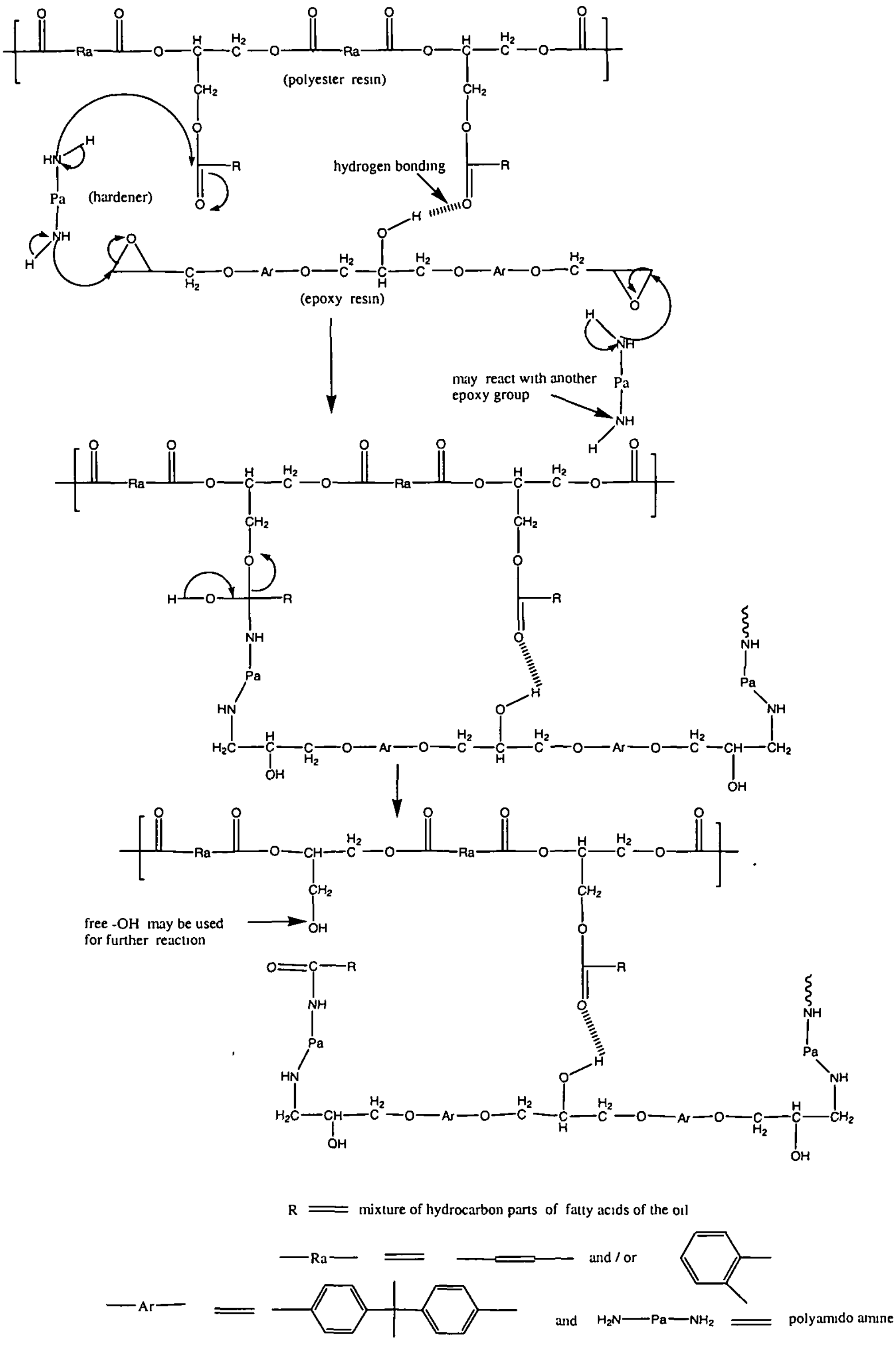


Fig. 4.1 FT-IR spectra of P-1, P-2, P-3 and P-4

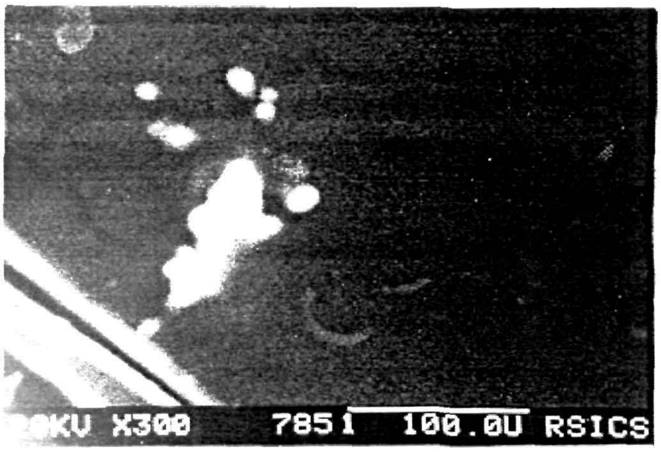


Scheme 4.1 Schematic representation of the phenomenon occurring during the crosslinking of the blend

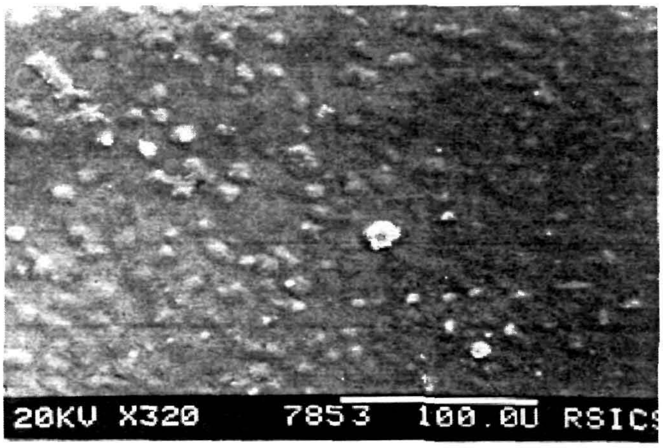
4.3.2 Blend Morphology

The ability to produce blends with improved combination of properties of the individual component depends on the degree of compatibility of the system. Alkyd resins in general show good compatibility with epoxy resin in industrially used solvent system. However, two or more distinct layers may be formed, depending on the number of incompatible ingredients present in blends[26]. Even two miscible polymers may form two-phase mixture when dissolved in certain solvent. So, a large variety of combinations of solvents were tested to achieve the desired solvent compatibility, evaporation rate and ultimately uniform phase formation. A solvent system consisting of equal weight mixture of benzene and petroleum ether was found to be the best for this purpose and showed a clear single-phase solution. Hence, that solvent mixture was used to prepare blends through out this study.

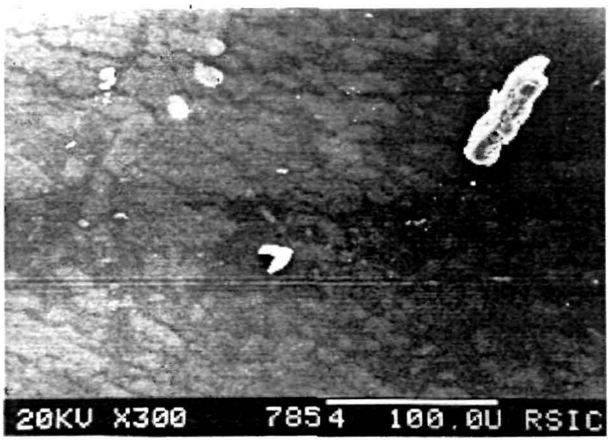
Among these SEM micrographs (Fig. 4.2), the blend containing polyester resin based on 100% phthalic anhydride (PA), Fig. 4.2 (P-1) shows excellent dispersion in epoxy resin. There is no observable phase separation in this blend. However, addition of maleic anhydride (MA) in polyester resin gives rise to phase separation [Fig. 4.2 (P-2) and (P-3)]. The complete phase separation is observed in the blend containing 50 PA:50 MA. The SEM study reveals that addition of MA in polyester produces phase separation. In all cases, the haziness or turbidity was effectively eliminated by this solution blending technique. Thus, the morphology of solvent cast film of polymer blends depends on the composition of the blends, the nature of solution, the rate of evaporation of solvent and solution viscosity. However, the size of the domain of the disperse phase is largely governed by the level of polymer miscibility that is physical and chemical nature of the blend components. The domain reduction and relatively good interfacial adhesion of PA based polyester and epoxy resin blend (Fig. 4.2, P-1) may be explained by the better compatibility of the aromatic moiety present in both resins as well as polar-polar interaction between π-bonds of aromatic rings in both resins. In addition to that, the higher compatibility may be due to better interpenetrating network formation through the amine reaction of ester groups present in PA based alkyd resin along with normal crosslinking of hydroxyl or epoxy resin by amine hardener[1]. There is a possibility of crosslinking by the hydroxyl groups of polyester resins present in the fatty acid originally or generated during crosslinking reactions with the epoxy groups of epoxy resin in the presence of amine hardener, which is also a base. Along with this, there is the possibility of H-bonding between C=O of the polyester resins with the O-H of epoxy resin present in the systems. All these phenomenon are shown in Scheme 4.1.



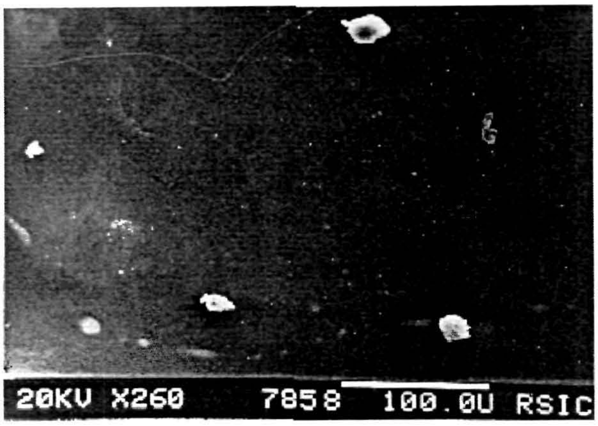
P-1



P-2



P-3



P-4

Fig. 4.2 SEM micrographs of P-1, P-2, P-3 and P-4

4.3.3 Performance of Blends as Coatings

In the process of drying of polyester resin of non-drying oil, the crosslinking is mainly radical reactions by absorbing oxygen from the atmosphere, which converts the resin from the liquid state to solid state. So it requires a long time for hard drying. The drying time of all the polyester resins improved significantly from several hours to several minutes (Table 4.4) by blending with epoxy resin. This is due to high rate of curing of epoxy resin by the amine hardener. Also, there is a possibility of chemical reactions[20] of hydroxyl/epoxide of epoxy resin with hydroxyl groups of polyester resin, in the presence of amine hardener along with reactions of the hydroxyl/ester groups of polyester resin with amine groups of the hardener. Further, the hydroxyl groups of epoxy resin may undergo self-condensation reaction to form ether linkages[20]. However, by using only peroxide with cobalt octate, the blend could not dried even for 8 h at 150 ^{O}C. This may be due to the fact that epoxy resin totally remains uncured at that time, as there is no radical reaction is possible for epoxy resin. Also the reaction of hydroxyl of polyester with epoxy resin is not occurring in this case, under these conditions. Even by using combination of curing systems, which were used for individual resin, the drying time was much higher (8 –9) h at 150 ^{O}C. It has also been found that the blends are dried even without using amine hardener. However, the time for drying was long (7 –8) h and temperature was high ~200 ^{O}C.

The film thickness of the cured films was (60-65) μm. From Table 4.4, it has been found that the hardness of blends, as measured by different grades of pencils, were improved from individual polyester resin may be due to the increase of crosslinking density. However, the improvement is more prominent in case of blend P-1, may be due to the presence of higher amount of rigid aromatic moiety in the matrix.

Table 4.4

Performance characteristics of Resin A, Resin B, Resin C, P-1, P-2, P-3 and P-4

Polymer code	Hard drying time	Gloss (60^0)	Flexibility	Pencil hardness	Adhesion (%)
Resin A	9h at 175 ^{0}C*	85	Pass	H	5B
Resin B	7h at 150 ^{0}C*	81	Pass	HB	5B
Resin C	6h at 150 ^{0}C*	70	Pass	2B	5B
P-1	55 min at 125 ^{0}C	62	Pass	3H	5B
P-2	45 min at 125 ^{0}C	66	Pass	2H	5B
P-3	40 min at 125 ^{0}C	60	Pass	2H	5B
P-4	30 min at 100 ^{0}C	52	Pass	4H	5B

*The performance characteristics of Resin A, Resin B and Resin C are reproduced from Table 3.4 of chapter 3, section 3.3.6

Gloss refers to specular reflection or the light reflected at the same angle as the angle of incidence. The gloss of the coated surface depends upon the amount of light absorbed or transmitted by the coating material that is influenced by the smoothness or texture of the surface. In general, polyesters show good gloss, which is observed in our case also (Table 4.4). The gloss of polyester resin is much higher compared to epoxy resin only. Thus epoxy resin has low gloss characteristics (P-4), which was improved by blending with alkyd resins in all cases, (Table 4.4). This improvement may be due to better compatibility of these blends and good light stability of the alkyd resins for which blends showed good gloss. Though P-1, P-2 and P-3 show improved gloss characteristic than P-4 but all of them show lower gloss than individual alkyd resin. This may be due to blushing nature of films caused by the humid weather[27].

All blends were tested for flexibility by bending the tin coated panel at 180^0, but no crack, or damage or peeling of films was observed (Table 4.4). This is indicating excellent flexibility of all blends. This is mainly due to two reasons, firstly non-drying oil acts as permanent plasticizer[28], and secondly polyamidoamine imparts good flexibility[29]. All blends showed good adhesion due to the fact that both resins possess different polar functional groups including ether linkages (Table 4.4).

4.3.4 Thermal Study

From the Fig. 4.3, it was found that blends degrade by a single step pattern with the char residues 5%, 2%, 8% and 7% upto 600 °C for blends P-1, P-2, P-3 and P-4 respectively. However, generally the alkyd resins are lesser thermostable and started to degrade at ~200 °C. But, the studied alkyd resins have relatively high thermostability as discussed in the previous chapter, section 3.3.7. Even then, the thermostability of blends further improved by blending with epoxy resin (Fig. 4.3). This higher thermostability of blends compared to polyester resins may be due to crosslinking between the free hydroxy groups present in the fatty acids of the oil originally or generated during amine crosslinking reaction (Scheme 4.1) as well as better physical interactions[30] through H-bonding, polar-polar interactions, etc. Thus, due to better compatibility between alkyd and epoxy resins, the thermostability of the blends got improved to a significant extent.

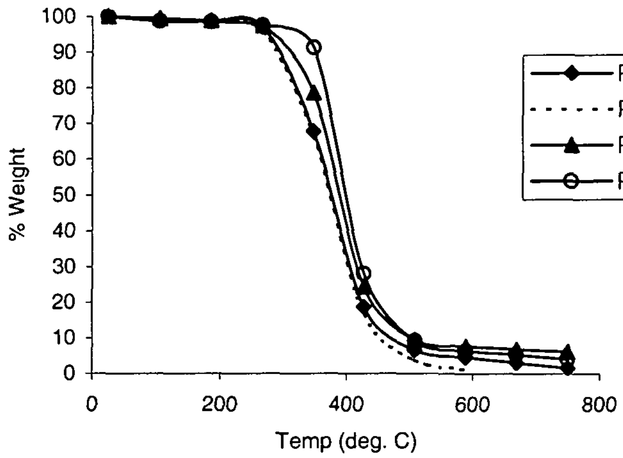


Fig. 4.3 TG traces for the blends (P-1 to P-3) and amine cured epoxy resin (P-4)

4.3.5 Chemical Resistance

Results of chemical resistance are shown in Table 4.5. Both alkyd and epoxy resins having good water and salt solution (aqueous NaCl solution) resistance, so also the blends. The acid resistance of P-1, P-2 and P-3 is excellent, but P-4 showed inferior resistance to acid solution (25% HCl) compared to other blends. This may be due to the fact that the amount of amide groups present in the cured epoxy resin are much higher compared to all other blends and hence attracted much more toward the H^+ ion of the acid and thus the acid affected the film. However, the alkali resistance of blends has improved to a significant extent due to better alkali resistance of epoxy resin. Blends showed relatively good resistance upto 5% aqueous NaOH solution compared to the individual alkyd resin, which got easily affected by 0.5% NaOH solution. In the blend, the epoxy component having good resistance to alkali may be due to absence of any alkali hydrolyzable groups[15], presence of alkali resistant amide bonds and the presence of alkali stable ether linkages[15]. Among blends, the blend P-1 showed relatively better alkali resistance, this is due to the presence of more rigid aromatic moiety in the alkyd resin[31].

Table 4.5

Chemical resistance test of P-1, P-2, P-3 and P-4

Type of media	P-1	P-2	P-3	P-4
Alkali (5%)	Good	Peeled off	Peeled off	Excellent
HCl (25%)	Excellent	Excellent	Excellent	Good
NaCl (25%)	Excellent	Excellent	Excellent	Excellent
Distilled water	Excellent	Excellent	Excellent	Excellent

4.4 Conclusions

From this study, it has been found that the blends of polyester resins based on Nahar seed oil and epoxy resin showed a significant improvement of properties from the individual component. The properties such as drying time, pencil hardness, alkali resistance and thermal stability of the polyester resins are improved by blending with epoxy resin, whereas acid resistance and gloss of epoxy resin are improved by blending with polyester resins. This indicates that the alkyd and epoxy resins have good compatibility and thus may used as multipurpose coating materials.

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Chapter 5

Blends of *Mesua ferrea* L. Seed Oil Modified Polyester and Melamine-Formaldehyde Resins

5.1 Introduction

The vegetable oil modified polyester (alkyd) resins have widely been used for several decades in different applications[1] as already discussed previously. Again these polyesters are classified as short, medium and long oil polyesters depending on the oil content[2]. Among all three types of resins, short oil polyesters are generally preferred for non-drying oils. The resin prepared from non-drying oil will not dry under ambient condition[3]. They also suffer from low alkali resistance[4], relatively low hardness[5], etc. So, there is a strong demand of improving these performance characteristics of this resin for advance applications. Since short oil polyester resin has sufficient amount of free hydroxyl groups, which ensure good compatibility with polar amino resin and serve reactive sites for polycondensation[6]. So, the above drawbacks of polyester resin may be improved by blending with a suitable amino resin such as melamine-formaldehyde, urea-formaldehyde, etc. Among these, melamine-formaldehyde resin is one of the most important resins in surface coating industry[7, 8]. This resin can produce high performance coatings[9] with respect to hardness, chemical resistance, scratch hardness, color retention, durability, good electrical insulation property, thermostability, etc. But as it forms very hard and brittle coatings with poor adhesion after baking, so it cannot be used solely[10]. It is always, therefore used in combination with resins having flexible backbone with some polar groups[11, 12]. Since oil modified polyester resins exhibit high flexibility due to the presence of long linear hydrocarbon chain in their structures, so a combination of polyester resin with melamine-formaldehyde resin may result a film with good flexibility as well as good chemical resistance, hardness, thermostability, etc. The cross-linking reactions between polyester and melamine-formaldehyde resins are accomplished by heating or by using acid catalyst or by combination of both[6, 13, 14].

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There are a few reports on improvement of coating properties of polyester resins of different vegetable oils by blending with melamine-formaldehyde resin[6, 8, 15-18]. In the previous chapter, the improvement of *Mesua ferrea* L. seed oil modified polyester resins (55% oil length) by blending with commercial bisphenol-A based epoxy resin has been studied. As the cost of melamine-formaldehyde resin is much lower than epoxy resin, so the objective of the present investigation is to study the performance characteristics of blends of *Mesua ferrea* L. seed oil modified short oil polyester resin and partially butylated melamine-formaldehyde resin at different ratios.

5.2 Experimental

5.2.1 Materials

Mesua ferrea L. (Nahar) seeds were utilized for isolation of oil by solvent extraction method. The solvent was removed by distillation and then the oil was purified as described in chapter 2, section 2.2.1.

Phthalic anhydride (S. D. Fine Chem.), glycerol (Merck), and lead mono-oxide (Loba Chemie) were used as received. The specifications of these have already been discussed in chapter 3, section 3.2.1. *p*-toluene sulfonic acid was obtained from BDH, England (m.p. 103-105°C, Assay > 98%) and used as such.

Partially n-butylated melamine–formaldehyde (MF) resin was received from Berger Paint India Ltd., Kolkata and used as received. The technical specifications of MF resin are as given in Table 5.1.

Table 5.1

Technical specifications of used MF resin

Properties	Values
Acid value (mg KOH/g)	1.5
Non-volatile matter (%)	60 ± 2
Specific gravity (30°C)	1.02
White spirit tolerance	1:4-6

5.2.2 Instruments and Test Methods

The morphology of blends was studied by the scanning electron microscopy (SEM) analysis using JSM 6360 (JEOL) after gold coating. The thermogravimetric analysis of blends was performed using Mattler Toledo TGA analyzer/SDTA 821^e under the nitrogen atmosphere with heating rate of 20 ^{0}C/min. FT-IR spectra of the resins and blends were recorded in FT-IR spectrophotometer (Impact-410, Nicolet, USA) using KBr pellet. The molecular weight of the polyester resin was determined by GPC (Waters, USA, Model 515) using THF as the solvent. The viscosity of the polyester and MF resin was measured using Brookfield viscometer (Model LVT, Serial number 201543, USA).

The physical properties such as acid value, iodine value, saponification value, and specific gravity of the short oil polyester resin were determined by standard methods as mentioned in chapter 2, section 2.2.2. The hydroxyl value of the resin was determined by the standard method IS 6746: 1994.

The film thickness of the cured films was measured by Pentest, coating thickness gauge (Sheen Instrument Ltd., Model 1117, UK). Coating performance of the cured films was evaluated by determining pencil hardness using pencils of different grade ranging from 6B to 6H (Mitsubishi Uni Pressure Proofed High Density Lead), gloss using glossmeter (Sheen Instrument Ltd., Model No. 160, UK), flexibility using flexibility apparatus (PEI, Kolkata), adhesion using commercial cello tape respectively. All methods of the above tests are same as described in the chapter 2, section 2.2.2. The impact resistance of the cured films coated on mild steel panel was measured using a falling weight impact tester (2 pound weight, Byk, Big Chemie, Germany) as per the standard method[19]. The chemical resistance of the cured blends was tested by immersing the coated mild steel strips in different media for 4 days followed by the observation for any change.

Method of Preparation of Short Oil Polyester Resin

The oil modified polyester resin was prepared as per the formulation given in Table 5.2 by the alcoholysis process as reported in chapter 3, section 3.2.2. After obtaining the desired level of acid value (30 mg KOH/g), the reaction mixture was cooled to 120 ^{0}C and diluted to about 60% solid content by addition of xylene as the diluent.

Table 5.2

Composition of the short oil polyester resin

Ingredients	Amount (g)
Oil	80
Glycerol	41.40
Phthalic anhydride	89.93
Lead mono-oxide	0.12

Preparation and Curing of the Blends

Blends of above polyester and MF resins were prepared by mixing them at different weight ratios (Table 5.3) with 0.5% (by weight with respect to the total resin) *p*-toluene sulfonic acid (as 2% w/v of acetone solution). After hand stirring for 10-15 min, each blend was uniformly coated in the form of a thin film on mild steel plates of size (50 mm X 20 mm X 1.5 mm) and (100 mm X 50 mm X 1.5 mm) and tin plates of size (100 mm X 50 mm X 0.315 mm) for different tests and cured at 120 ^{0}C for 1 h.

Table 5.3

Composition of blends

Polymer code*	Polyester resin (%)	MF resin (%)
P-80	80	20
P-70	70	30
P-60	60	40
P-50	50	50
P-20	20	80
P-0	—	100

*digit indicates the weight percentage of polyester resin in blends

5.3 Results and Discussion

5.3.1 Characterization of Resin

The physical properties like acid value, iodine value, saponification value, non-volatile content, hydroxyl value, viscosity and average molecular weight, etc. of the polyester resin are given in Table 5.4. From the table, it has been found that this short oil polyester resin (oil length 40%) exhibits moderate acid value, which indicates its moderate reactivity for paint and coating applications. This will also help the resin to be used as matrix for polar fibre such as cellulosic fibre to prepare fibre reinforced composite. The iodine value of the resin is comparatively low due to the short oil length of the resin and non-drying nature of the oil. The high saponification value is due to the same reason of short oil length. The higher viscosity value of the resin is supported by high molecular weight as determined by GPC. The relatively low polydispersity index and higher weight average molecular weight indicate that the resin will offer good mechanical properties. The relatively high hydroxyl value indicates that the resin will have good interaction with MF resin[6]. The IR spectra of the oil modified polyester resin shows the presence of important linkages such as OH, COOR, C=C and other characteristics peaks (Table 5.5). The IR data (Table 5.6) of the MF resin indicate the presence of different linkages[20, 21] such as C-N, N-H, N-CH_2-OR, etc.

Table 5.4

Different properties of the short oil polyester resin

Properties	Values
Oil content (%)	40
Non-volatile matter (%)	62.51
Saponification value (mg KOH/g)	328.50
Iodine value (g I_2 per 100 g)	38.865
Acid value (mg KOH/g)	30
Hydroxyl value (mg KOH/g)	145.58
Viscosity (cp, spindle 2, speed 1.5, temp. 31 ^{0}C)	1750
Weight average molecular weight (M_w)	4282
Number average molecular weight (M_n)	1365
Polydispersity index	3.137

Table 5.5

Important FT-IR peaks of short oil modified polyester and the corresponding functional groups

Peak (cm^{-1})	Functional groups
3466	OH stretching frequency
2925-2853	C-H stretching vibration
1731	C=O stretching vibration
1599	C=C stretching frequency
1123	C-O stretching frequency of ester
987	C-C stretching frequency
743	Aromatic C-H stretching frequency

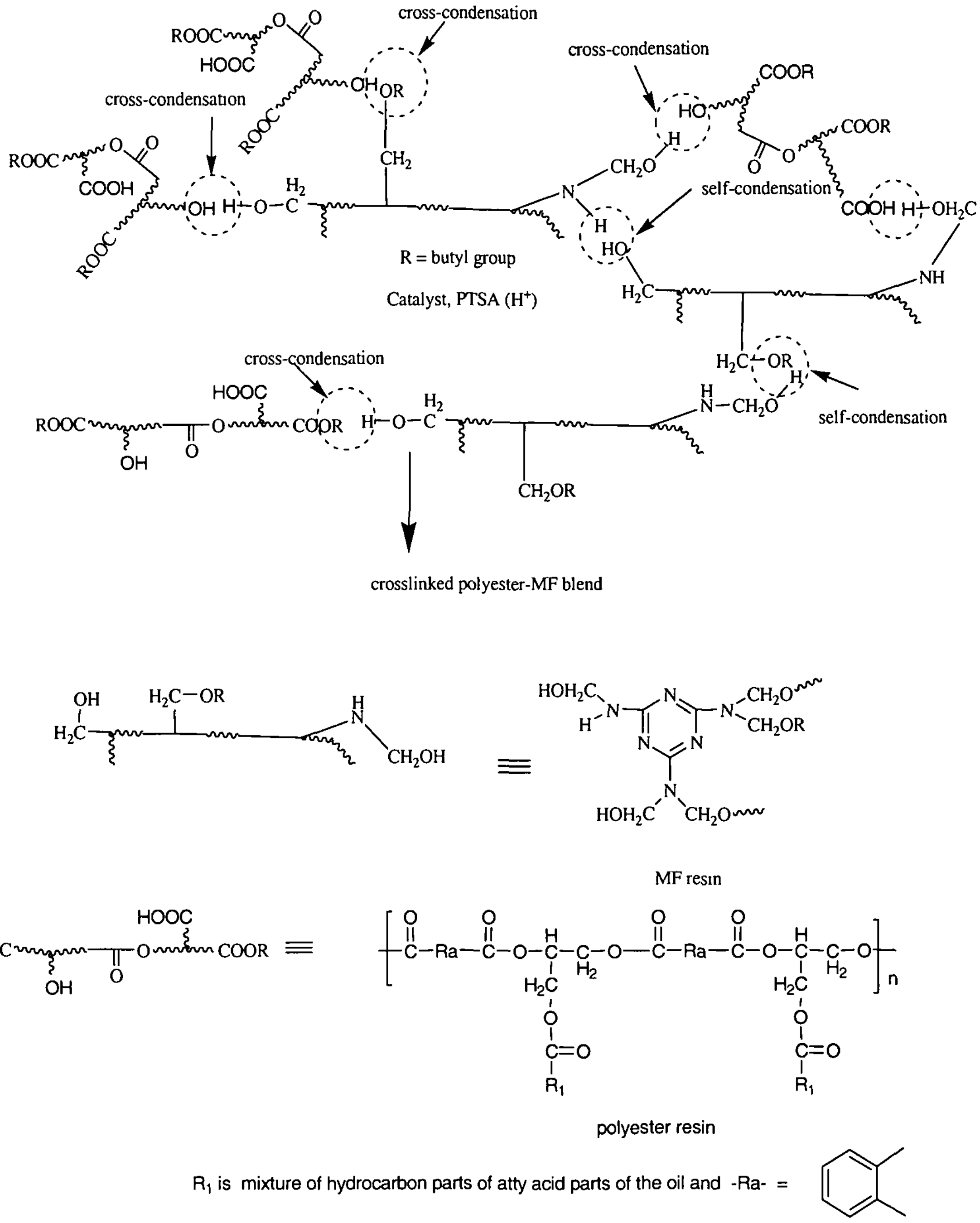
Table 5.6

Important FT-IR peaks of MF resin and the corresponding functional groups

Peak (cm^{-1})	Functional groups
3360	Overlap of N-H and O-H stretching frequency
2958-2870	C-H stretching
1548	Overlap of N-H deformation and C-N stretching
1387	C-H bending
815	Triazine ring
932	C-H rocking of $N-CH_2$

5.3.2 Curing Study

The curing mechanism associated with the conventional oil modified polyester and MF resins is a complex phenomenon due to the presence of a large number of functionalities such as –OH, -OR, -COOR, -COOH, -NH, $>NH_2$, etc. in resins. Thus a variety of reactions are possible between these two resins[6, 20, 22]. The principal reaction takes place during the curing process is between the alkoxymethyl or methylol group of amino resin and hydroxyl group of polyester resin, which leads to the formation of ether linkages. The major reactions of interest, which may occur during the curing process and the general structure of resins are shown in Scheme 5.1. These curing reactions are supported by FT-IR study. The FT-IR spectrum of each blend was recorded before and after curing. The spectra showed the broad peak (Fig.5.1, before curing) at (3435-3360) cm^{-1} of the blends before curing. This is due to the overlapping of bands of –OH group of polyester resin and –OH and / or >N-H group of MF resin. After curing all blends at 120 ^{0}C for 1 h, the above mentioned peak get sharpen, which indicates the involvement of –OH groups of polyester and MF resin and >NH group of MF resin in the crosslinking reaction.



R_1 is mixture of hydrocarbon parts of atty acid parts of the oil and -Ra- =

Scheme 5.1 Proposed crosslinking reactions and general structures of the resins

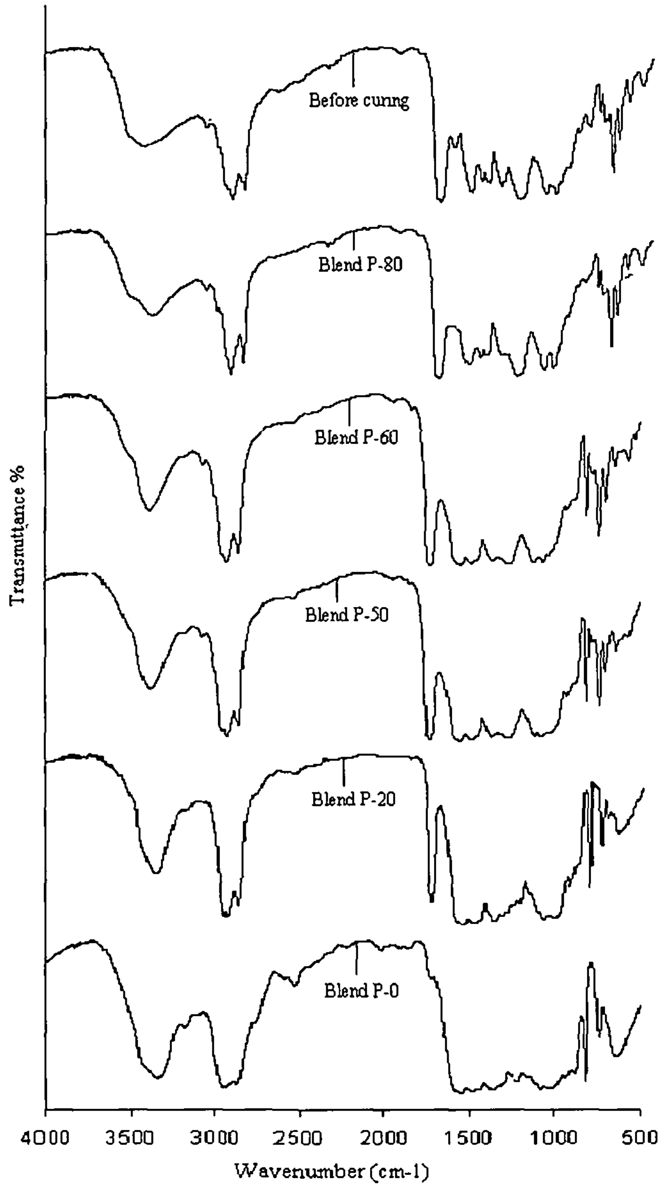
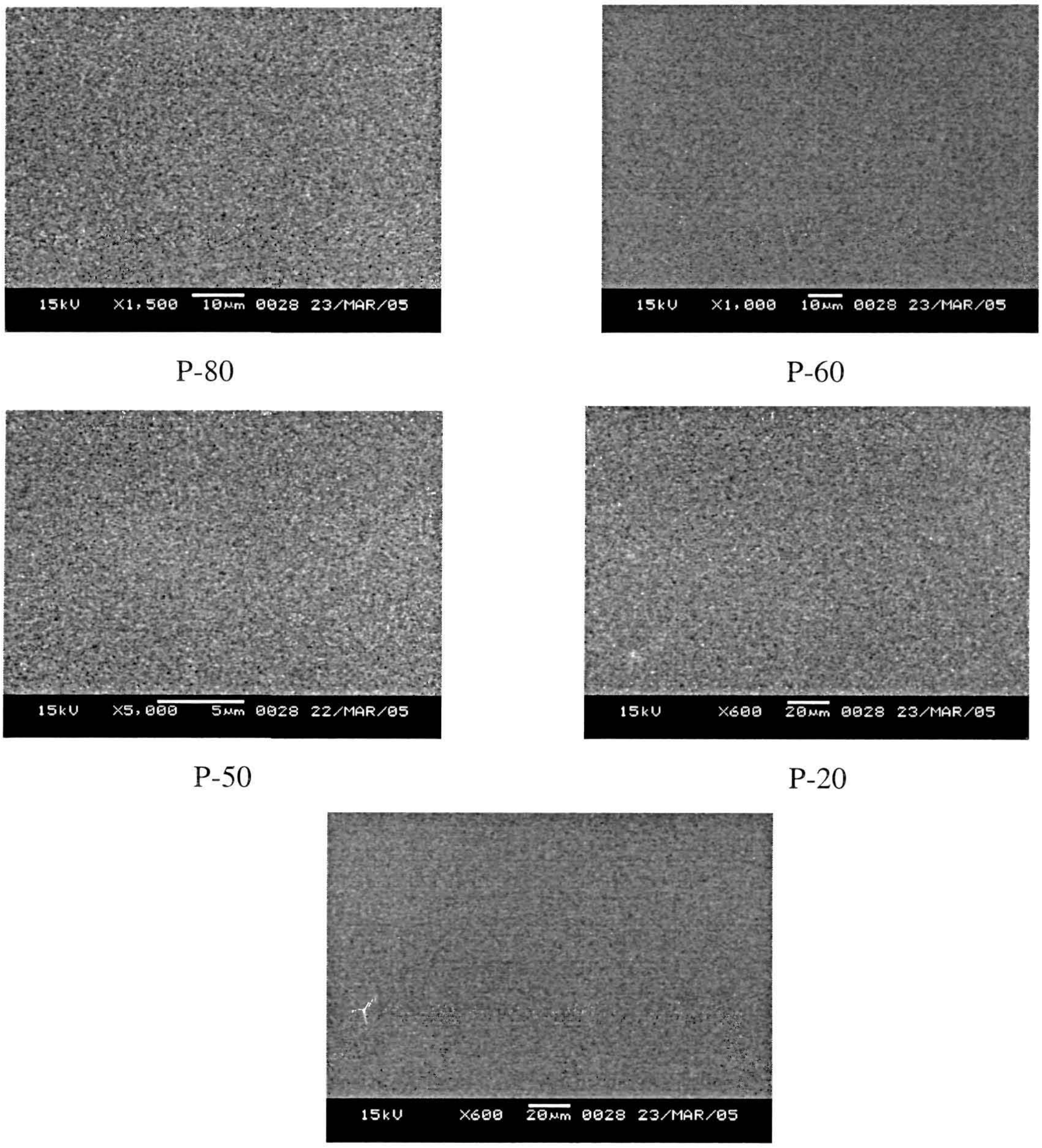


Fig. 5.1 FT-IR spectra of blends before (representative one) and after curing (P-80, P-60, P-50, P-20 and P-0)

5.3.3 Morphology of Blends

The ability to produce blends with improved combination of properties of the individual component depends on the degree of compatibility of the system. The oil modified polyester resin, in general, shows a good compatibility with MF resin by solution blending technique. The solvent system used in this study based on desired solvent compatibility, evaporation rate and ultimately uniform phase formation with the blend. All blends (P-80, P-60, P-50, P-20) show very clear and homogeneous micrographs in SEM study (Fig. 5.2). By comparing the micrographs of the cured blends with pure MF resin (P-0), it is observed that blends are compatible in any proportion and there is no phase separation. Thus, this study indicates that the Nahar seed oil modified short oil polyester has excellent dispersion characteristic in MF resin. This is mainly due to the fact that the different functionalities of both the resins directly involved in crosslinking reaction, which makes them a single phase system. The better dispersion of the blend components may also be due to good compatibility of aromatic moieties present in both resins as well as polar-polar and H-bonding interaction between the resins.



P-80 P-60

P-50 P-20

P-0

Fig. 5.2 SEM micrographs of the blends P-80, P-60, P-50, P-20 and P-0

5.3.4 Performance Characteristics

The film thickness of the cured blends as measured by Pentest was (45-50) μm. The cured samples were tested for different performance characteristics, results of which are given in Table 5.7. It has been found that the gloss increases with the increase of the percentage of MF resin, which is due to the higher clarity[23, 24] of MF resin compared to the polyester resin[16]. Again the increase of MF resin content decreases the flexibility of the cured blends, may be due to the fact that higher MF concentration in the blend leads to more self-polymerization reaction. This results higher degree of crosslinking, which increases the hardness of the network and that is reflected in the increase of pencil hardness with the increase of MF resin content in blends[16, 25]. The increase of hardness is also due to increase of rigid triazine moiety in the matrix with the increase of MF resin content in blends. The impact resistance of blends increases initially with the increase of the amount of MF resin but after a particular amount it decreases. This initial increase of impact resistance may be due to increase of strength property due to increase of crosslink density. But after a certain point, the decrease of impact resistance value at higher MF content in the blends is observed which is due to the increase in brittleness[25] of the network and also decreases in adhesion[25] with the substrate. The adhesive strength of blends decrease with the increase of MF resin content[25], as the amount of free polar groups such as -OH and -COOH groups decrease as a result of higher crosslinking reactions. Also as the amount of polyester resin increases, the transetherification reaction will be more feasible over self-condensation reactions. This leads to the formation of more flexible ether linkages, which facilitates the diffusion of the resin in the substrate and hence increase the adhesive strength[26].

Table 5.7

Performance characteristics of the blends

Polymer code	Flexibility*	Gloss (60^0)	Adhesion	Impact resistance (at 2 lb, cm)	Pencil hardness
P-80	Pass	100.2	5B	20 Pass	2B pass B fail
P-70	Pass	101.5	3B	50 Pass	B pass HB fail
P-60	Fail	103.9	3B	100 Pass	H pass 2H fail
P-50	Fail	105.9	2B	100 Pass	2H pass 3H fail
P-20	Fail	107	cut failure	20 Pass	3H pass 4H fail
P-0	Fail	114.5	cut failure	10 Pass	3H pass 4H fail

5.3.5 Thermal Properties

It has been found that the cured blends P-80, P-60, P-50 and P-20 along with 100% MF resin (P-0) possess good thermal stability under the nitrogen atmosphere. The thermostability increases[25] with the increasing amount of MF resin (Fig. 5.3). This may be due to the fact that higher concentration of MF resin favors the self-condensation reactions[27].

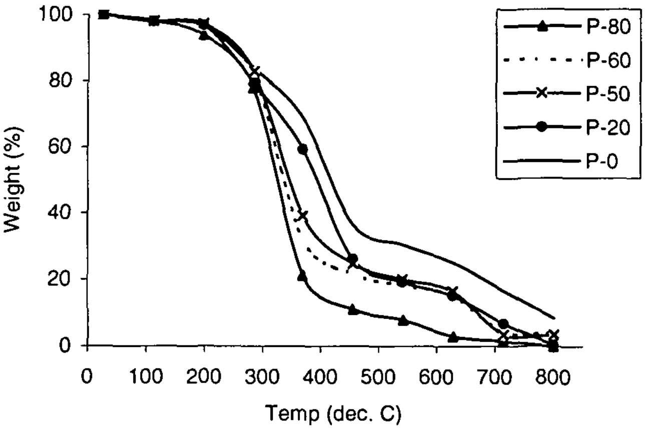


Fig. 5.3 TG traces of the blends (P-80, P-60, P-50, P-20 and P-0)

These self-condensation reactions increase the crosslinking density through the formation of three dimensional network structure, which is due to branched structure of MF resin. Also as the MF resin content increases in the blend, the amount of thermostable triazine moiety increases, which further enhance the thermostability of the matrix. It has also been found that blends degrade by a prominent single step pattern. From the DSC curves (not shown here) of blends, it is found that the degradation of blends occurs mainly through a very broad endothermic reaction. The char residues for the blends P-80, P-60, P-50, P-20 and 100% MF resin (P-0) are 1.46%, 4.31%, 3.45%, 6.8% and16.73% at 700 ^{0}C respectively.

5.3.6 Chemical Resistance

The chemical resistance of blends was tested by immersing the coated plates in different media for 4 days. The qualitative results of chemical resistance are shown in Table 5.8. It has been found that blends are unaffected in water, aqueous salt solution and less affected in aqueous H_2SO_4, HCl and CH_3COOH solutions. However with the increase of MF resin content in blends, the acid resistance decreases, which may be due to the reaction of stronger acid such as H_2SO_4, HCl with the –NH of MF resin. But alkali resistance increases[25] with the increase of MF resin and this may be due to the decrease of alkali hydrolyzable ester groups and increase of stable triazine moiety in blends.

Table 5.8

Chemical resistance of the blends

Type of media	P-80	P-70	P-60	P-50	P-20	P-0
NaOH (5%)	1	3	3	4	4	4
HCl (10%)	4	4	4	2	2	2
NaCl (10%)	3	3	3	3	4	4
Distilled Water	4	4	4	4	4	4
CH_3COOH (10%)	3	3	3	3	3	3
H_2SO_4 (10%)	3	3	3	3	2	1

1: fully damaged, 2: film peeled off with slight damage, 3: film peeled off but unaffected and 4: unaffected

5.4 Conclusions

From the above study, it has been found that the short oil polyester from *Mesua Ferrea L.* seed oil provides a way to utilize sustainable resource as a binder for coating material by suitable blending with MF resin. The study indicates that the polyester and MF resins have excellent compatibility with each other. Blends with high content of MF resin exhibit good thermostability, alkali resistance, gloss and pencil hardness. Whereas blends with high polyester content exhibit better flexibility, adhesion and acid resistance. The impact resistance is better for 60:40 (polyester resin: MF resin) and 50:50 (polyester resin: MF resin) blends. Thus, the blend ratio 60:40 of polyester and MF resins may be taken as the best ratio for getting optimum performance as coating material.

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Chapter 6

Stoving Paint from *Mesua ferrea* L. Seed Oil Modified Polyester and Melamine–Formaldehyde Resins

6.1 Introduction

Paints are industrial products mainly used for the protection of objects from destructive external attacks and for the decoration. Prehistoric men decorated their caves by paintings using natural paints, so that the use of paints is as old as civilization started[1]. The basic components of paints are vehicle consists of binder, solvent and pigments. In addition to these components, modern paints may contain additives[1, 2] of various kinds, such as dispersing agents, wetting agents, viscosity controlling agents, anti-settling agents, anti-skinning agents, antioxidants, antifoaming agents, adhesion promoters, desiccants, driers, biocides, light stabilizers, etc. The binder is the key component of the paint, which includes natural and synthetic resins, vegetable oils and natural fats, etc. The binders are the film forming materials in paints. The main function of the binder is to hold the different components together and to adhere to the applied surface[1]. The basic properties of paints such as drying, gloss, hardness, durability, flexibility,. abrasion resistance, impact resistance, chemical resistance, adhesion, etc. are solely governed by the binder system used in paint formulation, though some minor variations can be made by modifying the other components of paints. The pigment is a fine powder, whose function is to offer the film its desired color and hiding property. Pigments also provide protection of paints against UV light and corrosive environments. It increases hardness and major contributor to the cost of paints[2, 3]. The function of solvent is to reduce the viscosity of the binder to ease the processing and wetting of pigments. Thus, it helps in application, improve flow level, gloss and wetting of the substrate. The solvent system, may be a mixture of solvents or a single solvent, is not the part of the final film. Thus, the solvent has to be volatile and is only a member during journey of the paint from production to its final destination[2].

Among different binder systems, oil modified polyester (alkyd) resin is the most widely used binder for different paints. Non-drying short oil polyester in combination with melamine-formaldehyde resin is used as binder for stoving paint[4]. Stoving paints based on alkyd-amino resin combinations are highly durable[5] and the drying time is shortened with less opportunity for dirt collection on the finish[3]. For long time, they were used as the basis of automotive finishing paints[6, 7], but now a days they are used for sewing machines, fans, original equipment machines finishes, etc.

Since the studied oil is non-drying in nature, and blend of short oil polyester resin of this oil and commercially available partially butylated melamine-formaldehyde (MF) resin exhibits satisfactory performance characteristics as surface coating materials (discussed in chapter 5), so the main objectives of work reported in this chapter is to utilize the blend of short oil polyester based on Nahar seed oil (test resin) and MF resin as binder material for an industrial stoving paint (test paint). The performance characteristics of this paint was compared with an industrially used similar type of stoving paint (standard paint) obtained from castor oil based polyester resin (standard resin). Therefore, preparation, characterization and properties of stoving paints have been studied in this chapter. The maximum part of this work has been carried out in Berger Paints India Ltd., Kolkata.

6.2 Experimental

6.2.1 Materials

Nahar seeds have been collected from Jorhat (Assam) and the oil has been obtained by solvent extraction method using hexane as the solvent. The oil was purified as described in chapter 2 section 2.2.1.

Phthalic anhydride, glycerol, lithium hydroxide, xylene, naphtha, carbon black, methyl-ethyl ketoxime, silicone oil, ethanol, n-butanol all were obtained from Berger Paints India Ltd. Kolkata. The technical specifications of partially butylated melamine formaldehyde resin (MF) have already been mentioned in chapter 5.

6.2.2 Instruments and Methods

The morphology of both paints was studied by the scanning electron microscopy (SEM) analysis using LEO 1430 VP (SEM Instrument, Germany) after gold coating. The thermogravimetric analysis of blends was performed using Mattler Toledo TGA analyzer/SDTA 821^e under the nitrogen atmosphere with heating rate of 20 ^{0}C/min.

The physical properties such as acid value and non-volatile matter content and of the Nahar seed oil based polyester resin and castor oil based polyester resin were determined by using the standard methods. Viscosity[8] was determined by using PRS tubes, which is similar to Bubble viscometer standardized by Paint Research Society.

The fineness of grinding during paint preparation was checked using Hegman Gauge (Sheen Instrument Ltd., UK).

The film thicknesses of both the paints were determined by Pentest, coating thickness gauge (Sheen Instrument Ltd., Model 1117, UK). The coating performance of paints was evaluated by determining pencil hardness using pencils of different grades ranging from 6B to 6H (Mitsubishi Uni Pressure Proofed High Density Lead), gloss using glossmeter (Sheen Instrument Ltd., Model No. 160, UK), flexibility using flexibility apparatus (PEI, Kolkata), adhesion by commercial cello tape respectively. All the methods of these tests are same as described in chapter 2, section 2.2.2. The impact resistance of the paints coated on mild steel panel was measured using a falling weight impact tester (2 pound weight, Byk, Big Chemie, Germany) as per the standard method[9]. The salt spray test[10] and humidity test[11] of both paints coated on mild steel panel were performed using the standard IS methods after 96 h.

Resinification Reaction

The Nahar seed oil based short oil polyester resin was prepared by the conventional alcoholysis process with glycerol followed by polycondensation with phthalic anhydride using azeotropic distillation technique as described below.

509.6 g of Nahar oil, 128 g of glycerol and 0.4 g of LiOH were taken in a resin kettle fitted with a mechanical stirrer, a thermometer and a Dean-Stark apparatus. The resulting mixture was heated to (230±5) ^{0}C with constant stirring and maintained at this temperature for about half an hour until monoglyceride was formed as confirmed by the solubility test in methanol at ambient temperature. After the formation of monoglyceride, the reaction mixture was cooled down to (130±5) ^{0}C and 475.6 g of phthalic anhydride, 109.8 g of glycerol and 40 g of xylene were added into the kettle. Further, the reaction mixture was heated to (220±4) ^{0}C until the desired level of acid value was obtained. The progress of the reaction was monitored by measuring the acid value of the mixture, time to time. After reaching the desired level of acid value, the reaction mixture was allowed to cool to (140±2) ^{0}C and diluted to 60% solid content by addition of xylene. However, the stirring was continued until the reaction mixture reached to ambient temperature.

By using the same procedure, short oil polyester resin based on castor oil was also prepared.

Preparation of Paints

Paints from both oils were prepared using the following recipe (Table 6.1)

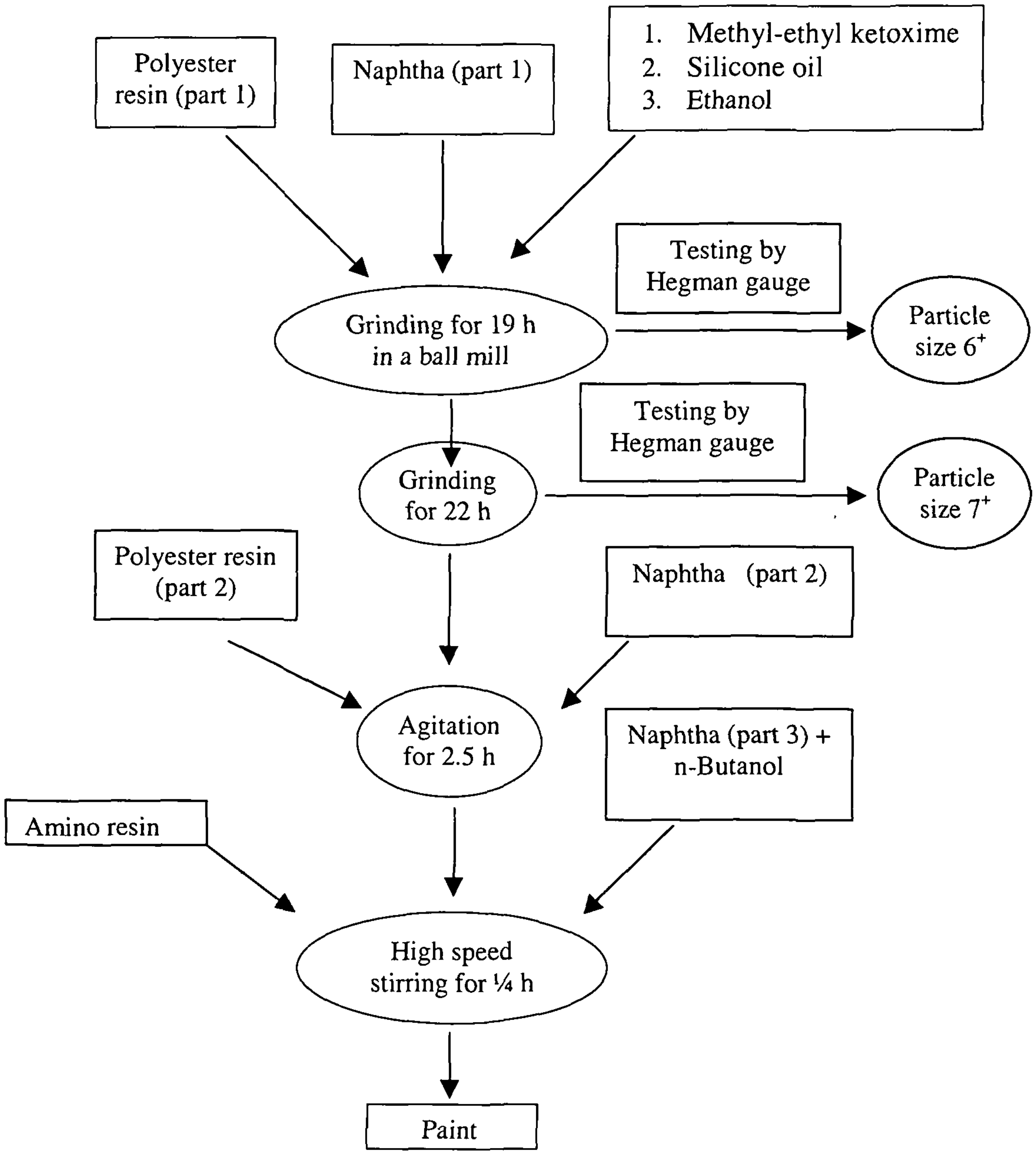
Table 6.1

Recipe of paint formulation and function of the ingredients

Ingredients	Amount (weight %)	Function
Polyester resin	48.04	Binder
Naphtha	21.87	Solvent
C-black	1.5	Pigment
Methyl-ethyl ketoxime	1	Antioxidant
Silicone oil	1	Antifoaming agent
Ethanol	1	Solvent
n-Butanol	5	Solvent
Amino resin	20.59	Binder

At first 6.86% of polyester (60% solid content) resin was mixed with 1.5% of carbon black, 1% of silicone oil, 1% of methyl ethyl ketoxime, 1% of ethanol and 11.67% naphtha in a ball mill and ran for 19 h at ambient condition followed by checking of dispersion of additives in the resin using Hegman gauge. Again, the ball mill was run for another 22 h. Then further 6.86% of polyester resin, and 6.5% of naphtha were added and the mill was allowed to run for another 2.5 h. After that 20.58% of MF resin (60% solid content), 34.31% of polyester resin, 5% of n-butanol and 3.7% of naphtha were added in the mixture and agitated with the help of high-speed stirrer for 15 min. Finally the mixture was kept for 24 h for better wetting before panel preparation for further study.

The whole process of paint preparation is shown in the following flow diagram



Scheme 6.1 The flow sheet for preparation of stoving paint

Preparation of Panels and Stoving

The prepared paint was diluted to 46% solid content by adding xylene. This was sprayed with the help of specific gravity type spray gun from a distance of 15-20 inch on the mild steel plates (145 mm X 68.9 mm X 0.70 mm) and tin plates (100 mm X 50 mm X 0.315 mm) placed on spray booth. After the panels were painted, those were kept in open air for 10 min followed by drying in an oven at 120 ^{0}C for 30 min.

6.3 Results and Discussion

6.3.1 Kinetics of Esterification

During resinification reaction, the change of acid value with an increasing reaction time for Nahar oil based polyester resin is shown in Fig 6.1. The extent of reaction, p and average degree of polymerization, DP with respect to the acid value were calculated using the following equation[12-14]

$$p = C_0 - C_t / C_0$$

where C_0 is the acid value at zero reaction time and C_t is the acid value after time t, respectively.

The average degree of polymerization, DP is given by $DP = (1 - p)^{-1}$

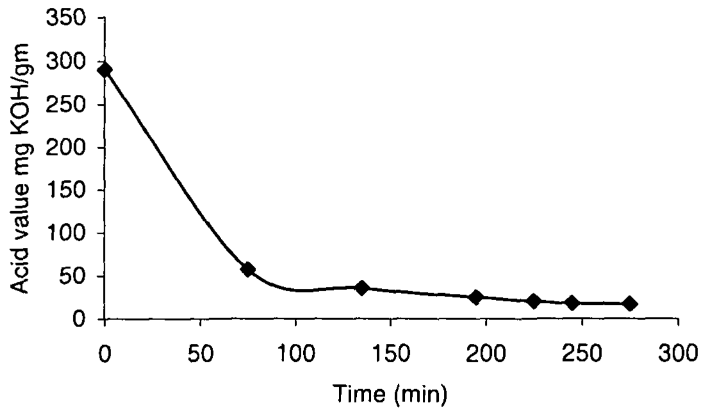


Fig. 6.1 Variation of acid value with time

From Fig. 6.1, it has been observed that the acid value decreases with the increase of reaction time. The decrease in acid value is more rapid during the early stage of resinification reaction though at the later stage of reaction, the rate of decrease of acid value became slow. The change of acid value is due to the fact that the primary hydroxyl groups of glycerol (monoglyceride) react much faster with phthalic anhydride than the secondary hydroxyl groups. Thus it is believed that rapid decrease in acid value[15] at the early stage of polycondensation reaction corresponds to the reaction of primary hydroxyl groups, while the slower rate is due to the reaction of less reactive secondary hydroxyl groups. It has been reported by Aigbodion and Okieimen[12] that the period when change in acid value during polycondensation reaction is slow, probably then the crossliniking of resin has started to form a three-dimensional network structure. Thus, it may be inferred that during this stage of polycondensation reaction, probably crosslinking started.

The monofunctional and polyfunctional condensation reactions can be considered as equivalent as essentially they are the reaction between functional groups, so their rate of reaction can be expressed as a second-order rate law[16]

$$(1-p)^{-1} = C_0kt + 1$$

where C_0 is the initial concentration of reactant, t is the time of reaction, p is the extent of reaction and k is the rate constant of the reaction. Here the acid value is substituted for concentration. Thus the plot of (1/1-p) versus time should be linear, if the rate constant k is constant throughout the reaction. But the plot (Fig. 6.2) shows a non-linear variation indicates that rate change during resinification reaction.

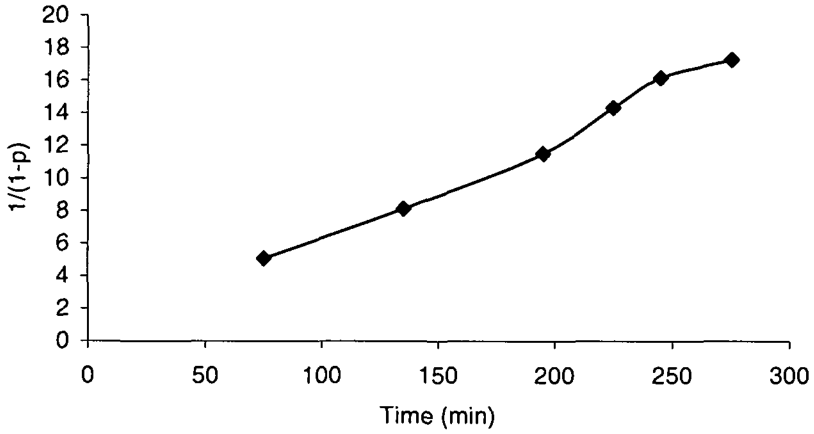


Fig. 6.2 Plot of $(1-p)^{-1}$ versus time

Even though, initially the variation of $(1-p)^{-1}$ versus time is linear, but after a certain point it deviates from linearity. The similar observation was reported in preparationof different oil modified polyester resins[12, 17]. This trend of variation may be due to the fact that the first linear portion is considered to represent time of formation of linear chains, but the second non-linear portion may represent onset period of cross linking that is three dimensional network formation of the resin, which is very insignificant in this case. The extent of reaction and the average degree of polymerization were calculated for the resin at the point of deviation from linearity and are given in Table 6.2. The result indicates that the extent of reaction at this region is about 90%. Although this result is little higher than the value (75-80%) obtained by reaction of phthalic anhydride with glycerol[18], but is much higher than results reported for African locustbean[17] and rubber seed[12] oil modified polyester resins. The average degree of polymerization value indicates the formation of chains with relatively medium molecular weight at that point and also cross-linking started at the same time. The second order rate constant value of the resin (Table 6.2) obtained from the linear portion of the plot indicates that the rate of resinification reaction depends on the ratio of reactants used in the formulation. From this study, it is clear that the preparation of short oil polyester resin is relatively easier in this case without gel formation.

Table 6.2

Extent of reaction (p, %), average degree of polymerization (DP) and second order rate constant (k, g(mg KOH)$^{-1}$ min^{-1}) at the onset of gelation (t_{onset}, min)

Parameter	Value
t_{onset}	195
p	91.3
DP	11.49
k	18.2 X10^{-5}

6.3.2 Physical Properties

The oil content, viscosity, acid value and non-volatile matter of both resins are given in Table 6.3.

Table 6.3

Different properties of the test and the standard resins

Properties	Test resin	Standard resin
Oil content (%)	43.73	41
Acid value (mg KOH/g)	14.56	16
Viscosity* (PRS)	12^+	10-12
Non-volatile matter (%)	60	60

* at 50% solid content

6.3.3 Paint Preparation

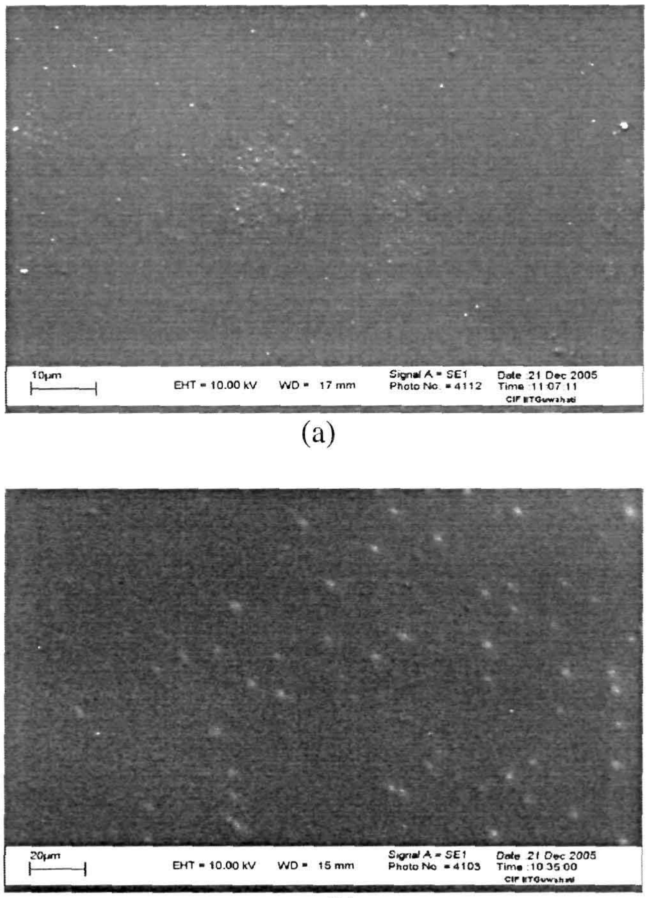
In the previous chapter we observed that 60:40 ratio of polyester and MF resins blend results the optimum performance as coating material. But in the present investigation, 70:30 ratio of polyester and MF resins blend has been used in order to decrease the ultimate cost of the paint as the cost of MF is higher than polyester resin. Further this blend also satisfies industrial requirements for this type of paint, as observed in the earlier chapter (Chapter 5).

In dry condition, the pigment particles exist largely in the form of clusters or aggregates and breaking down of these particles is necessary for the dispersion of individual particle in the paint medium. In the first step of paint preparation, pigment was grinded in the vehicle in order to incorporate[19] pigment particles in the medium to yield fine particle dispersion. All other additives were also dispersed along with the pigment during the same period. The degree of dispersion at this stage was not acceptable (Hegman unit 6^+), so again grinding was continued until the dispersion became acceptable (Hegman unit 7^+) for the stoving paint[20]. The next step is the stabilization of dispersed particles in the binder medium through wetting and thereby forming a stable dispersion. The main motive of this step is to surround the particles with sufficient amount of vehicle so that particle-to-particle contact is thereafter to be avoided[19]. In the final step, high-speed stirring was performed in order to let down the dispersion with additional vehicle to get the final paint composition having optimum level of application and performance[19].

The ultimate cost is the combined cost of raw materials and production[3]. Between two paints, as all raw materials except the vegetable oil and process of production are same, so difference in cost of two paints only depends on the cost of vegetable oil. As it is expected that the cost of Nahar oil will be lower than castor oil because of its easy availability. So, the paint based on Nahar oil may be cheaper than that of castor oil.

6.3.4 Morphological Study

From the SEM micrographs of both paints (Fig. 6.3), it has been observed that the disperse phases are more uniformly distributed throughout the matrix in case of castor oil based paint (Fig. 6.3 a) compared to Nahar oil based paint (Fig. 6.3 b). This may be due to higher viscosity of the test resin compared to the standard resin (Table 6.3). Because of the same reason, the domain sizes of disperse phases in the test paint are smaller than the standard paint as the mechanical stress during milling is higher in case of the test paint, which facilitates the breakdown of the disperse phase in the matrix.



(a)

(b)

Fig. 6.3 SEM micrographs of the test paint (a) and the standard paint (b)

6.3.5 Performance Study

The performance characteristics of both paints (film thickness 35-40 μm) are given in Table 6.4. The gloss of Nahar oil based paint is very good and comparable to the industrially used castor oil based paint (Table 6.4). This high gloss of paints is due to the fact that both resins used in the paints possess high gloss[21-23] and also due to the better smoothness of blends. This higher surface smoothness is due to higher crosslink density of the blend through self- and co-condensation reactions of MF and polyester resin. Denser the network formation better is the dimension stability and that makes the surface much smoother. The pencil hardness of the test paint is relatively lower compared to the standard paint. Though this lower value is sufficient to fulfill the service requirement for applications of the stoving paint. This lower pencil hardness of the former is due to the lower degree of crosslink density compared to the latter. This higher crosslink density of castor oil based paint may be due to the presence of free hydroxyl groups in the fatty acid chain (recenoleic acid), which undergo cross-condensation reaction with MF resin, in addition to other cross- and self-condensation reactions. Because of these polar hydroxyl groups as well as resulted ether linkages, adhesion of the standard paint is better than the test paint (Table 6.4). These hydroxyl groups increased polarity when they are free as well as when they are forming polar ether linkages. The impact resistance of both paints is quite satisfactory (Table 6.4), which may be due to good mechanical strength arises from optimum crosslinking density and better flexibility[23] coming from the flexible hydrocarbon chains present in the fatty acids as well as from ether linkages. The higher flexibility is supported by the flexibility test (Table 6.4).

In humidity test, both paints show the formation of a few micro blisters. The humidity test is more useful to determine corrosion resistance because of good correlation with actual field performance of paints. The first appearance of blistering is an indication of initial breakdown of paints. It is mainly attack of moisture through oxidation or rust formation on the metal surface[24], the by-product of which is hydrogen gas and that causes blistering. The results indicate that both paints exhibit satisfactory corrosion resistance as very less number of micro blisters are formed. This is further supported by adhesion test after humidity test, which shows good results in both cases. The better adhesion for both paints may be due to the better wetting and physical anchoring with the metal surface.

Table 6.4

Performance characteristics of test and standard paints

Properties	Test paint	Standard paint
Gloss (20^0)	76.7	76.6
Gloss (60^0)	94.9	94.6
Impact resistance	100 cm pass	100 cm pass
Pencil hardness test	B	F
Adhesion	3B	4B
Flexibility	Pass	Pass
Salt spray resistance	2 mm corrosion	2 mm corrosion
Humidity resistance	Few microblisters	Few microblisters
Adhesion*	5B	5B

*after performing salt spray test and also after humidity test

The salt spray test of both paints indicates 2 mm corrosion from both edges of the cross cut portion of the test panel. These results satisfy service requirement for their applications. The cross cut adhesion test for both paints after the salt spray test indicates equal and good adhesion. The satisfactory corrosion resistance in both tests indicates the penetration of corrosive chemicals such as moisture, NaCl salts, etc. through the paint films is restricted. This may be due to satisfactory dimensional stability through three dimensional network formation and due to presence of rigid triazine and phenyl moieties in the structure. However, in this case both resins exhibit equivalent results may be due to maturation, which causes same extent of dimensional stability as samples were kept for 7 days after curing before testing.

6.3.6 Thermal Study

From the TG traces of both paints (Fig. 6.4), it has been observed that the initial decomposition of the standard paint is lower than the tested paint. This may be due to higher molecular weight as measured by viscosity of Nahar oil based polyester compared to castor oil based polyester. TG traces for both paints show prominent single step decomposition pattern. The overall thermostability of both paints is quite satisfactory as the 50% decomposition occurred above 340 ^{0}C for both cases. The char residue for the test paint at 600^0 is 8.2%, whereas for the standard paint the value is

5.7%. This overall better thermostability is coming mainly from the binder system, which contain thermostable triazine moieties[23] in their structures.

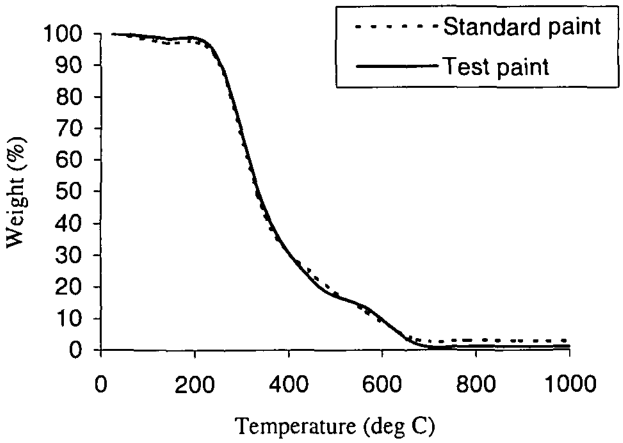


Fig. 6.4 TG traces of test and standard paints

6.4 Conclusions

From this study, it can be concluded that Nahar oil based short oil polyester resin has been successfully utilized for the preparation of an industrial stoving paint in combination with partially n-butylated melamine-formaldehyde resin. The performance characteristics of this paint are comparable with the industrially used castor oil based paint having same recipe and processing conditions. Furthermore, Nahar oil based paint is expected to be of lower cost than industrially used castor oil based stoving paint.

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Chapter 7

Summary and Conclusions

7.1 Summary and Conclusion

The present thesis works on development of polyester resins from *Mesua ferrea* L. (Nahar) seed oil. The thesis describes the brief review on polyester resins from vegetable oils including the importance, general techniques of preparation, characterization, properties and applications. The whole technical work of the present investigation is divided into five different parts.

In the first part, the purified Nahar oil was characterized and properties were evaluated as a coating material before and after heat treatment at two different temperatures.

In the second part, the synthesis, characterizations and properties evaluation of three different polyester resins based on different composition of phthalic anhydride and maleic anhydride from the above purified oil were described.

The third part of the technical work studied on improvement of coating performance characteristics of above polyester resins by blending with commercially available bisphenol-A based epoxy resin.

A 100% phthalic anhydride based short oil polyester resin of Nahar oil was prepared and blended with partially butylated melamine-formaldehyde resin to investigate the coating performance characteristics of the material. This was described as fourth part of the work.

The final part of the technical work is on utilization of the short oil polyester resin as a binder material for preparation of an industrial stoving paint.

From the present investigation the following conclusions can be drawn

i) Nahar seeds contain a-exceptionally high amount of oil.

ii) The heat treatment of Nahar oil can cause significant change in structural characteristics and rheological behavior. Heat treatment reduces the drying time of heated oil compared to the unheated oil.

iii) Nahar oil was successfully utilized for preparation of polyester resins based on 100% phthalic anhydride, 50% phthalic anhydride with 50% maleic anhydride and 25% phthalic anhydride with 75% maleic anhydride.

iv) The prepared resins were successfully characterized by determining the physical properties and structural analysis.

v) Blending of the prepared resins with commercially available bisphenol-A based epoxy resin led to significant improvement in drying time from several hours to several minutes as well as film properties like hardness, alkali resistance and thermal stability. Thus, these materials can be utilized as surface coating materials.

vi) Blends of Nahar seed oil based short oil polyester resin with partially butylated melamine-formaldehyde resin showed very good compatibility at different proportions of blends. The blend at 60:40 ratio of polyester resin to melamine-formaldehyde resin showed optimum performance.

vii) The blend with 70: 30 ratio of polyester resin to melamine-formaldehyde resin was successfully utilized for the preparation of an industrial stoving paint. The performance characteristics of this paint were compared with an industrially used standard castor oil based stoving paint and it was found that both exhibited comparable results. Thus, Nahar seed oil based polyester resin may replace castor oil based stoving paint.

Thus the overall major achievement of the present investigation is the utilization of a less significant renewable raw material to a great significant industrially useful product.

7.2 Future Scopes

There are many future scopes for further utilization of Nahar seed oil based polyester resins in different applications. Some of these are

i) Investigation of water borne polyester resins.

ii) Preparation of polyester resins after blending of Nahar oil with other commercially useful vegetable oils.

iii) Investigation of flame retardant polyester resins.

iv) Utilization of Nahar oil based polyester resins as the binder for green composites and nanocomposites.

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