SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCHED AND AIR DRYING FATTY ACID BASED RESINS

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCHED AND AIR DRYING FATTY ACID BASED RESINS

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There has been a considerable effort in the last years to decrease the amount of volatile organic compounds (VOCs) present in organic coatings. The risks to human health and environmental hazards associated with VOCs, governmental directives, and economic factors are the main driving forces behind this effort. One way of achieving less or no VOC containing coating systems is to produce low viscosity resins. Hyperbranched resins owing to their globular structure have low viscosities and are promising materials for decreasing the VOCs. In this research hyperbranched resins having properties close to alkyds were synthesized. Dipentaerythritol, which was used as the core was esterified with dimethylol propionic acid. The hyperbranched polyester was then esterified with the castor oil fatty acids

(Castor FA). The hydroxyl group of the ricinoleic acid present in the castor FA was modified with different amounts of linseed oil fatty acids (Linseed FA) and benzoic acid.

The chemical characterization of the resins was achieved by FTIR spectroscopy and the thermal properties were determined by DSC. Then, the physical and the mechanical tests were carried out. The resins containing the Castor FA only and 32.5 % Linseed FA in addition to the Castor FA had 24 and 68 Persoz hardness, respectively. The viscosity of the resins decreased from 17.3 Pa·s to 5.8 Pa·s as the amount of the Linseed FA was increased. The resins showed excellent adhesion, gloss, flexibility and formability.

Keywords: Hyperbranched, Castor oil, Ricinoleic acid, Air drying, Linseed oil

ÖZ

AŞIRI DALLI VE HAVADA KURUYAN YAĞ ASİDİ KÖKENLİ REÇİNE YAPIMI VE ÖZELLİKLERİNİN BELİRLENMESİ

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Son yıllarda organik kaplamalardaki uçucu organik bileşik miktarını azaltmak için önemli çaba sarf edilmektedir. Uçucu organik bileşiklerin insan sağlığına ve çevreye olan zararları, yasal düzenlemeler ve ekonomik etmenler bu çabanın ana itici güçleri olmuştur. Az miktarda ya da hiç uçucu organik bileşik içermeyen organik kaplama sistemleri elde etmenin bir yolu düşük viskoziteli reçineler üretmektir. Aşırı dallı reçineler küresel yapıları sayesinde düşük viskoziteye sahiptirler ve uçucu organik bileşikleri azaltmak için umut vaad eden malzemelerdir. Bu çalışmada alkit reçinelerinin özelliklerine yakın özelliklere sahip aşırı dallı reçineler sentezlenmiştir. Çekirdek molekül olarak kullanılan dipentaeritritol, dimetilol propiyonik asit ile tepkimeye sokularak esterleştirilmiştir. Elde edilen aşırı dallı polyester daha sonra hint yağı asitleri ile esterleştirilmiştir. Hint yağı asitlerinde bulunan risinoleik asidin hidroksil grubu değişik miktarlarda keten yağı asitleri ve benzoik asitle tepkimeye sokulmuştur.

Reçinelerin kimyasal yapısı FTIR spektroskopisiyle, ısıl özellikler ise DSC ile belirlenmiştir. Daha sonra fiziksel ve mekanik testler yapılmıştır. Sadece hint yağı asitleri içeren reçinenin sertliği 24 Persoz iken % 32.5 keten yağı asitleri içeren reçinenin sertliği 68 Persoz ölçülmüştür. Keten yağı asidi miktarı arttıkça akma direnci 17.3 Pa·s'den 5.8 Pa·s'ye düşmüştür. Tüm reçineler mükemmel derecede yüzeye yapışma, parlaklık, esneklik ve şekillendirilebilirlik göstermiştir.

Anahtar Sözcükler: Aşırı dallı, Hint yağı, Risinoleik asit, Havada kuruyan, Keten Yağı

To My Family
&
Arzu

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TABLE OF CONTENTS

APPENDIX

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

NOMENCLATURE

Castor FA	Castor oil fatty acids
Dipenta	Dipentaerythritol
DMPA	Dimethylol propionic acid
EB	Electron beam
HAP	Hazardous air pollutant
HBP	Hyperbranched polyester
HBR	Hyperbranched resin
KHP	Potassium hydrogen phthalate
Linseed FA	Linseed oil fatty acids
M_w	Weight average molecular weight
M_n	Number average molecular weight
M_w/M_n	Polydisperdsity index
PET	Poly(ethylene terephthalate)
PP	Polypropylene
p-TSA	Para toluene sulfonic acid
T_g	Glass transition temperature
UV	Ultraviolet
VOC	Volatile organic compound
σ	Standard deviation

CHAPTER 1

INTRODUCTION

The ‘rationality’ principle in classical economics, which aims at maximization of profit, has revealed some argumentative results especially in the last few decades. The more and more production throughout the world, not taking into account the environmental side-effects caused some reversible/irreversible hazards to the environment. In the early 1970s more than 90 % of the paint and coatings sold worldwide consisted of low solids (5-20 % by weight) solvent borne coatings [1]. These coatings containing very high levels of solvents, more accurately volatile organic compounds (VOCs) play a major role in global warming and in photochemical ozone creation which is toxic to plants and animals including humans.

The fact of globalization has forced the coatings industry to face tough competition as well as the other industries. The competitive environment of the industry provides the drive needed to develop coatings that utilize less expensive material [1]. The changing consumer expectations and concerns manifested themselves into the main driving force behind a transition from conventional solvent borne coatings to new and novel coating technologies. The oil embargo in the 1970s caused many manufacturers to reconsider the cost associated with operating the ovens used to volatilize solvents during the cure of a coating. A shortage of gas and oil highlighted the need to develop coatings that either contained less solvent or exhibited lower energy cure process [1].

Environmental concerns and the governmental directives especially in Europe and United States and has stimulated research to develop environment friendly coatings having very low VOC content or no VOC at all [1-7]. Several options are available for meeting this limitation on VOCs [2].

- No solvent / powder coatings (industrial use only)
- Water-based acrylic dispersions
- Water-based alkyd emulsions
- Air drying, high solids alkyds

However, conventional dispersion technology has failed, so far, to provide the gloss performance that can be achieved with solvent based alkyd systems. Alkyd emulsion systems appear to have gloss advantage over conventional dispersion. These products have generated some interest among manufacturers. Currently, the most realistic method of producing low VOC gloss coatings seems to be the application of high solids alkyd paints. Although, recently ultra low VOC levels could not be achieved with these systems, they can significantly reduce the emission of organic compounds in comparison with conventional alkyd paint [3]. Apart from the lower solvent emission of these high solids paints there is also a technical benefit; thicker layers can be applied in one go, providing better protection of the painted surface and more hiding power [2].

In the development of a high solids alkyd, the main problem is to reduce the viscosity while keeping the properties on that high level. There are several theoretical options [2].

- Increasing oil length
- Use of reactive diluents
- Narrow molecular weight distribution

Increasing oil length lowers molecular weight, leads to a reduction of intermolecular action due to increased C=C bonds and leads to less hydrogen bond forming groups [2]. However, low molecular weight resins possess unsatisfactory properties such as slow drying and sagging [3]. A reactive diluent functions as a solvent in the formulation of the coating and is converted into an integral part of the film during curing [3, 4, 8]. High and low molecular weight resins can be reduced by designing resins with narrow molecular weight distribution. Narrow molecular weight distribution is desirable as this leads to lower solution viscosity for high solids and a more homogeneous network, which improves overall film properties. In order to obtain narrow molecular weight distribution, highly branched chains are useful, because at the same molecular weight a lower viscosity can be reached as compared to linear counterparts and less chemical drying is needed to form a network.

In the early 1950s Flory published a paper about the condensation reactions of AB_x monomers, which yield highly branched structures without gelation [9-14]. However, the field remained almost unexplored until the late 1970s [9, 13]. The development of the divergent synthesis of ‘true dendrimers’ was first presented in 1984. The article describing the preparation of poly-(amidoamine) polymer used the term ‘dendrimer’ for the first time [13]. The term hyperbranched polymer was first coined by Kim and Webster after the one step synthesis of first hyperbranched polyphenylenes [14-16]. These highly branched polymers were named dendritic polymers and are accepted as the fourth major class of polymeric architecture. Dendritic polymers consist of three major subgroups: Dendrimers, hyperbranched polymers, and dendrigrafts. The signature for such a distinction is the unique repertoire of new properties manifested by this class of polymers [14]. Dendritic polymers have high solubility and lower solution and melt viscosity compared to their linear analogues. Their globular shape eliminates the entanglements leading to Newtonian behavior. They can also be tailored with respect to functionality and polarity to adjust the properties for certain applications. The difference between the dendrimers and hyperbranched polymers is that dendrimers are perfectly built onto a core molecule while hyperbranched polymers are polydisperse and not fully reacted at every repeating unit. The synthesis routes of dendrimers are often time consuming, require repetitive isolation and purification steps and often produce low yield products. This makes dendrimers rather costly to produce and less attractive for large volume applications. Hyperbranched polymers on the other hand can be produced in large scale at a reasonable cost making them more attractive in several areas [5, 17]. The use of hyperbranched polymers in several coating applications has been presented in the literature [5, 18].

Hyperbranched alkyd resins have been studied in order to obtain low viscosity resins with rapid air drying [3, 5, 18, 19]. The common part in these works is that all the works modify the hydroxyl groups at the outer periphery of a hyperbranched polyester with different fatty acids. In this research the hyperbranched polymer synthesized through a pseudo-one step procedure using dipentaerythritol as core molecule and dimethylol propionic acid as chain extender. The synthesized polymer was first reacted with the castor oil fatty acids. The obtained resin was then further reacted with the linseed oil fatty acids in different amounts. The last resin was modified with benzoic acid and the linseed fatty acids. Internal functionalization of the alkyd resins has been accomplished by this route. Films were casted on glass and metal plates and were dried in an oven at 90 °C for 12 hours. Four different resins have been characterized in terms of chemical structure, the mechanical and the physical properties.

CHAPTER 2

LITERATURE SURVEY

2.1 Coatings

2.1.1 Definition & Uses

Surface coatings are solid or liquid materials, that can be applied as one or more thin layers to the surface of an object and dry to form well adhering films [20]. Paint and coating terms are often used interchangeably. However it has become common practice to use coatings as the broader term and to restrict paints to the familiar architectural and household coatings [21]. There are three broad categories of coatings: architectural, OEM (Original equipment manufacturers) and special purpose coatings. Today coatings are used for one or more of three reasons [21]:

- decoration
- protection
- some functional purpose

2.1.2 History

Coatings have been used for various purposes for thousands of years. Archeologists have found cave drawings in color and etchings on rocks which were executed before the last Ice Age. Paleolithic artists used chalk, charcoal, red and yellow ocher. Naturally these drawings had no durability except in a favorable environment as in caves [22]. The finest specimens have been found in Altamira, Spain (15000 B.C.) where a landslide sealed the cave for thousands of years [23]. Findings in the Libyan Desert indicate that this kind of drawing was taken up many years later by Egyptians. Eastern civilizations developed colored pencils for decorative purposes (4000 B.C.). There are many examples of the decorative arts in the form of tomb frescoes, wall paintings, papyrus manuscripts, which belong to early Egyptian period. First synthetic pigments were made during this period. Egyptians employed gum arabic, egg white as well as egg yolk, gelatin and bees wax for preparing their binders. Although drying oils were known and flax was grown for its seed, there is little evidence that the oils were used for paint.

The paint and varnish industry was first described as we know it today in 1773. After industrial revolution turpentine was employed as the thinner. Grinders for pigments were used. The first varnish factory was established in England in 1790. Great Britain and the Netherlands were the first to place varnish manufacture upon a truly technical basis [22].

Up until about 1900 varnish formulations experienced minor changes only. Progress at the beginning of the 20th century was naturally slow at first and then each innovation produced a major revolution. After the turn of the century progress became rapid and at present time it has a pace which is difficult to follow. Titanium and Zinc pigments were discovered and many oils other than linseed oil were employed in paint formulations. The works of Baekeland in 1909 laid the foundations for the present resin and plastics industry. Starting from 1929 a rapid increase in favor with which the synthetic resins (phenolic & alkyd resins were introduced in 1928) have met for varnish use lead to the replacement of the naturally occurring resins with the synthetic ones [22].

2.1.3 Composition of Coatings

Organic coatings are complex mixtures of chemical substances that can be grouped into four broad categories [21]:

- Binders
- Pigments
- Volatile components (solvents)
- Additives

2.1.3.1 Binders

Binders are the materials that form the continuous film that adheres to the substrate (adhesive forces), binds together the other substances (cohesive forces) in the coating to form a film and that presents an adequately hard outer surface. The binders used today are polymers. In some cases, these polymers are prepared and incorporated into the coating before the application; in other cases, final polymerization takes place after the coating has been applied. The binder governs, to a large extent, the final properties of the coating film [21].

2.1.3.2 Pigments

Pigments are finely divided insoluble solids that are dispersed in the vehicle (binder & volatile components) and remain suspended in the binder after film formation. Generally the primary purpose of pigments is to provide color and opacity to the coating film. However, they also have substantial effects on application characteristics and on film properties (such as hardness, abrasion, and weathering resistance) [20]. Particle size affects color strength, transparency or opacity, exterior durability, solvent resistance and other properties of pigments.

A large fraction of the coatings contain **white pigment**. White pigments are used not only in white coatings but also in a substantial fraction of the other pigmented coatings to give lighter colors than would be obtained using color pigments alone. Furthermore, many color pigments give transparent films and the white pigment provides a major part of the hiding power of the coating. Most widely used white pigment is TiO_2.

Inert pigments absorb little, if any, light and have high refractive indices close enough to those of binders that they give little light scattering when used as pigments. Commonly, but not always they reduce cost of a coating. The principal function of most inert pigments is to occupy volume in a film. Calcium carbonate, magnesium silicate, silicon dioxide, barium sulfate pigments are used as inerts.

Functional pigments are used to modify the application characteristics, appearance or film properties of coatings. Complex zinc chromate, red lead and zinc phosphate are used as primers to inhibit corrosion of steel by passivation of anodic areas. Other functional pigments are used as fungicide, biocide, fire retardant, and viscosity modifiers.

2.1.3.3 Volatile Components

Volatile components are included in a majority of all coatings. They play a major role in the process of applying coatings; they are liquids that make the coating fluid enough for application, and they evaporate during and after application. Most methods of application require coating viscosities of 50 – 1000 mPa·s (= cP) [24]. Today, most coatings, including water-borne coatings, contain at least some volatile organic solvents. Exceptions are powder coatings and radiation curable coatings [21].

An important characteristic of solvents is rate of evaporation. Rates of solvent loss are controlled by vapor pressure and temperature, partial pressure of the solvent over the surface, and thus the air-flow rate over the surface, and the ratio of surface area to volume. When coatings are applied by spray gun, the atomized particles have a very high ratio of surface area to volume, and hence solvent evaporation is more rapid during the time when the atomized particles are traveling from the orifice of the spray gun to the surface being coated than from the film of the coating on the surface [24].

All solvents are toxic at some level of exposure. Generally the greatest potential risk comes from inhalation. Since the 1950s it has been realized that the presence of organic compounds in atmosphere can lead to serious air pollution problems. Three end effects of VOC emissions into the atmosphere are important: formation of eye irritants, particulates, and toxic oxidants, especially ozone. While ozone is a naturally occurring component of the atmosphere, it is toxic to plants and animals. Plants and animals, including humans evolved in the presence of some ozone and can tolerate its presence up to a point. However, with the rapid growth of VOC emissions from man-made sources since 1900, ozone levels on many days of the year in many parts of the world have exceeded the levels that many plants can withstand and endanger human health. The largest source of man-made VOC emissions comes from transportation auto and truck tailpipe emissions, along with fuel leakage during distribution. The second largest source is coatings; in 1995, coatings and adhesives accounted for 11.6 % of man-made volatile organic compound emissions.

Photochemical reactions are complex and dependent on many variables in addition to the amount and structure of VOCs, especially the concentration of various nitrogen oxides. Some reactions that have been proposed to explain ozone generation are shown below.

$$\begin{aligned}
\mathrm{RH} + {}^{\bullet}\mathrm{OH} &\longrightarrow \mathrm{H_2O} + \mathrm{R}^{\bullet} \\
\mathrm{R}^{\bullet} + \mathrm{O_2} &\longrightarrow \mathrm{ROO}^{\bullet} \\
\mathrm{ROO}^{\bullet} + \mathrm{NO} &\longrightarrow \mathrm{RO}^{\bullet} + \mathrm{NO_2} \\
\mathrm{NO_2} + h\nu &\longrightarrow \mathrm{NO} + \mathrm{O} \\
\mathrm{O_2} + \mathrm{O} &\longrightarrow \mathrm{O_3}
\end{aligned}$$

Figure 2.1 Reactions proposed to explain ozone generation.

2.1.3.4 Additives

Additives are materials that are included in small quantities to modify some property of the coating. Some of the additives used in coatings are as follows [23]:

Driers catalyze the decomposition of peroxides and hydroperoxides formed by the action of atmospheric oxygen on binders like alkyd resins. This promotes the formation of radicals and polymerization of the binders is thus initiated and accelerated. **Anti-skinning agents** are mostly antioxidants that counteract the tendency of drier containing paints to form an insoluble surface skin on contact with atmospheric oxygen. In the film they promote uniform drying and thus hinder wrinkling. During film formation they evaporate together with the solvents and therefore do not extend drying time. **Curing agents** act as catalysts in chemically cross-linking binder systems. They allow stoving enamels to be cured in shorter times and/or at lower temperatures. **Levelling agents** promote the formation of smooth and uniform coating films from uneven patterned layers of wet paint. **Wetting, anti-floating and anti-flooding agents** maintain gloss, hiding power and uniformity of shade. **Dispersion agents** counteract the settling tendency of pigments. **Matting agents** are used to obtain flat layers with satin gloss.

2.1.4 Film Formation

Most coatings are liquids with a viscosity appropriate for the application method to be used, generally in the range 0.05 to 1 Pa·s at high shear rates [21]. After the application, the liquid is converted to a ‘dry’ that is solid film. During film formation process the coating is transformed to a film that adheres tightly to the surface. The quality of the dry coating depends on the composition of the coating, the nature and pretreatment of the substrate, and the processing conditions [23]. Four routes of film formation are implemented either alone or in combination:

a) Evaporation of organic solvents from polymer solutions or dispersions
b) Evaporation of water from polymer solutions or dispersions
c) Cooling of polymer melts
d) Reaction of low molecular weight substances and or polymers to form macromolecules by polymerization and cross-linking.

Physically drying systems use high molecular weight substances as binder to satisfy flexibility and durability requirements. The glass transition temperatures of these binders usually exceed 25 °C. They include cellulose esters, chlorinated rubber, vinyl resins, acrylics, styrene copolymers, polyesters, polyamides, and polyolefins. All physically dried coating films are sensitive to solvents that swell or dissolve them.

Chemically drying systems form films consisting of cross-linked macromolecules. The cross-linked films may swell in the presence of a solvent but cannot be dissolved. The film forming substances are mixtures of low molecular mass compounds. Due to their comparatively low viscosity, they normally need less solvent than physically drying systems. Three reactions are used for the curing of coating materials: chain polymerization, polycondensation, and polyaddition.

2.1.5 Properties of Coatings

The critical properties of most coating films relate their ability to withstand use without damage and form an opinion about ease of application appearance of films.

2.1.5.1 Rheology

Rheology is the science of flow and deformation. A liquid exerts resistance to flow called **viscosity**, η, defined as the ratio of *shear stress*, τ, to *shear rate*, γ^*. This type of viscosity is correctly called *simple shear viscosity*.

$$\eta \equiv \frac{\tau}{\dot{\gamma}} \tag{Eq. 1}$$

When the ratio of shear stress to shear rate is constant fluids are called **Newtonian** fluids. A plot of shear rate as a function of shear stress is linear (See Fig. 2.2). Some fluids are **non-Newtonian**. One class of non-Newtonian liquids exhibits decreasing viscosity as the shear rate increases; these are called **shear thinning** *(pseudoplastic)* fluids. In some cases no detectable flow occurs unless a minimum shear stress is exceeded. Such materials are called **Bingham plastics**. Another class of fluids exhibits increasing viscosity as the shear rate increases. Such fluids are called **shear thickening** *or* **dilatant** liquids.

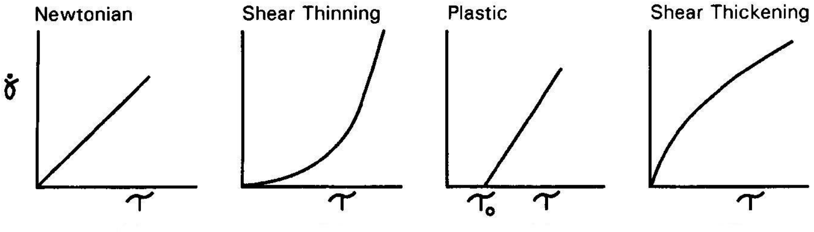


Figure 2.2 Schematic plots of flow of different types of liquids [21].

Some fluids show reversible time or shear history dependence of viscosity. When sheared at constant rate or stress the viscosity of a **thixotropic** liquid will decrease over a period of time, implying a progressive breakdown of structure. Thixotropic behavior is important in the coatings industry, where smooth and even application with brush or roller is required, but it is desirable for the coating on the surface to ‘set up’ to avoid drips and runs after application. The opposite sort of behavior is manifested by **rheopectic** liquids [25].

Paint brushability, leveling and sagging are highly dependent on viscosity. To evaluate the force required for brushing the viscosity should be measured at a high shear rate of about 10,000 s^{-1}. Sagging is the downward movement of a coating film that occurs between the time of application and setting. The viscosity should be measured at a shear rate of at most 1 s^{-1} in order to assess sagging on vertical walls. Levelling is the ability of a coating to flow out after application (e.g. to obliterate brush marks) [23].

A wide variety of instruments are used in measuring the viscosity of coatings. e.g. capillary viscometers, rheometers, rotating disk viscometers, bubble viscometers, efflux cups, and paddle viscometers.

2.1.5.2 Adhesion

Adhesion is an essential characteristic of most coatings. A distinction is often made between *mechanical* and *specific* adhesion. The former is supposed to arise by a purely mechanical entanglement of the film in microscopic irregularities on the surface of the substrate. Specific adhesion is seen as the result of chemical binding forces between the film and substrate. In one or two cases it may be that specific adhesion is the result of primary valencies, but, in general adhesion is a phenomenon which is attributable only to van der Waals forces and hydrogen bonds. Cleaning of the substrate frees the active centers on the surface from saturating impurities which prevent them from coming into intimate contact with the active groups in the coating. Mechanical cleaning of a surface makes it rough and increases surface area with the result that specific adhesion is increased owing to the increased number of active sites which are available [20]. Surface roughness can be a disadvantage. If the coating can not penetrate into the microscopic pores and crevices in the surface, dovetail effects are not realized and the actual, interfacial contact area can be smaller than the geometric area. Rate of penetration of coating is greatest if the surface tension of the coating is high. However, the rate is strongly affected by the contact angle. The rate is fastest when cosine of the contact angle is 1, that is when the contact angle is zero. The cosine can only be 1 if the surface tension of the liquid is less than the solid substrate (complete wetting of the substrate by the coating). The lower the viscosity of the continuous phase of a coating is the more rapid the penetration. Since viscosity of resins increase with molecular weight, lower molecular weight resins would provide a superior adhesion after crosslinking everything else being equal. Coatings with slow evaporating solvents and relatively low crosslinking rates in general give better adhesion.

The presence of polar groups in a binder improves its adhesion. Which polar groups are most effective in this respect, depends, however, on the chemical nature of the substrate at the time of application. Carboxyl group is effective in the majority of cases in increasing adhesion more or less independently of the nature of the substrate. The establishment of hydrogen bond also leads to good adhesion.

Internal stresses in coatings amount to forces that counteract adhesion. Internal stresses result from the inability of coatings to shrink as they form films on rigid substrates. When solvent evaporates T_g rises and free volume is reduced, it becomes more difficult for the polymer to accommodate the voids from the solvent evaporation, so it becomes fixed in unstable conformations, and internal stress (energy) increases. Stresses can also result from volume expansions. In thermosetting coatings, crosslinking reactions lead to formation of covalent bonds that are shorter than the distance between two molecules before they react. When such reactions occur near the T_g of the film, stresses result from the inability of the coating to undergo shrinkage. As the rate of cross-linking increases, stresses also tend to increase, since less time is available for polymer relaxation to occur.

2.1.5.3 Hardness

An important requirement is that a film of a coating, within a reasonable time of application, shall reach a degree of hardness, suited to the purpose which the object is to fulfill. Hardness is a property which is usually defined as the resistance to deformation caused by attempted penetration of another body.

Depending on the nature of the outer forces giving rise to deformation three types of hardness are defined [20].

Scratch hardness is represented by the force which must be applied to a hard or more or less pointed object in order that it shall cause a scratch in the film. **Indentation hardness** depends on measurement of depth of indentation by the use of micro-hardness testers. The indenter itself may take different forms, e.g. pyramid, cone, or a ball. **Pendulum hardness** is measured by means of a swinging pendulum with its fulcrum resting on the film. It depends on the fact that the film uses up energy transmitted to it by pendulum in the repeated compressions and recoveries which take place as the pendulum swings. As the pendulum loses kinetic energy in this way its amplitude of swing decreases. The softer the film the greater will be the deformations and the more the energy absorbed so that the damping of the pendulum swings will occur the more rapidly.

2.1.5.4 Abrasion Resistance

Abrasion is the wearing away of a substance. The assumption that hard materials are less likely to fail by abrasion than soft materials is true in some cases but in many other cases softer materials are more abrasion resistant. Energy to break values of films can be related to abrasion resistance of films. The coefficient of friction of the coating can be an important variable in abrasion resistance. As the energy to break values increase and coefficient of friction decreases abrasion resistance increases [21].

2.1.5.5 Formability and Flexibility

In many cases a coated metal object is subjected to mechanical forces either to make a product, as in forming bottle caps, or in use. To avoid film cracking during such distensions, the elongation at break must be greater than the extension of the film under the conditions of fabrication or distortion. Cross-linked coatings have low elongations-at-break when below T_g.

Properties are affected by the extent to which cross-linking has been carried to completion. If the cross-linking reaction was not complete, the reaction may continue decreasing flexibility. Another possible factor with baked films is densification. If a coating is heated above its T_g and then cooled rapidly, the density is commonly found to be lower than if the sample had been cooled slowly. During rapid cooling, more and/or larger free volume holes are frozen into the matrix. On storage, the molecules slowly move and free volume decreases, causing densification; it is also called physical aging.

2.1.5.6 Gloss

Gloss and gloss retention are properties which are of great importance for most surface coatings. This importance is not only confined to aesthetic considerations; in many cases technical considerations are of equal weight. For instance the property of a surface to collect dirt is to a large extent bound up with its gloss, being reduced by an increase in gloss. In judging the resistance of a film to the effects of destructive agents, loss of gloss is one of the most important criteria [20].

Gloss is a complex phenomenon associated with the physical nature of a surface and the way in which the nature of the surface affects the reflection of incident light. Two extreme cases of reflectivity of a surface may be distinguished, ideal mirror reflection, and an ideal diffuse or matt reflection. The perfect mirror surface is a plane surface reflecting all the incident light flux unidirectionally according to the angles of incidence. As primary surfaces for gloss standards, optically plane highly polished black glass surfaces are often used. They are ascribed an arbitrary value of 100 for all angles of incident and reflected light. From Fresnel’s formula it is clear that the amount of light reflected increases with increasing angle of incidence. Therefore, in the measurement of specular gloss 20° is recommended for glossy surfaces and 85° for matt surfaces. A perfectly matt surface is one which spreads the reflected light equally in all directions (See Fig. 2.3). Perfectly matt surfaces are extremely rare in practice. In almost all cases differences in brightness will be apparent if the surface is viewed from different directions. Such a surface having luster will show a greater intensity of reflected light in the direction of specular reflection.

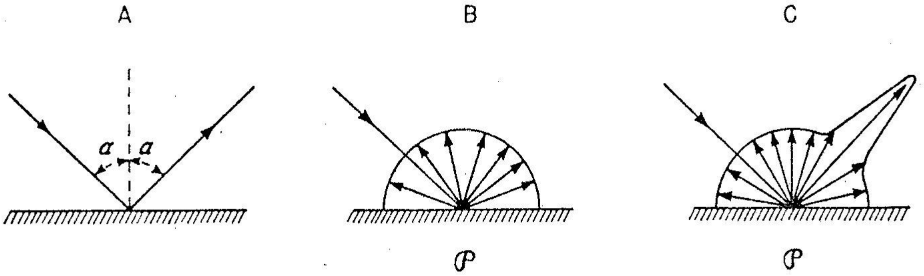
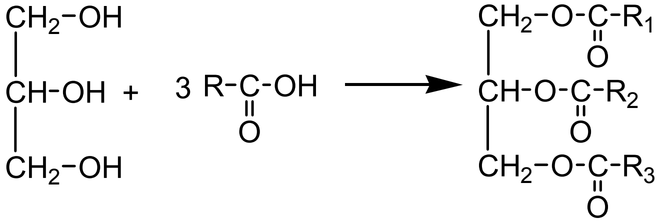


Figure 2.3 Three main types of reflection A: Ideal mirror reflection B: Ideal diffuse or matt reflection C: Sheen (luster) [20]

2.2 *Glyceride Oils*

Glyderide oils are naturally occurring vegetable and marine animal oils. They occur as triglycerides of long chain fatty acids and are the reaction products of one mole of glycerol with three moles of a fatty acid [26] (See Fig. 2.4).



$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array} + 3\ R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH \longrightarrow \begin{array}{l} CH_2\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}R_1 \\ | \\ CH\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}R_2 \\ | \\ CH_2\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}R_3 \end{array}$$

Figure 2.4 The reaction of glycerol with fatty acids to form glyceride oil.

This esterification reaction is carried out by enzymes in living organisms. In coatings industry the reverse of this reaction is employed to obtain fatty acids or monoglycerides [27]. Most importantly they are raw materials for binders such as alkyd resins, epoxy resins and uralkyds. The oils that are commercially important in organic coatings are listed in Table 2.1 [28].

Table 2.1 Commercially important glyceride oils

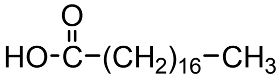
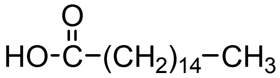
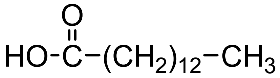
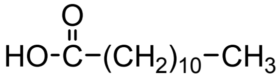
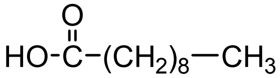
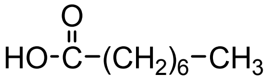
Group 1	**Group 2**
Linseed	Tung
Safflower	Oiticica
Soya	Castor
Tall oil acids	Dehydrated castor
Cottonseed	Fish
Coconut	

The grouping in Table 2.1 is based on composition and consequent properties. The chain length of fatty acid can vary from C_{12} to C_{22}, but C_{18} is the most common. The variations in properties, encountered with different oils, are a function of the variation in fatty acid structure. Although having the same general formula the fatty acids can vary considerably in terms of:

a) The degree of unsaturation (number of C=C bonds)
b) The relative positions of the double bonds (degree of conjugation)
c) The presence (or absence) of polar groups (such as OH or C=O) on the carbon backbone

As the degree of unsaturation increases oil becomes liquid, and as the degree of saturation increases oil becomes solid. Degree of unsaturation also determines the drying property of oils. As the degree of unsaturation increases, drying rate increases. Glyceride oils are generally classified as drying, semi drying and non drying. The oils in the second group contain one or more fatty acids that are not present in other oils. These distinctive fatty acids impart special properties to each oil. With the exception of castor oil, the oils in Group 2 contain a major or substantial proportion of conjugated fatty acids, which promote the fast drying. Saturated and unsaturated fatty acids found in glyceride oils are given in Table 2.2 and 2.3. Table 2.4 gives the fatty acid compositions and analytical constants of the oils.

Table 2.2 Saturated fatty acids commonly found in glyceride oils [27].

Acid	# of C atoms	Formula
Stearic	18	 $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_{16}-CH_3$
Palmitic	16	 $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_{14}-CH_3$
Myristic	14	 $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_{12}-CH_3$
Lauric	12	 $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}-CH_3$
Capric	10	 $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_8-CH_3$
Caprylic	8	 $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_6-CH_3$

2.2.1 Drying of Glyceride Oils

Glyceride oils are usually classified as drying, semi drying or non-drying. These divisions reflect the ability of the oil to ‘air dry’, i.e. to form a coherent film on exposure to atmosphere. This ability is directly related to the fatty acid composition. The speed with which air drying occurs is greater if the double bonds are conjugated. Drying oils will form a tack free film whereas semi drying films form films that are never tack free [26].

Table 2.3 Unsaturated fatty acids commonly found in glyceride oils [27]

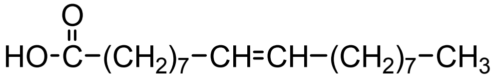
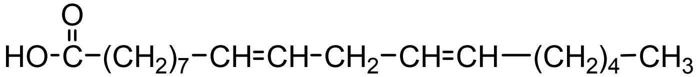
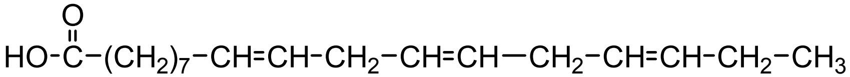
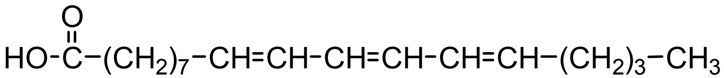
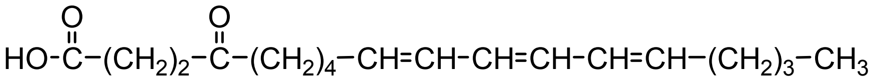
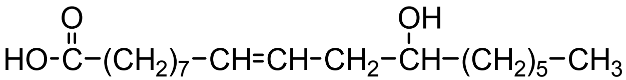
Group 1	**# of C atoms**	**Double bonds**	**Formula**
Oleic	18	1	 $HO{-}\overset{O}{\overset{\parallel}{C}}{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}CH_3$
Linoleic	18	2	 $HO{-}\overset{O}{\overset{\parallel}{C}}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_4{-}CH_3$
Linolenic	18	3	 $HO{-}\overset{O}{\overset{\parallel}{C}}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3$
Group 2			
Eleostearic (Tung oil)	18	3	 $HO{-}\overset{O}{\overset{\parallel}{C}}{-}(CH_2)_7{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_3{-}CH_3$
Licanic (Oiticica oil)	18	3	 $HO{-}\overset{O}{\overset{\parallel}{C}}{-}(CH_2)_2{-}\overset{O}{\overset{\parallel}{C}}{-}(CH_2)_4{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_3{-}CH_3$
Ricinoleic (Castor oil)	18	1	 $HO{-}\overset{O}{\overset{\parallel}{C}}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}\overset{OH}{\overset{\vert}{C}}H{-}(CH_2)_5{-}CH_3$

Table 2.4 Fatty acid compositions and analytical constants of the oils [26]

Fatty Acids		Unsaturation	Coconut Oil	Castor Oil	Grape Seed Oil	Linseed Oil	Oiticica Oil	Palm Oil	Palm Kernal Oil	Safflower Oil	Sunflower Oil	Soya Bean Oil	Tung Oil	Tall Oil*	Dehydrated Castor Oil*
8 Caprylic	$C_8H_{16}O_2$		6						3						
10 Capric	$C_{10}H_{20}O_2$		6				Contains 4% hydroxy acids		4						
12 Lauric	$C_{12}H_{22}O_2$		44						51						
14 Myrtstic	$C_{14}H_{28}O_2$		18					1	17						
16 Palmitic	$C_{16}H_{32}O_2$		11	2	9	6	7	48	8	8	11	11	4	5	
18 Stearic	$C_{18}H_{36}O_2$		6	1	4	4	5	4	2	3	6	4	1	2	
Oleic	$C_{18}H_{34}O_2$	(—2H)	7	7	20	22	6	38	13	13	29	25	8	48	9
Ricinoleic	$C_{18}H_{34}O_2$	(—2H)		87											8
Linoleic	$C_{18}H_{34}O_2$	(—4H)	2	3	67	16		9	2	75	52	51	4	45	83
Linolenic	$C_{18}H_{30}O_2$	(—6H)				52				1	2	9	3		
Eleostearic	$C_{18}H_{30}O_2$	(—6H)											80		
Licanic	$C_{18}H_{28}O_2$	(—6H)					78								
Approximate analytic constants															
Iodine Value			7.5–10.5	81–91	130–140	155–205	140–160	44–54	14–23	140–150	125–136	120–141	160–175	130–138	145–155
Saponification Value			250–264	176–187	185–195	188–196	186–193	195–205	245–255	188–194	188–194	185–195	189–195	192–194	200–204
Melting Point °C			23–26					27–50	24–26						
Titre °C			20–24		–17	19–21	42–47	40–47	20–28	15–18	16–20	20–21	36–37		
Uses			Short Oil non-drying Alkyd resins Epoxy resins	Plasticiser in ink systems Plasticising alkyds	Alkyd resins	Oleo-resinous varnish Long oil alkyd	Oleoresin varnish Alkyd resins	Short oil non-drying Alkyd resins		Alkyd resins	Alkyd resins	Alkyd resins	Oleo-resinous varnish Alkyd resins	Alkyd resins	Alkyd resins

**Typical tall oil fatty acids (2% rosin) and dehydrated castor oil shown for completeness*

Air drying ability is quantified by the *drying index,*

$$\text{Drying Index} = (\%\ \text{linoleic acid} + 2 \times \%\ \text{linolenic acid}) \qquad \text{(Eq. 2)}$$

A drying index of greater than 70 indicates a drying oil. Iodine value, which gives the amount of iodine needed to react with double bonds of the oil, is also used in predicting the drying nature of the oil. An iodine value of about 160 would normally indicate a drying oil [27].

In general, conjugated and non-conjugated systems dry by cross-linking. The simplest approach is to postulate oxygen attack at the site of the activated methylene which is alpha to the C=C bond. This gives rise to hydroperoxide formation which subsequently breaks down with the formation of a link to a neighboring fatty acid chain. The process somewhat differs for conjugated and non-conjugated systems.

Non-conjugated systems

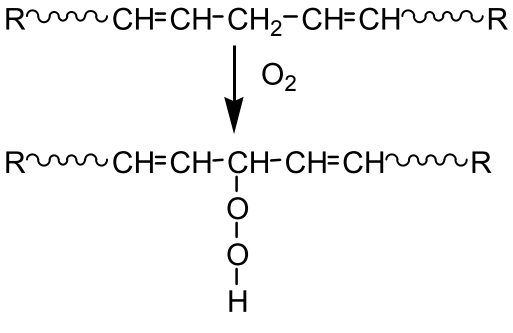


Figure 2.5 Hydroperoxide formation.

The hydroperoxide then decomposes by the dissociation of the O–O bond, leading to a variety of products including intermolecular linkage as can be seen in Figure 6.

$$\mathrm{R\text{-}OOH} \longrightarrow \mathrm{RO^{\bullet}} + \mathrm{{}^{\bullet}OH}$$

$$2\ \mathrm{R\text{-}OOH} \longrightarrow \mathrm{RO^{\bullet}} + \mathrm{ROO^{\bullet}} + \mathrm{H_2O}$$

$$\mathrm{RO^{\bullet}} + \mathrm{R_1} \longrightarrow \mathrm{ROH} + \mathrm{{}^{\bullet}R_1}$$

$$\mathrm{R^{\bullet}} + \mathrm{R^{\bullet}} \longrightarrow \mathrm{R\text{-}R}$$

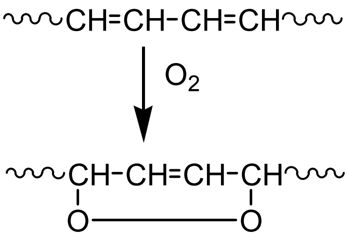
$$\mathrm{RO^{\bullet}} + \mathrm{R^{\bullet}} \longrightarrow \mathrm{R\text{-}O\text{-}R}$$

$$\mathrm{RO^{\bullet}} + \mathrm{RO^{\bullet}} \longrightarrow \mathrm{R\text{-}O\text{-}O\text{-}R}$$

Figure 2.6 Decomposition of hydroperoxides and possible intermolecular linkage reactions.

Conjugated Systems

The reaction of the oil with oxygen is given in Figure 2.7.



$$\sim\!\mathrm{CH{=}CH{-}CH{=}CH}\!\sim \xrightarrow{O_2} \sim\!\mathrm{CH(O{-})\text{-}CH{=}CH\text{-}CH(O{-})}\!\sim$$

Figure 2.7 Reaction of oxygen with the oil having conjugated fatty acid.

The film formed differs from that formed by a non-conjugated structure in that the linkages are predominantly C–C suggesting a vinyl polymerization mechanism (See Fig. 2.8).

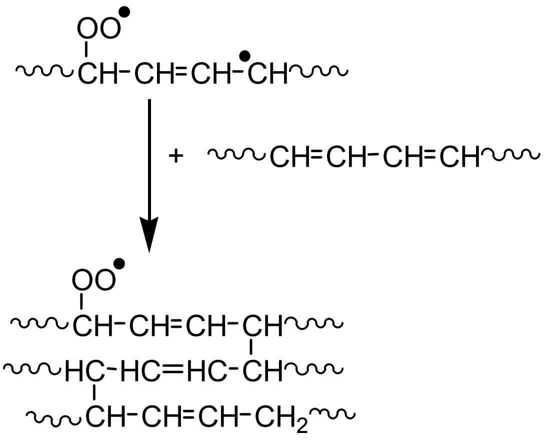


Figure 2.8 Formation of crosslinks in conjugated systems

In practice the length of the polymerization chain is short because the probability of chain termination by oxygen is high. A crosslinked film may be represented schematically as in Figure 2.9 where FA represents fatty acid.

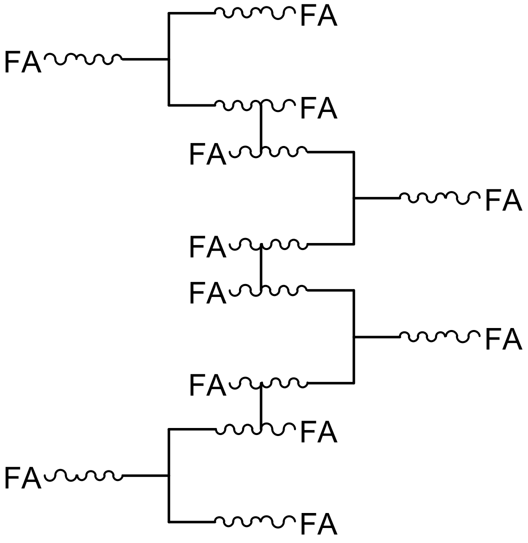


Figure 2.9 Schematic representation of the crosslinked film.

2.2.2 Driers

Driers are used in some types of organic coatings to accelerate the conversion of the liquid coating to the dry film. They are heavy metal soaps of organic acids. The early driers were lead, cobalt, and manganese soaps of linseed fatty acids and rosin acids; these are known as linoleate driers and resinate driers respectively [29]. It is extremely important that driers maintain good solubility and stability in solution and in combination with various organic coatings. Since linoleate, rosinate, and tallate driers are made of oxidizable acids they show some tendency to change on aging. The naphthenate and octoate driers are made from saturated organic acids which are non-oxidizing, therefore they are more stable. Naphthenates are made from naphthenic acids obtained as a by product in petroleum refining. They contain very small amount of color bodies, and they have a somewhat objectionable odor. Both features are eliminated by using octoates which are made of octoic acid. But it is more expensive than naphthenic acid.

Manganese and Cobalt promote the rapid surface drying of the film. They are normally employed in amounts varying from 0.005 to 0.1 % **metal** (percentage of metal in driers varies for each drier metal). An excess of cobalt and manganese driers may produce a wrinkled finish particularly if the film is slightly thicker than normal. Zinc, calcium, or barium do not have direct effect on the oxidation alone but they act as synergists, and considerably increase the rate of oxygen uptake of the oil. Zirconium and lead are through driers and catalyze drying throughout the film. The amounts of driers should be kept to the minimum possible level, since they not only catalyze drying but also catalyze the reactions that cause postdrying embrittlement, discoloration and cleavage.

2.3 Alkyd Resins

Alkyd resins were first synthesized by Kienle and the name alkyd was coined to express the fact that these resins are products of an al–cohol and an a–

cid, the ‘cid’ being altered to ‘kyd’ to indicate the pronunciation and to avoid too close a similarity to the word acid in print [20]. Alkyd resins first came out in 1920s but found wide use after the Second World War [27]. They were the largest volume resins produced for many years. While no longer the largest volume binders in coatings, alkyd resins still are of major importance [21]. The reasons for this popularity are; excellent surface appearance, cost, and versatility.

Alkyd resins are relatively inexpensive in terms of raw material and manufacturing costs and since they are readily soluble in the less expensive solvents [26]. Whilst other polymer types may offer improved properties in specific areas, alkyd resins have the widest spectrum of acceptable properties in terms of surface coating usage. They are easy to pigment and are compatible with most substances used in surface coatings e.g. nitrocellulose, polyurethanes, amino resins, phenolics. In addition they are tolerant of most substrates and are easily modified for specialist applications. Alkyd resins find applications in:

- Printing inks
- Decorative paints
- Air drying and stoving industrial paints
- Metal decorating coatings, also a variety of other areas including water soluble and electrodeposition systems

Alkyd resins are essentially short branched polyester chains, formed by the polycondensation of a di-basic acid and a polyhydric alcohol in the presence of a glyceride oil or oil derived fatty acid. The presence of oil confers to good pigment wetting properties and when unsaturated, allows coherent films to be formed on cure. The polyester chain confers hardness and durability to the film and improved drying speed. The presence of oil also adversely affects color and gloss retention, whilst the nature of the ester linked chain means that the film can be attacked by strong alkalis and acids.

2.3.1 Techniques Used in Alkyd Manufacture

2.3.1.1 Alcoholysis of the Oil (Monoglyceride Technique)

In this technique the oil is pre-reacted with a polyol, to give a product capable of taking part in the polycondensation reaction. During alcoholysis ester interchange is brought about between the polyol and oil. The triglyceride oil is converted into reactive monoglyceride. The idealized equation in Figure 2.10 shows the reaction between an oil and glycerol.

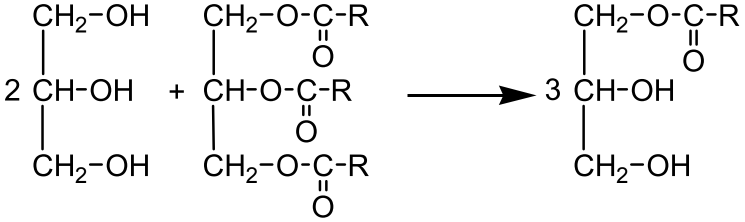


Figure 2.10 Alcoholysis reaction

Alcoholysis requires temperatures of 240 °C–260 °C and ester interchange is greatly speeded up by the use of basic catalysts. Lithium or sodium hydroxide, 0.01-0.03 % w/w on the oil charge is used as catalyst. The reaction is normally carried out under a slightly positive inert gas pressure to prevent ingress of air, which would otherwise result in discoloration of the product.

2.3.1.2 *Acidolysis of the Oil*

In this technique oil is pre reacted with the fatty acid (See Fig. 2.11).

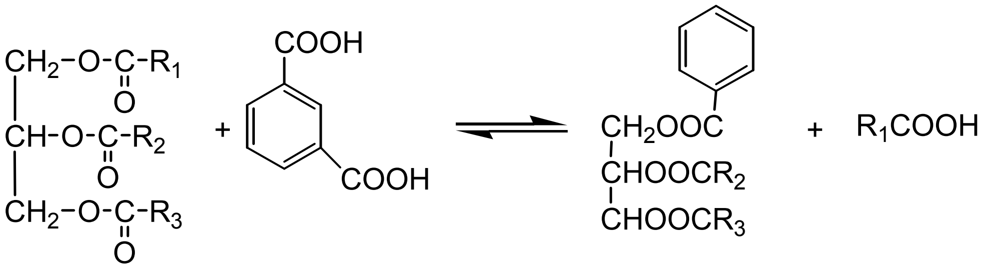


Figure 2.11 Acidolysis reaction

Temperatures of above 260 °C are required for acidolysis and although tin catalysts may be used to speed up the reaction rate, the process takes longer than that for alcoholysis. As a result of the higher temperature and longer process time there is more risk of color deterioration and polymerization of the oil. Acidolysis is normally used, only where there are problems associated with the solubility or reactivity of the dicarboxylic acid which may be overcome by prereaction with the oil.

2.3.1.3 *The Fatty Acid Process*

This technique employs fatty acids derived from oils rather than the oils themselves. The carboxylic group on the fatty acid is able to react directly with the polyol. Thus, the fatty acid, the polyol, and the di-acid can be charged to the reactor and polycondensation brought about without the need for alcoholysis or acidolysis. Although fatty acids are more expensive than oils, the shorter process times conferred by the fatty acid process are attractive.

There are some advantages and disadvantages of using the fatty acids as opposed to oils:

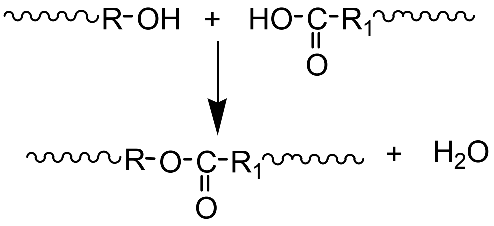
Advantages

- Lighter colored products
- Shorter process time
- Synthetic fatty acids not normally obtained as glyceride oils can be employed.
- Freedom of choice of polyol. When an oil is used in alkyd resin, part of the overall polyol content is provided by the glycerol from the oil.

Disadvantages

- More expensive raw material cost
- Separation of the more saturated components of the fatty acids can occur.

The polycondensation reaction consists of a series of simple esterification reactions. A hydroxyl group reacts with a carboxyl group to form an ester link with the elimination of a molecule of water as illustrated in Figure 2.12.



$$\sim R{-}OH + HO{-}\underset{\underset{O}{\|}}{C}{-}R_1\sim \longrightarrow \sim R{-}O{-}\underset{\underset{O}{\|}}{C}{-}R_1\sim + H_2O$$

Figure 2.12 Esterification reaction

2.3.2 Classification of Alkyd Resins

Alkyd Resins are characterized in terms of oil length and oil type.

2.3.2.1 Oil Length

This is the amount of oil (or fatty acid expressed as triglyceride oil) present as a percentage of the total non-volatile content. Although it does little to describe the complex polymer system which is modern alkyd, it is universally used throughout the surface coating industry and as such is a convenient method of classification. Alkyds can be classified as;

- Long oil – oil content greater than 55 % w/w
- Medium oil – oil content 45 – 55 % w/w
- Short oil – oil content less than 45 % w/w

Oil length can be calculated by the following formulas [21]:

$$\text{Oil Length} = \frac{\text{Weight of oil}}{\text{Weight of alkyd - Water evolved}} \times 100 \qquad \text{(Eq. 3)}$$

$$\text{Oil Length} = \frac{1.04 \times \text{Weight of fatty acids}}{\text{Weight of alkyd - Water evolved}} \times 100 \qquad \text{(Eq. 4)}$$

2.3.2.2 Oil Type

Alkyds can be further classified by oil type as follows:

An **oxidizing alkyd** contains drying or semi drying oils or fatty acids, and is able to film form by oxidation. This type of alkyd usually has an oil length in excess of 45 %.

A **non-oxidizing** alkyd contains non-drying oils or fatty acids and is not capable of coherent film formation by oxidation. They are reacted with other polymer types to produce cured films. Non oxidizing alkyds have oil lengths usually below 45 %.

2.4 Dendritic Polymers

Dendritic polymers are highly branched globular macromolecules which can be subdivided into the three different categories, namely dendrimers, dendrigrafts, and hyperbranched polymers. The term '*dendrimer*' is derived from the Greek words dendron (tree) and meros (part). The dendritic topology has now been recognized as a fourth major class of macromolecular architecture [13, 14] (See Fig. 2.13). Dendrimers are highly uniform, three-dimensional, monodisperse polymers (M_w/M_n = 1.01 – 1.0001 and less) with a tree-like, globular structure. A dendrimer is a symmetrical, layered macromolecule that consists of three distinct areas: the polyfunctional central core or focal point, which represents the center of symmetry, various well-defined, radial-symmetrical layers of repeating units (so-called generations, G), and the end groups, which are also termed peripheral or terminal groups. Hyperbranched polymers represent another class of highly branched macromolecules which –unlike dendrimers– exhibit polydispersity (M_w/M_n = 2-10) and irregularity in terms of branching and structure. Schematic representations of hyperbranched polymers and dendrimers are given in Figure 2.14. Dendrigraft polymers reside between these two extremes of structural control, frequently manifesting rather narrow polydispersities (M_w/M_n = 1.1-1.5) depending on their mode of preparation. The progress in designing and synthesizing dendritic polymers having unique and different properties compared to their linear analogues, enables an unpredictable interdisciplinary variety of applications [13, 14, 30].

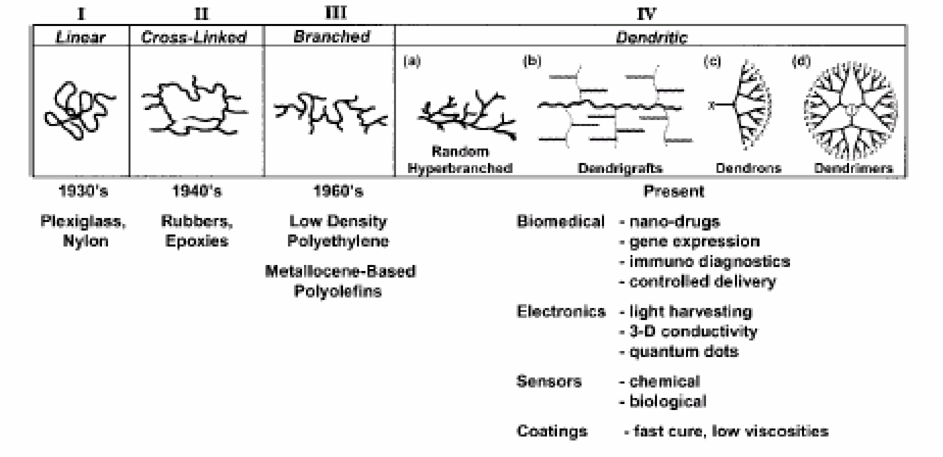
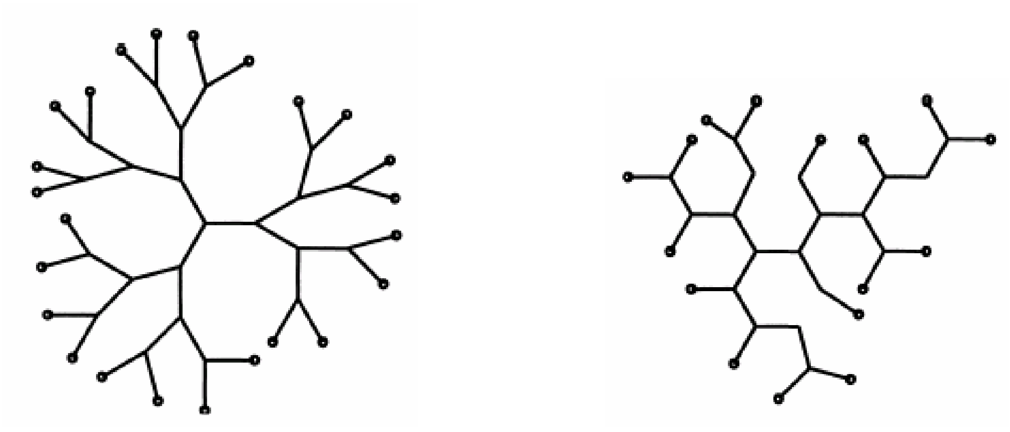


Figure 2.13 Polymeric architectures [13]



(a) (b)

Figure 2.14 Schematic representation of dendritic and hyperbranched polymers [36]

2.4.1 Synthesis of Dendritic Polymers

It was Paul Flory, in 1952, who first presumed the synthesis of branched condensation polymers from multifunctional monomers. But since he expected non-entangled, highly branched condensation polymers having a broad molecular weight distribution and therefore poor mechanical properties, he did not pursue this theoretical approach further. At the end of the 1970s, Vogtle and co-workers described the first cascade synthesis of dendrimers which was followed by the fundamental, pioneering synthetic methodology of Tomalia et al. for starburst dendrimers and Newkome et al. for cascade molecules. The latter methodology for the synthesis of dendrimers came to be known as the divergent growth approach (See Fig. 2.15). In 1989 Frechet et al. introduced an alternative synthetic strategy for the construction of dendritic macromolecules, the so-called convergent growth approach (See Fig. 2.16). Since then, many scientists have focused their attention on the synthesis of new dendrimers, fascinated by their unique structural features and potential applications [9 – 16, 30-38].

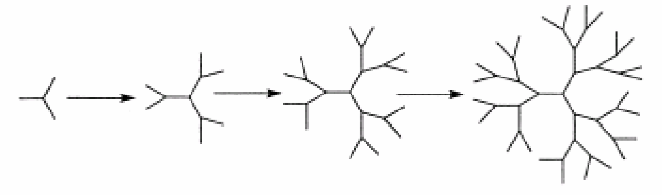


Figure 2.15 Representation of the divergent synthesis [36]

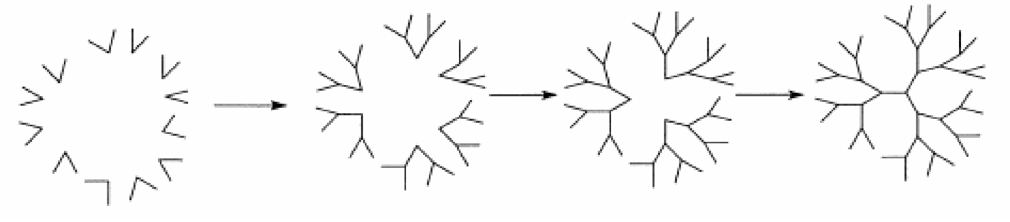


Figure 2.16 Representation of the convergent synthesis [36]

2.4.2 Hyperbranched Polymers

Highly branched polymers have so far mainly been used as oligomers in thermosets for high solids coating binders, alkyds, and in resins for composites. The most widely used of these is probably etherified hexamethylol melamine. The initial work on dendritic polymers focused on the preparation of perfect monodisperse dendrimers. These well-defined macromolecules have very interesting material properties, but the synthesis is often time-consuming and elaborate. For use as engineering materials they are far too complicated and costly to produce. In the early 1990s Kim and Webster were working on dendritic polymers as rheology control agents and as spherical multifunctional initiators. It was necessary to obtain the material rapidly and in large quantities. This forced them to develop a route for a one-step synthesis of dendritic polyphenylenes. These polymers were polydisperse, and had defects in the form of built-in linear segments but they were highly branched dendritic molecules. Kim and Webster named them *Hyperbranched Polymers* [10, 14-16, 30, 38]. The synthesis of hyperbranched polymers can often be simplified compared to that of dendrimers as it does not require the use of protection/deprotection steps. This is due to the fact that hyperbranched polymers are allowed to contain some linearly incorporated AB_x monomers. The most common synthesis route follows a one-pot procedure where AB_x monomers are condensed in the presence of a catalyst. Another method using a core molecule and an AB_x monomer has also been described. The lower cost of synthesizing hyperbranched polymers allows them to be produced on a large scale, giving them an advantage over dendrimers in applications involving large amounts of material, although the properties of hyperbranched polymers are intermediate between those of dendrimers and linear polymers [5, 10, 17].

Due to their highly branched, nanoscopic structure, their cavernous interiors, their large numbers of peripheral end groups and thus their unusual physical and chemical properties, a wide variety of applications of dendritic polymers was discussed and partially realized.

2.4.3 Properties of Dendritic Polymers

The urge of polymer scientists to develop new materials is driven by society's wish to substitute conventional materials by plastics and thereby gain in performance. One reason for the emerging interest in hyperbranched polymers and other macromolecular architectures is their different properties compared to conventional, linear polymers. Already Flory predicted that the number of entanglements would be lower for polymers based on AB_x monomers, with subsequent reduction in mechanical strength.

2.4.3.1 Solution Behavior

One of the first properties of dendritic polymers reported to differ from the linear analogues is the high solubility which depends to a large extent on the structure of the terminal groups. Not only good solubility but also solution behavior differs for dendritic polymers compared to linear polymers. They exhibit a very low α value in the Mark-Hauwink-Sakurada Equation and low intrinsic viscosities. This is consistent with highly branched, compact, globular non-entangled structures [10, 14, 30, 32] (See Fig. 2.17).

Another special feature of dendritic polymers is the possibility to combine an interior structure with one polarity, with terminal groups having another functionality, for instance a hydrophobic inner structure and a hydrophilic terminal (end) groups. The size of dendritic polymers in solution is greatly affected by the solution parameters such as polarity and pH.

The dilution properties of hyperbranched polymers also differ from those of linear polymers. In a comparison with two alkyd resin systems where one was a conventional high solid alkyd and the other based on a hyperbranched aliphatic polyester, the conventional high solid alkyd was seen to exhibit a higher viscosity. A more rapid decrease in viscosity with solvent content was noted for the hyperbranched alkyd when the polymers were diluted [10].

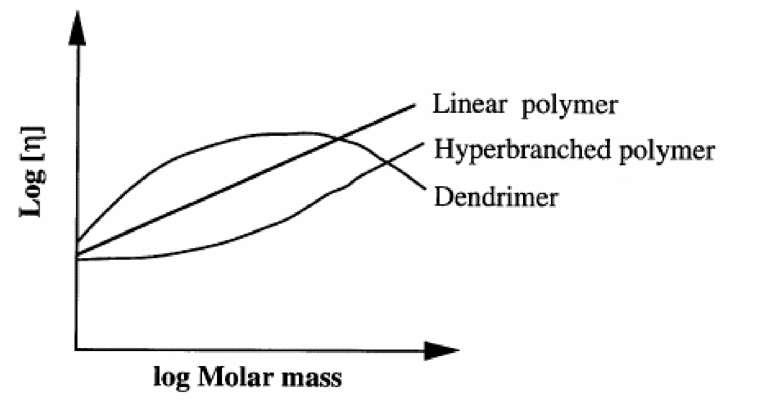


Figure 2.17 Comparison of the intrinsic viscosity vs. molar mass for linear, hyperbranched, and dendrimeric polymers on log–log scale (schematic) [10]

2.4.3.2 Thermal Properties

Since hyperbranched polymers are almost exclusively amorphous materials, the glass transition temperature is one of the most important features. The classical visualization of T_g is related to relatively large segmental motions in the polymer chain segments and the fact that the role of the end groups diminishes over a certain molecular weight. This is more difficult to conceive for dendritic polymers since segmental motions are affected by the branching points and the presence of numerous end groups. It has instead been proposed that the glass transition for hyperbranched polymers is a translational movement of the entire molecule instead of a segmental movement. Chemical nature also affects the T_g, for instance aliphatic polyester generally has a much lower T_g than an aromatic one. Several other factors such as degree of branching, steric interactions, backbone rigidity and polarity also play an important role for the T_g. The thermal stability of dendritic polymers is related to the chemical structure in the same manner as for linear polymers [10, 14, 30].

2.4.3.3 The Mechanical and Rheological Properties

A material must possess both suitable material and processing properties in order to find an appropriate use. The rheological properties of dendritic polymers are characterized by a Newtonian behavior in the molten state i.e. no shear thinning or thickening is observed indicating a lack of entanglements for these polymers. The non entangled state imposes rather poor mechanical properties resulting in brittle polymers. The large amount of branching also makes most of these polymers amorphous although exceptions exist. Hence, these materials are suitable as additives or thermosets when high mechanical strength is required for a certain application. The melt behavior has been shown to be greatly affected by the structure of the end groups where an increase in the polarity of the end groups can raise the viscosity by several orders of magnitude [10]. This is of great importance where low viscosity is essential for the processing of the material. Another very special feature of the dendritic polymers is the relationship between the molecular weight and melt viscosity. Increase in viscosity follows a different curve compared to linear polymers, it is less pronounced and levels off at higher molecular weights [10, 30].

2.4.4 Applications of Dendritic Polymers

The use of dendrimers is limited to speciality applications such as medicine because of their time consuming and expensive ways of synthesis which prevents large scale production. Hyperbranched polymers on the other hand have found important applications in industry owing to relatively easier production [10, 15, 30, 31]. Some applications of dendritic polymers are given below and some applications of hyperbranched polymers in Figure 2.18.

- surface modification of metals in order to passivate and block electrochemical reactions (in thin layers)
- rheology modifiers (low melt viscosity)
- tougheners in epoxy resins without compromising from other mechanical properties such as modulus
- Controlled drug release applications
- Non-linear optics applications

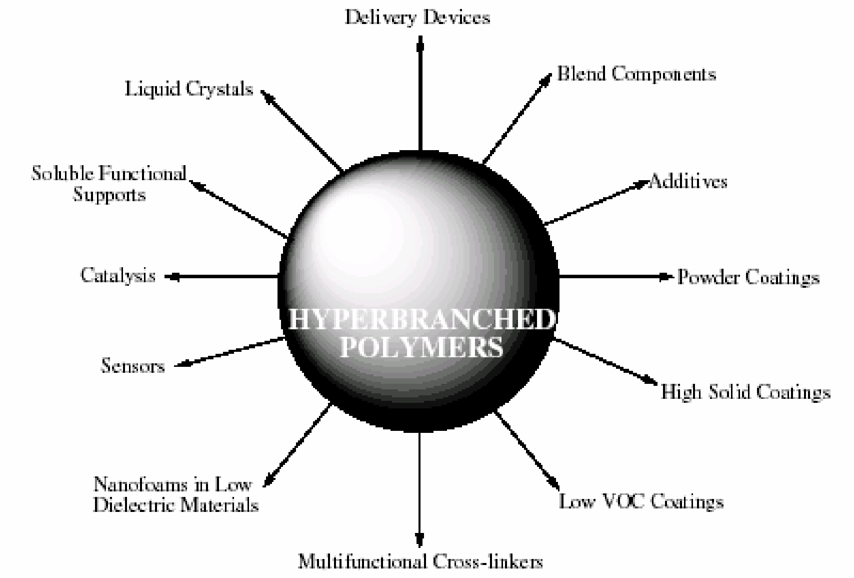


Figure 2.18 Applications of hyperbranched polymers [31]

2.4.5 Applications of Hyperbranched Polymers in Coatings

Thermosets is a potential area of interest for the applications of hyperbranched polymers. Their relatively low melt and solution viscosity can improve the processing properties and allow high solids formulations while extensive crosslinking can result in sufficient material strength. All or a fraction of the end groups can be functionalized with reactive groups, resulting in a crosslinkable polymer. The remaining functional end groups are accessible for further modifications. This implies the possibility to tailor the properties of the final network by two different routes, by changing either the crosslink density or the chemical structure of the nonreactive end groups.

Hult et. al. [40] were among the first to use dendritic polymers for thermoset applications. They modified hyperbranched hydroxy functional polyesters with various ratios of maleate allyl ether/alkyl ester end groups. Depending on this ratio, resins with different viscosities and different curing rates were obtained. Pettersson [19] has described a number of thermoset resin structures based on hyperbranched aliphatic polyesters. A comparative study was performed between an alkyd resin based on a hyperbranched aliphatic polyester and a conventional high solid alkyd which is a less branched alkyd. The hyperbranched resin had a substantially lower viscosity than the conventional resin that is less solvent was needed to obtain a suitable application viscosity. The hyperbranched resin also exhibited much shorter drying times. Manczyk et. al. [3] has also studied high solids alkyd resins based on highly branched structures. Hyperbranched, star like and conventional resins were synthesized and the properties were compared. Hyperbranched and star-like resins showed low viscosity, rapid drying but lower elasticity and lower hardness. Johansson et. al. [5] synthesized hyperbranched polyesters having hydroxyl end groups. They modified the end groups with different groups such as fatty acids, acrylate, maleate to obtain different types of resins such as alkyd, powder coating, UV curable resin. van Benthem [18] presented hyperbranched polyesteramides derived from cyclic carboxylic anhydrides and dialkanolamines. The hyperbranched resins were applied as powder coatings binder components. Hyperbranched polyurethanes were synthesized by Bruchmann et. al. [41] The hyperbranched polymers had either hydroxyl or isocyanate end groups. The products were tested as crosslinkers in two component coating formulations where they displayed better hardness than any other isocyanate raw material. Lange et. al. [42] presented use of acrylated and metacrylated hyperbranched polymers as barrier coatings for flexible packaging. The coatings were applied on PP and PET substrates and crosslinked by UV light. Their barrier against oxygen and water vapor were determined. The hyperbranched coatings gave a pronounced improvement in oxygen barrier on both substrates. However none of the resins improved water vapor barrier. Several works have been published on UV or EB-curable acrylic modified polyester, polyurethane, and polyamine esters [6, 43-52].

CHAPTER 3

EXPERIMENTAL

3.1 Raw Materials

1. Refined linseed oil (Betek Boya)
2. Castor oil (Akzo Nobel Kemipol)
3. Sodium hydroxide (NaOH), (Merck A. G.)
4. Sodium chloride (NaCl), (Technical Grade)
5. Sulfuric acid (95-98 %), (H_2SO_4), (Aldrich)
6. Magnesium sulfate hepta hydrate ($MgSO_4 \cdot 7H_2O$) (Technical Grade)
7. Ethyl alcohol (Technical grade)
8. Dimethylol propionic acid (DMPA), (Perstorp AB, Sweden)
9. Dipentaerythritol (Dipenrta), (Perstorp AB, Sweden)
10. Para-toluene sulfonic acid (p-TSA), (Merck A. G.)
11. Toluene (Best Kimya)
12. Isopropyl alcohol (Volkan Boya)
13. Potassium hydrogen phthalate (KHP) (Merck A. G.)
14. Cobalt naphthenate (Volkan Boya)
15. Lead Naphthenate (Volkan Boya)
16. Nitrogen gas (Oksan)

3.1.1 Dehydration of Raw Materials

Magnesium sulfate heptahydrate was ground and then dried in an oven at 120 °C for 2-4 hours and p-toluene sulfonic acid was dried for 1-2 hours at 85 °C up to a constant weight.

3.2 Production of Fatty Acids

The fatty acids of linseed oil and castor oil were produced first to be used as reactants in hyperbranched resin synthesis. The same procedure was followed for both oils. Firstly, the oils were saponified with sodium hydroxide. Stoichiometric amount of sodium hydroxide was dissolved 1:1 ethanol-distilled water solution (at least equivolumetric amount with the oil). The amount of NaOH needed was determined by the saponification value. Oil, NaOH, and ethanol-water mixture were placed in a reactor equipped with a mechanical stirrer. The mixture was left to react under reflux at 80 °C until a homogeneous mixture was obtained. The homogeneous mixture was then poured into a saturated NaCl solution in order to separate organic and inorganic phases. The soap rests on top of the solution. This two phase mixture was filtered through a filter paper under vacuum. Hence, most of the glycerol remained in the soap was removed. The soap was dissolved in distilled water in a beaker and then taken into a separatory funnel. The solution was reacted with stoichiometric amount (Figures 3.1 and 3.2) of sulfuric acid (app. 15–20 %) at room temperature. After the reaction, produced fatty acids (top layer) were separated by using the separatory funnel. The acids were washed with water several times to remove any remaining glycerol and other water soluble impurities. The obtained fatty acids were centrifuged to separate water and saturated fatty acids. Dried and ground $MgSO_4$ was added to further remove water and to settle suspended saturated fatty acids. The saponification occurs as follows:

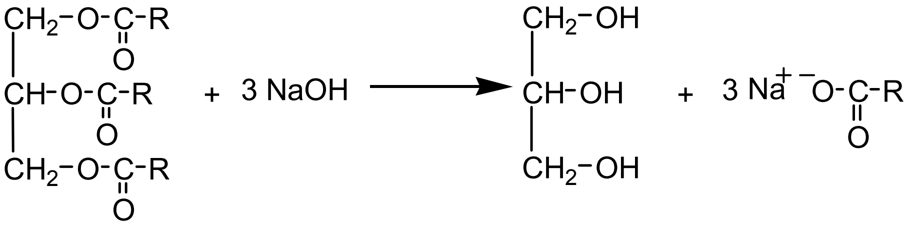
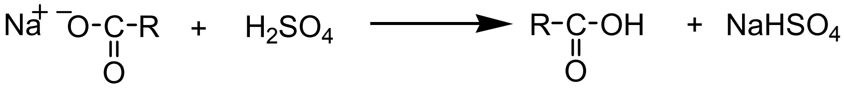


Figure 3.1 Saponification of the oil

The fatty acid is produced from the soap by the following reaction.



$$Na^{+}\,{}^{-}O-\underset{\underset{O}{\|}}{C}-R \;+\; H_2SO_4 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH \;+\; NaHSO_4$$

Figure 3.2 The reaction between the sulfuric acid and soap

3.3 Synthesis of the Hyperbranched Resin

At first a hyperbranched polyester (HBP) was synthesized in order to be used in the synthesis of the resins. A five necked flask equipped with a mechanical stirrer was used as reactor (Figure 3.4). Synthesis procedure of HBP from trimethylol propane and DMPA given in the literature was applied [53]. The synthesis of the HBP was achieved through a pseudo-one step procedure. This procedure was applied in order to obtain narrower molecular weight distribution [54, 55]. Dipentaerythritol was used as the core molecule and DMPA as chain extender. Both were fed to the reactor, in an amount corresponding to a perfect one generation. P-TSA was used as catalyst (0.4 % of DMPA fed). The reactor was immersed in an oil bath and reaction was carried out at 140 °C, under nitrogen atmosphere. The condensation product, water, was removed by nitrogen and azeotropic distillation with toluene. After the completion of the synthesis DMPA was added in an amount corresponding to second generation together with p-TSA. By the end of the reaction hyperbranched polyester is produced. The reaction scheme of the synthesis of the HBP is given in Figure 3.3. The HBP was then reacted with the castor FA which is mainly composed of ricinoleic, linoleic, and oleic acids at 220 °C. The acid value of the resin was determined in order to monitor the extent of the reaction.

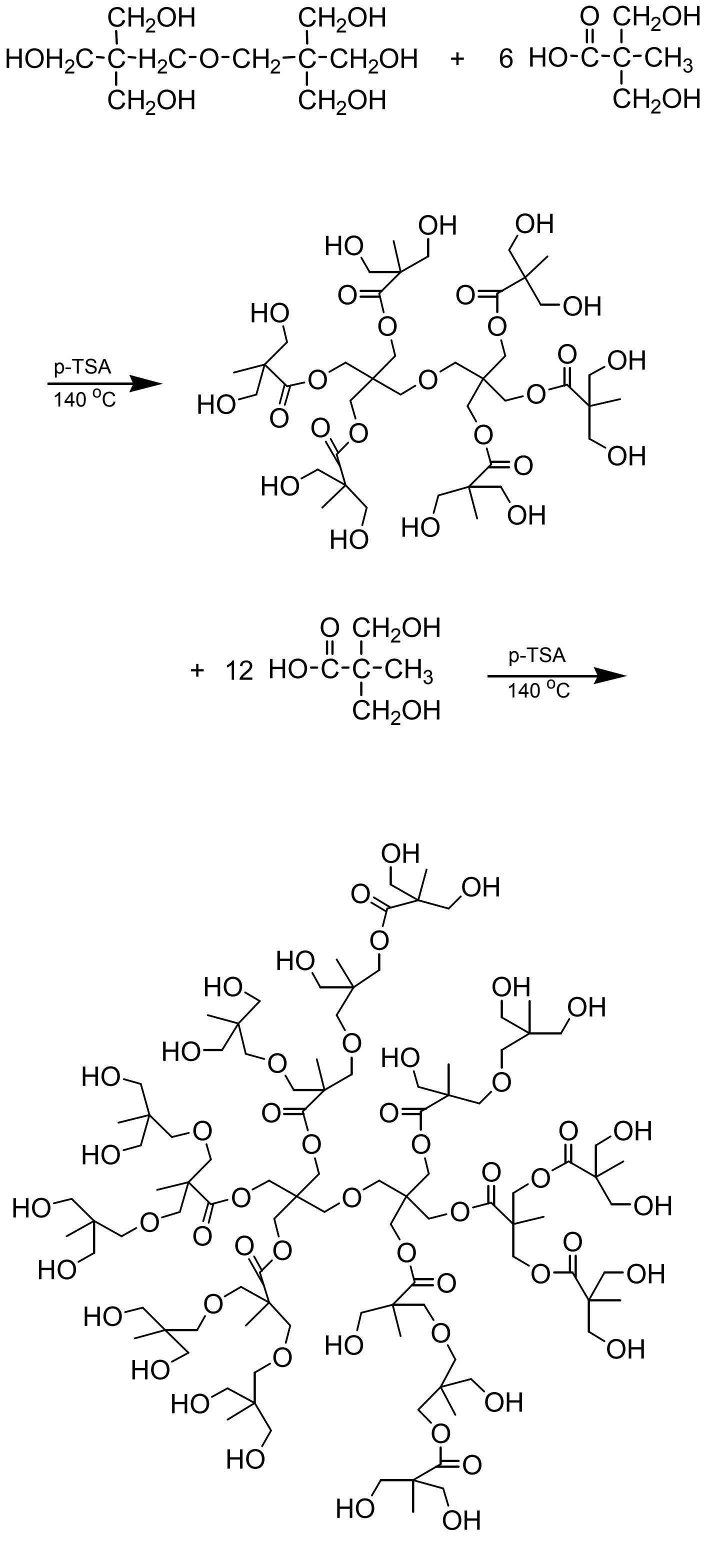


Figure 3.3 Synthesis of the HBP corresponding to second generation

As the acid value decreases the viscosity of the resin increases. The acid values of the resins were allowed to drop down to 15 mg KOH/g resin in order to prevent gelation and viscosity build up. The HBP modified with the castor oil fatty acids only is designated as HBR-1 (Hyperbranched Resin-1). HBR-1 was further reacted the linseed oil fatty acids and benzoic acid in different amounts to synthesize the other three resins HBR-2, 3, and 4. The composition of the resins on mole basis are given in Table 3.1. Percent fatty acids were calculated according to Eq. 4. Schematic representations of the resins are given in Figures 3.5 to 3.8. Since the esterification reactions did not go to completion and some side reactions may have occurred the figures are not exact but nearly ideal representations of the resins.

Table 3.1 Formulations and fatty acid contents of the resins

Resin	FA %	HBP (mole)	Castor FA (mole)	Linseed FA (mole)	Benzoic Acid (mole)
HBR-1	81.9	1.000	24.000	-	-
HBR-2	84.7	1.000	24.000	3.600	-
HBR-3	91.5	1.000	24.000	16.800	-
HBR-4	74.4	1.000	24.000	3.600	13.200

3.3.1 Addition of Driers

Cobalt naphthenate and lead naphthenate were added prior to application of the resin on the substrates. Slightly high amounts of driers were used since castor oil is non-drying. 0.6 % drier was added based on grams of resin one third of which was cobalt naphthenate and the rest was lead naphthenate.

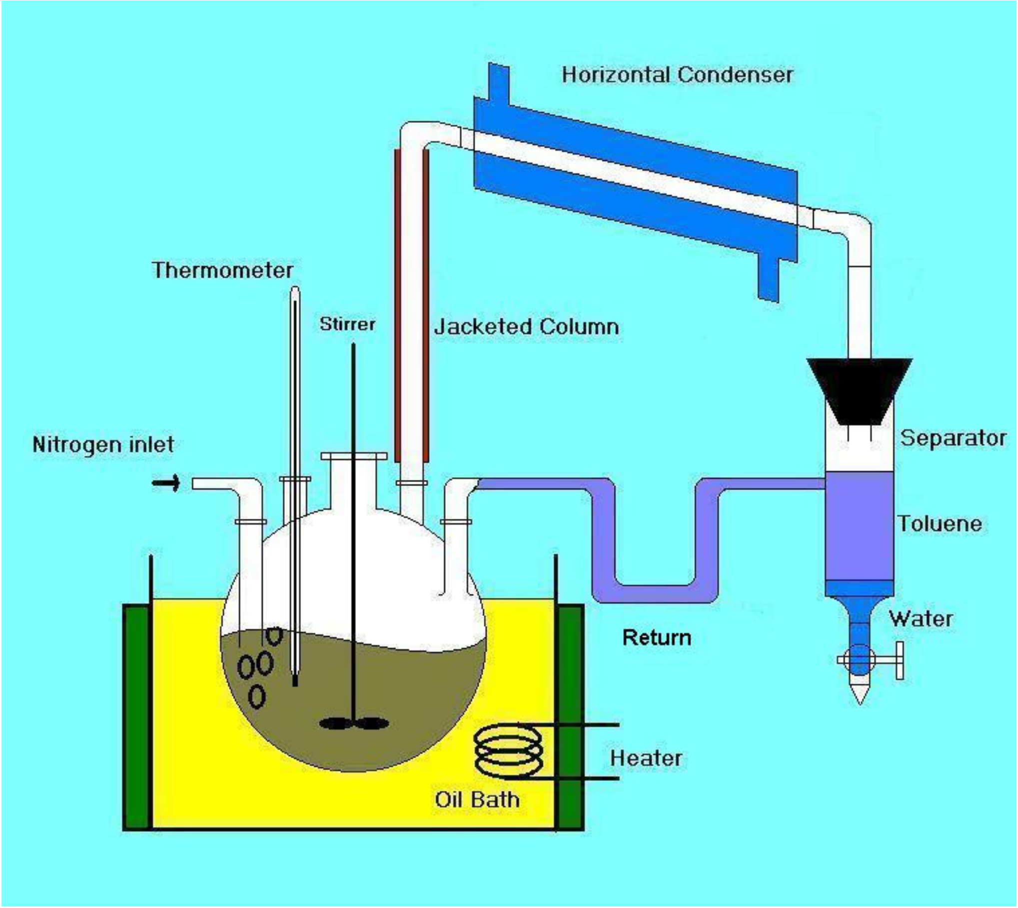


Figure 3.4 Experimental setup

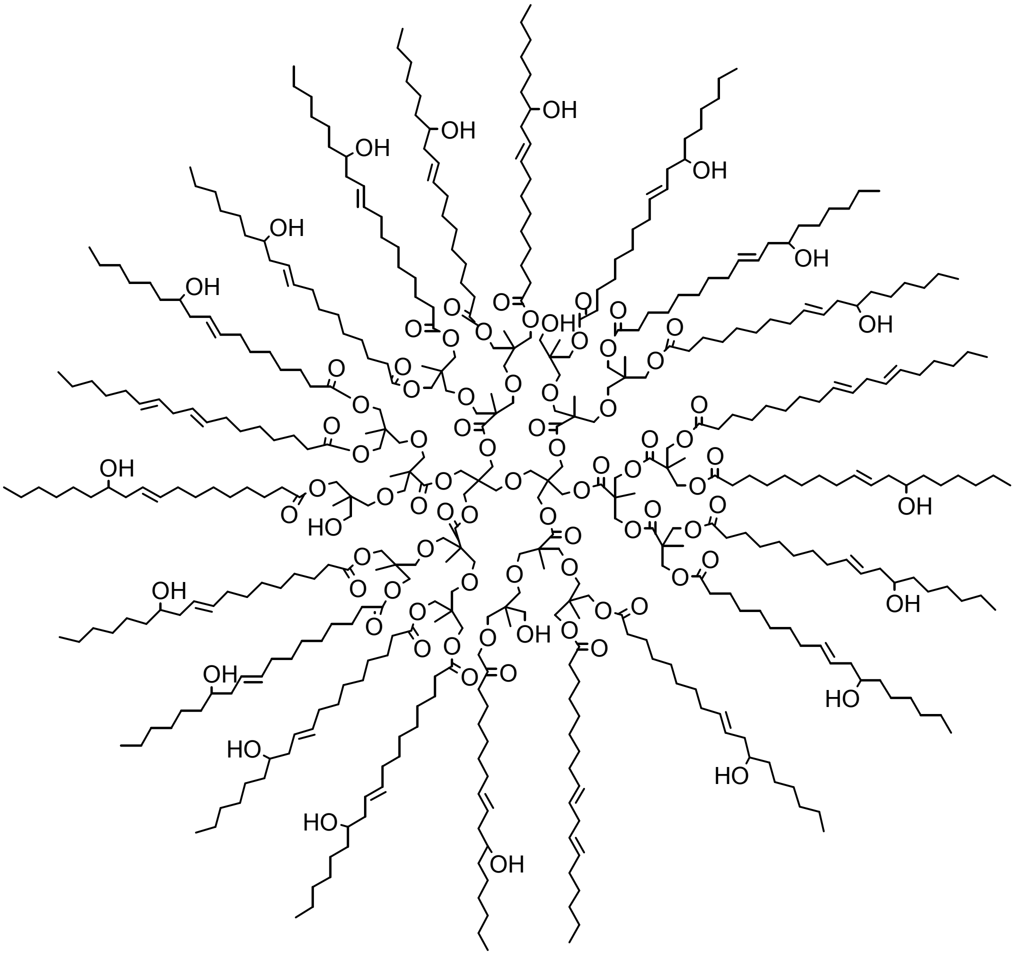


Figure 3.5 A schematic representation of HBP modified with the castor oil fatty acids (HBR-1)

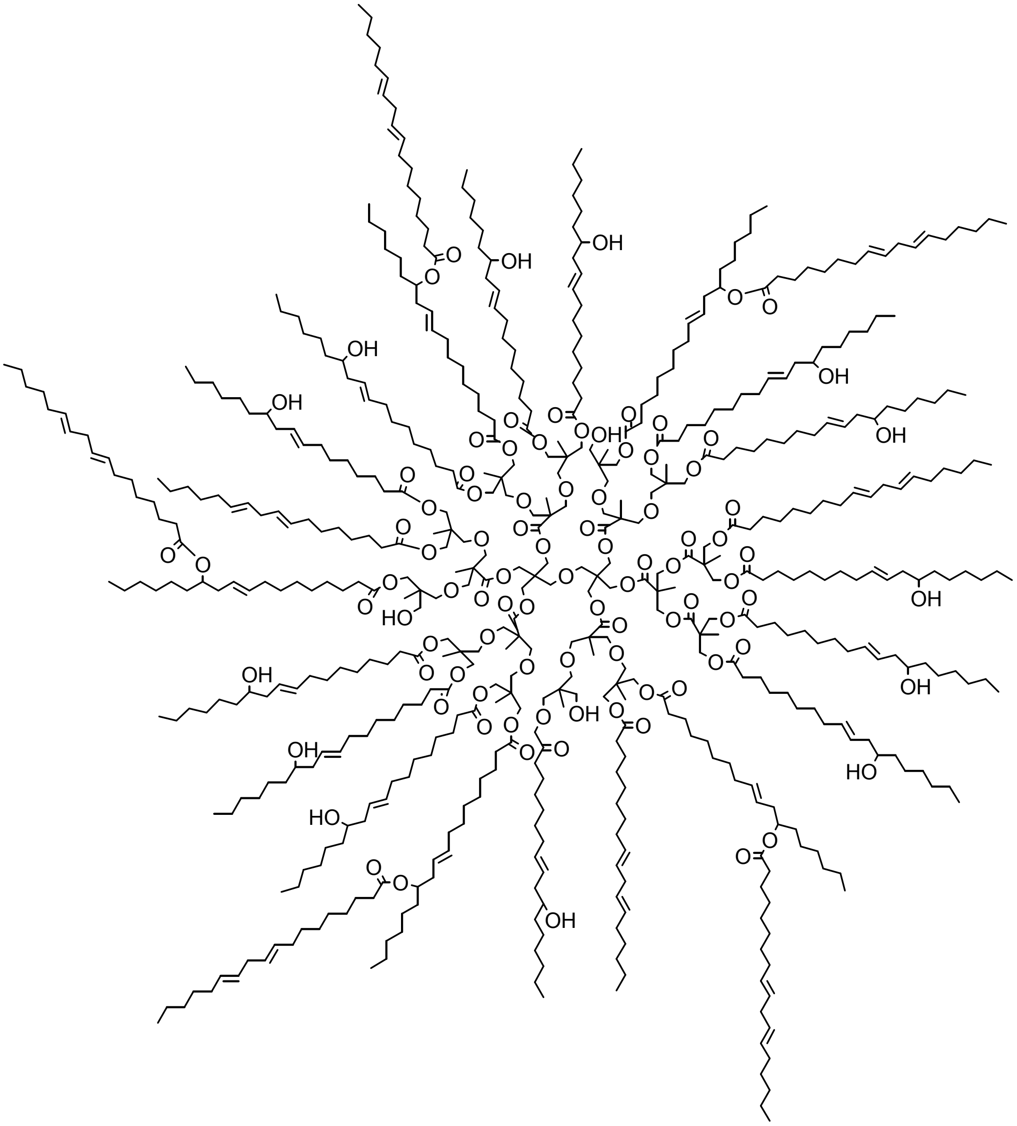


Figure 3.6 A schematic representation of HBR-1 modified with the linseed oil fatty acids (15 % of the castor FA used on mole basis) (HBR-2)

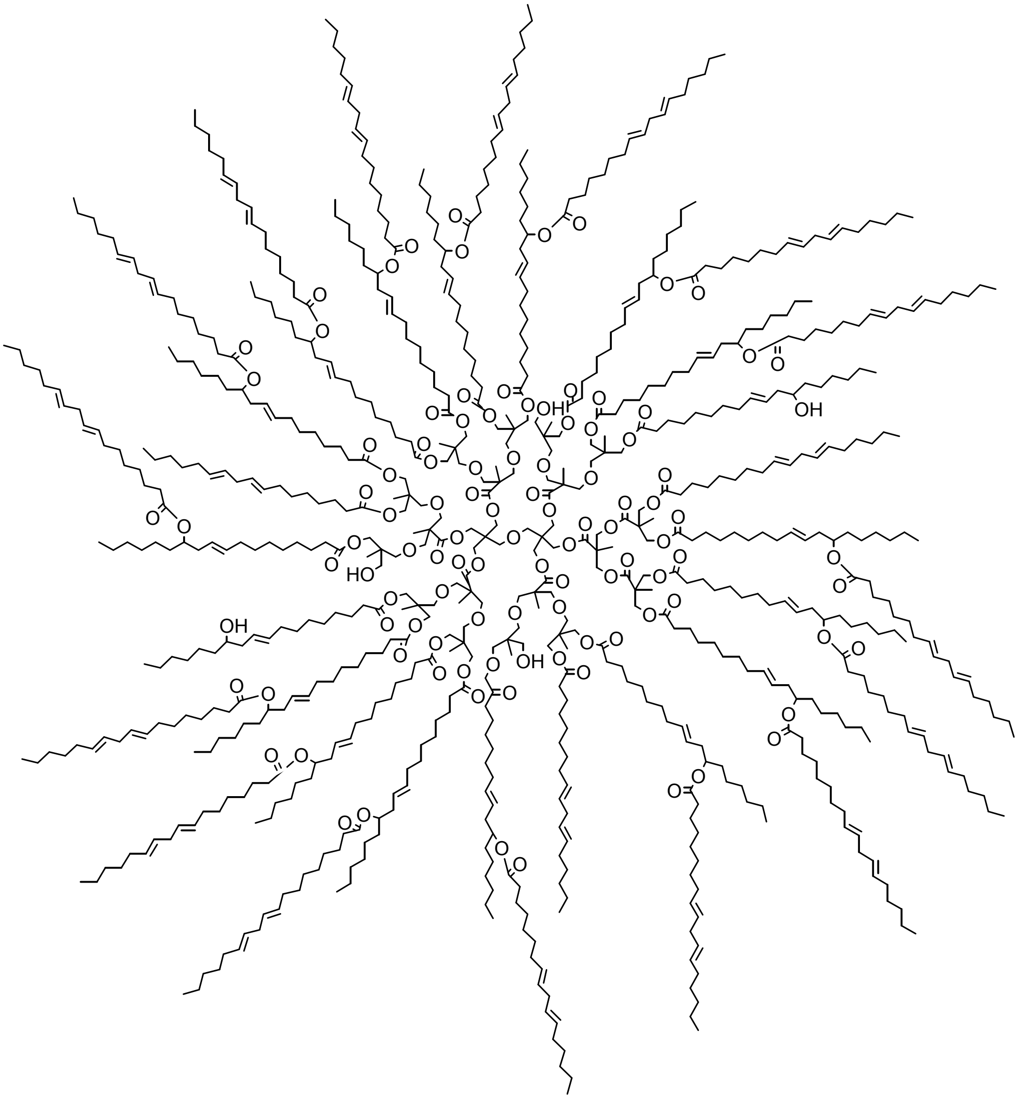


Figure 3.7 A schematic representation of HBR-1 modified with the linseed oil fatty acids (70 % of the castor FA used on mole basis) (HBR-3)

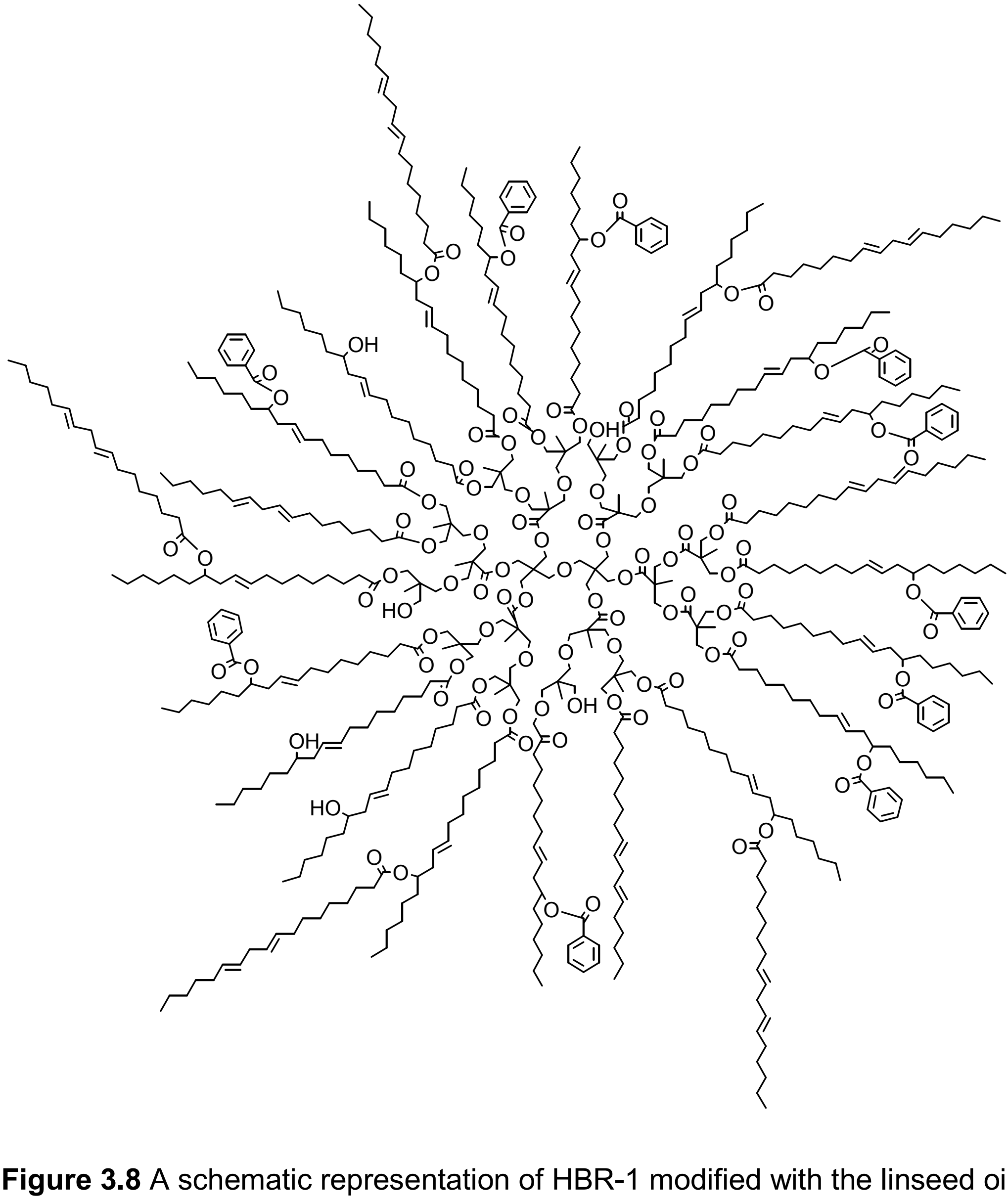


Figure 3.8 A schematic representation of HBR-1 modified with the linseed oil fatty acids (15 % of the castor FA used on mole basis) and benzoic acid (HBR-4)

3.4 Chemical Characterization

3.4.1 Fourier Transform Infrared (FTIR) Spectroscopy

Nicolet 510 FT Spectrophotometer was used to characterize the fatty acids and the resins. The samples were dispersed as thin films on NaCl discs.

3.5 Thermal Characterization

3.5.1 Differential Scanning Calorimetry (DSC)

Dupont (Model TA 910 S) differential scanning calorimeter was used. Samples of 2-3 mg weight were placed in stainless steel pans and heated at a rate of 10 °C/min.

3.6 Physical and Mechanical Tests

3.6.1 Preparation of Test Panels

Fifty micrometers wet film thickness was applied on glass and metal panels by a film casting knife (Braive Instruments). The test panels were dried in an oven at 90 °C for 12 hours and conditioned at room temperature for one week. A thickness gauge (Elcometer 345) was used to measure the film thickness of the coatings. The accuracy of the instrument is ± 1-3 % [56].

3.6.2 Pendulum Hardness Test

A Braive Instruments hardness tester (Model 3034) equipped with a Persoz pendulum was used. The hardness tester and the Persoz pendulum are given in Figure 3.9. The principle of the pendulum hardness test is based on the fact that the amplitude of oscillation of a pendulum swinging on a test specimen decreases more rapidly for the softer films. The time in seconds for the swing amplitude of the Persoz pendulum to decrease from 12° to 4° gives the Persoz hardness [57].

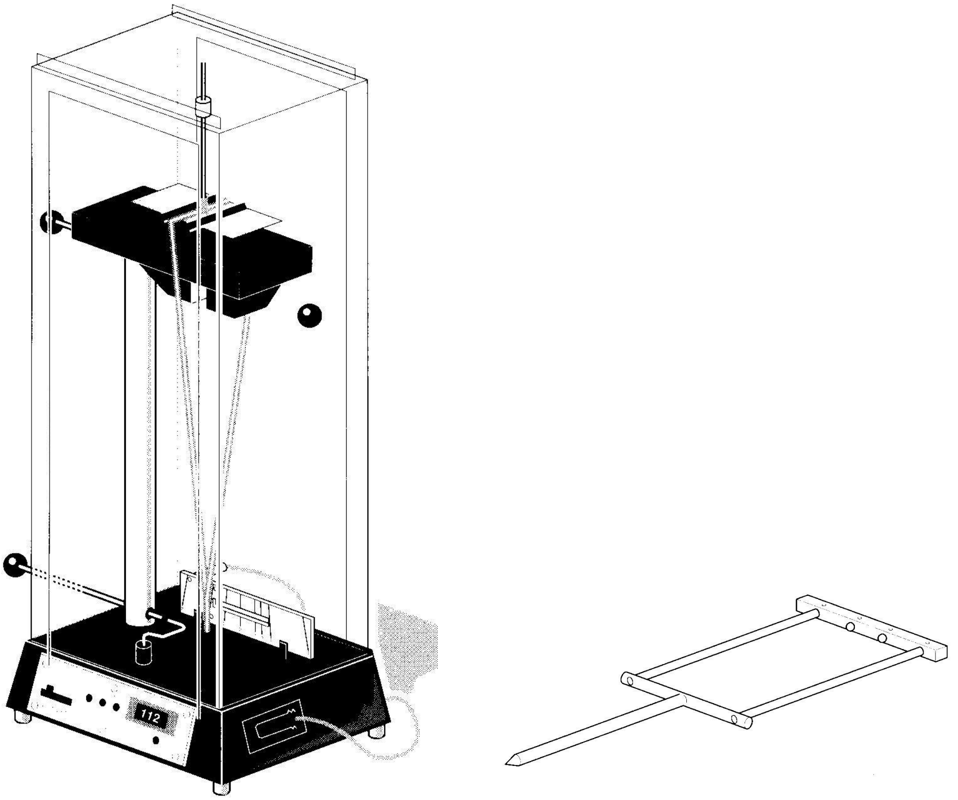


Figure 3.9 Hardness tester and Persoz pendulum

3.6.3 Impact Resistance Test

The method has been found to be useful in predicting the performance of organic coatings for their ability to resist cracking caused by impacts during manufacture of articles and their use in service. A Gardner Impact Tester (Model 5524) was used. A standard dropweight (1+1 kg) was dropped onto the coated surfaces from a specified distance. The potential energy needed to form cracks on the surface is found by the height at which cracks are observed [58]. The impact resistance tester and the dropweight are given in Figure 3.10.

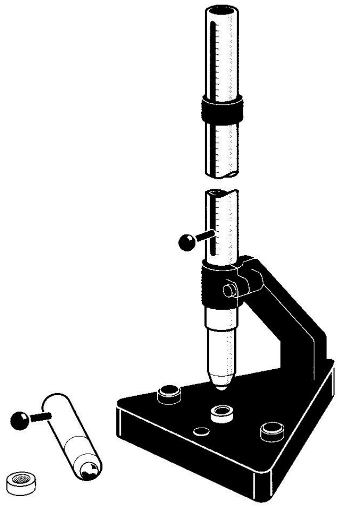


Figure 3.10 Impact resistance tester and dropweight

3.6.4 *Mandrel Bending Test*

The test is useful in rating attached coatings for their ability to resist cracking when elongated. A conical mandrel bending tester (Braive Instruments Model 1510) was used for the bending test (Figure 3.11). Coated metal plates were fastened and bent over the conical mandrel. The length of the crack formed from the tip of the mandrel is reported [59].

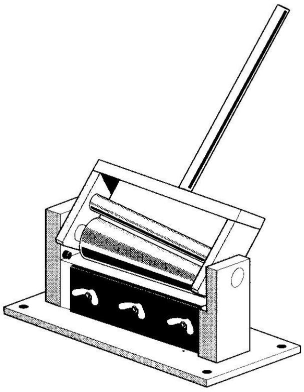


Figure 3.11 Conical Mandrel for bending test

3.6.5 Abrasion Resistance Test

The test is useful in determining the resistance of organic coatings to a falling abrasive. [60]. The apparatus used can be seen in Figure 3.12.

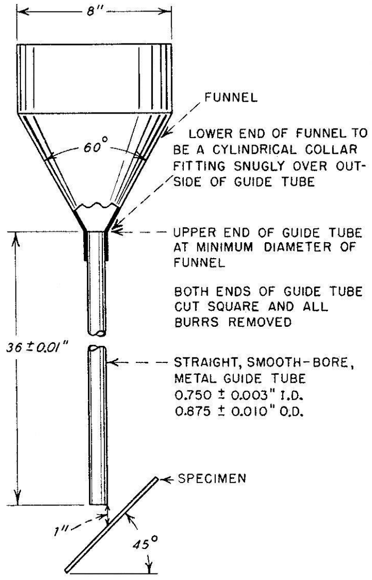
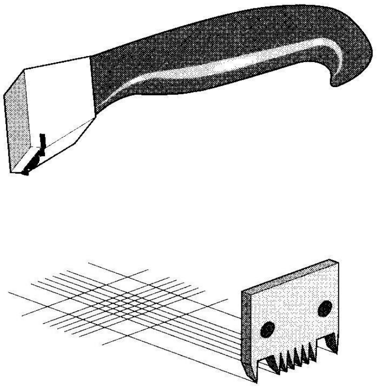


Figure 3.12 Abrasion resistance measurement instrument

3.6.6 Adhesion Test

A cross-hatch cutter was used to cut the substrate in order to produce a lattice pattern. After making the cuts the film was brushed with a soft tissue to remove any detached flakes or ribbons of coating. After that an adhesive tape was placed on the cut area and rubbed firmly to ensure good contact. The tape was pulled of rapidly (not jerked) back onto itself at as close to an angle of 180° as possible. The cross-cut area was inspected for the removal of coating from the substrate and rated the adhesion according to the following scale given in Figure 3.13 [61].



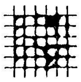
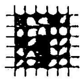
Classification	Surface of cross-cut area from which flaking has occurred. (Example for six parallel cuts)
5B	None
4B	
3B	
2B	
1B	
0B	Greater than 65%

Figure 3.13 Cross-hatch cutter and the scaling of adhesion

3.6.7 Specular Gloss

Gloss is associated with the capacity of a surface to reflect more light in some directions than in others. The directions associated with specular (or mirror) reflection normally have the highest reflectances. Measurements by this test method correlate with visual observations of surface shininess made at roughly the corresponding angles. A Rhopoint glossmeter was used [62].

3.6.8 Viscosity Measurements

Haake Rotovisco (Model CV 20) parallel disk rheometer was used in order to measure the viscosity of the resins. The diameter of the disk used was 19.25 mm. Measurements were made at 23 °C for five minutes until the shear rate reached to 200 s^{-1} and ten data were collected. Another ten data were collected for two minutes at 200 s^{-1} constant shear rate. The average of five measurements was given for each resin.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preliminary Experiments

Several attempts were made in order to synthesize the hyperbranched resin. First trial was to react dipenta with excess castor oil fatty acids at 140 °C. The reaction rate was very slow and some dipenta remained unreacted. It was seen that isolation of the unreacted fatty acids was difficult, therefore the stoichiometric amount of fatty acids were used for the second attempt. However, the reaction proceeded quite slow. Hence, it was decided to synthesize the hyperbranched polyester corresponding to second generation and then react it with the castor oil fatty acids. The reaction was carried out at 140 °C and observed to be very slow. By the end of the reaction a solid deposit remained at the bottom of the reactor. The liquid product applied in thin layers on the glass substrates formed well adhering films. In order to prevent the formation of the solid deposit the amount of solvent was increased and the experiment was repeated in the presence of 1 % catalyst. However the result was the same and the analysis showed that crosslinked ethers had formed. Then, the catalyst amount was decreased to 0.4 % (on chain extender basis) and the reaction temperature increased above 200 °C. The solid deposit disappeared and the reaction was much faster. Gelation occurred at acid values below 15; therefore the reaction was stopped when the acid number declined to 15.

4.2 Chemical Characterization

4.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of the castor oil fatty acids, linseed oil fatty acids, HBR-1, HBR-2, HBR-3, and HBR-4 are shown in Figures 4.1 and 4.2.

In Figure 4.1 the broad peak around 3400 cm^{-1} corresponds to the hydroxyl (O–H) groups of the ricinoleic acid. The strong hydrogen bonding in this molecule is the main cause for the broadening of the peaks in the spectrum. The spectra of the linseed oil fatty acids and the castor oil fatty acids are similar except this very broad and intense hydroxyl peak. The FTIR spectrum of the linseed oil fatty acids is also given in Figure 4.1. The peak at 3010 cm^{-1} is olefinic C–H stretching which is a clear indication of the unsaturated fatty acids. The peaks between 2850 cm^{-1} and 2930 cm^{-1} correspond to aliphatic C–H stretching. These peaks are broadened due to the hydrogen bonded O–H group of acids. The peak at 2670 cm^{-1} is also due to hydrogen bonded O–H group of acids. Carbonyl (C=O) peak can be seen in both spectra at 1710 cm^{-1}. The stretching of C–O is seen at 1280 cm^{-1}. The peaks at 1375 cm^{-1} and 1460 cm^{-1} correspond to symmetric and asymmetric bending of methyl groups. The peak at 1410 cm^{-1} indicates cis C=C group. The bending of O–H dimer of carboxylic acid gives a peak at about 936 cm^{-1}. Finally, the rocking of multiple (> 4) methylene groups is seen by the peak at 722 cm^{-1}.

The IR spectra of HBR-1, HBR-2, HBR-3, and HBR-4 are given in Figure 4.2. All of the spectra have most of the peaks in common since the structures are very similar. The broadest and the most intense O–H peak is seen around 3500 cm^{-1} in HBR-1 since none of the hydroxyl groups were modified. Olefinic C–H stretching due to fatty acids is seen at about 3010 cm^{-1} in all resins. The peaks at 2855 cm^{-1} and 2927 cm^{-1} are also common in all of the spectra corresponding to aliphatic C–H stretching. The stretching of aromatic C–H group gives a peak at 3060 cm^{-1} in HBR-4. The characteristic ester peak is seen in the spectra about 1735 cm^{-1}. About 1600 cm^{-1} stretching of aromatic C=C group is seen in HBR-4. The peaks at 1375 cm^{-1} and 1460 cm^{-1} correspond to symmetric and asymmetric bending of methyl groups. At 1240 cm^{-1} for HBR-1, 2, 3 and at 1270 cm^{-1} for HBR-4 O=C–O–C stretching of aliphatic esters shows a peak. The rocking of multiple (> 4) methylene groups is seen by the peak at 722 cm^{-1} in all of the spectra. Finally, the weak peaks around 580 cm^{-1} is seen, which correspond to C–O–C stretching of ether due to dipentaerythritol.

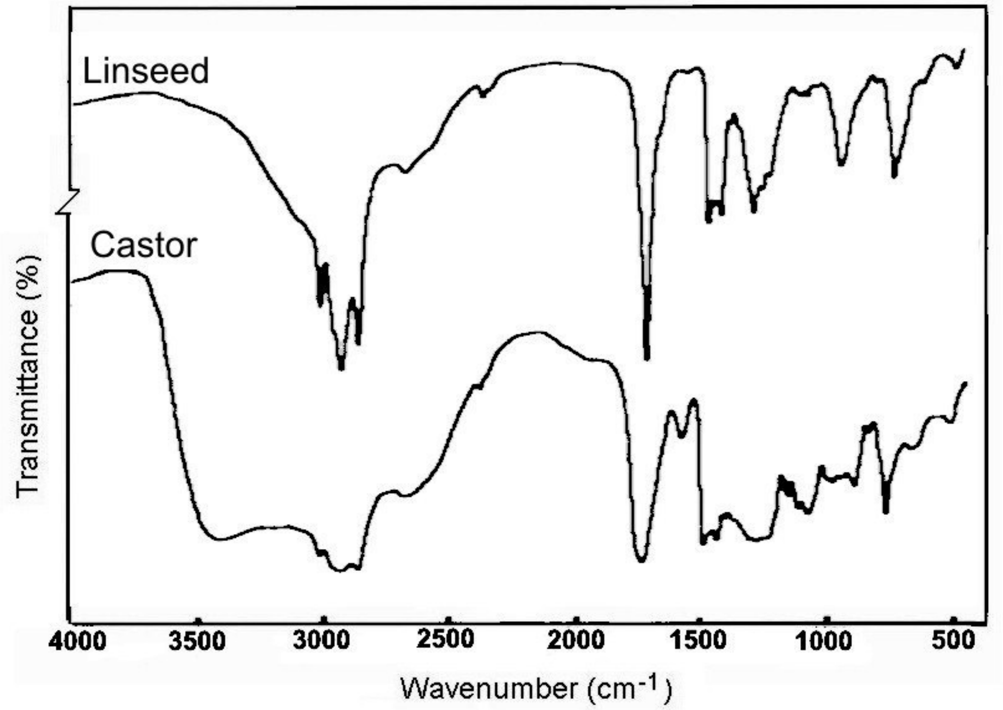


Figure 4.1 The FTIR spectra of the castor and linseed oil fatty acids

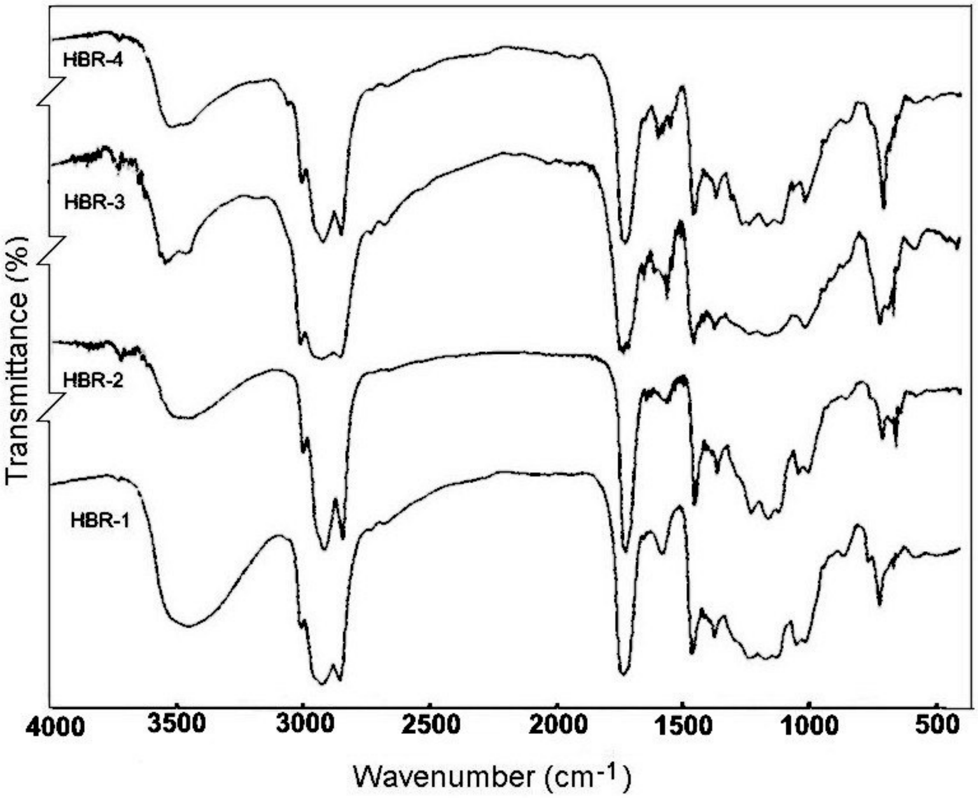


Figure 4.2 The FTIR spectra of HBR-1, 2, 3, and 4

4.3 Thermal Properties

4.3.1 Differential Scanning Calorimetry (DSC)

The DSC spectra of HBR-1, 2, 3 and, 4 are given in Figure 4.3. Since the cured resins had crosslinked structures thermal degradation temperatures of the resins could be detected only. Glass transition was not significant in the spectra. All of the resins were found to be thermally stable up to 300 °C. HBR-1 started degradation at 310 °C and the thermal degradation ended at 460 °C. Thermal degradation of HBR-2 started at 311 °C and ended at 393 °C. HBR-3 and 4 started degradation at 334 and 346 °C, respectively. Their thermal degradation ended at 389 and 395 °C, respectively. Since HBR-2, 3, and 4 have longer branches, their complete degradation occurred at lower temperatures compared to HBR-1. As the structure of the resin gets more compact thermal stability increases. HBR-1 had the most compact structure and thus the highest thermal stability. Bulky and rigid benzoic acid increased the thermal degradation temperature of HBR-4 only a little compared to HBR-2 and 3.

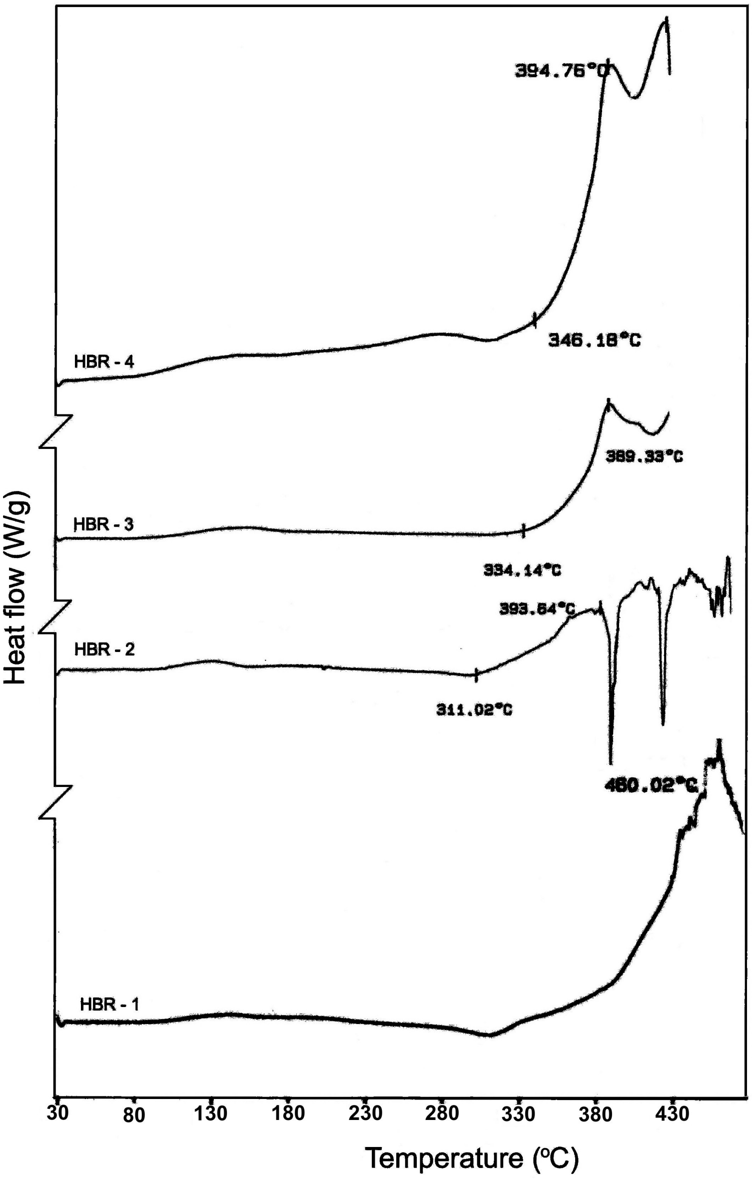


Figure 4.3 The DSC spectra of HBR-1, 2, 3, and 4.

4.4 The Physical and The Mechanical Properties

4.4.1 Pendulum Hardness

The change of pendulum hardness with the time of drying up to two weeks is given in Figure 4.4. The pendulum hardness values of the resins slightly increased by addition of the linseed FA in HBR-2. The modification with benzoic acid had no significant effect on the hardness of the resin. The most dramatic change in hardness values were observed in HBR-3. Increasing the amount of the linseed FA increased the hardness from 24 Persoz (HBR-1) to 68 Persoz (HBR-3). The increase in crosslink density was the main factor for this change. The addition of the linseed FA increased unsaturation which increased hydroperoxide formation and the formation of crosslinks. The resins showed the conventional alkyd resin characteristic with time. The hardness values increased with time and then reached a plateau.

Previously, it was reported that resins having hyperbranched structure showed just the reverse behavior compared with conventional alkyd resins [3]. The hardness of the resins were given as 75 Persoz after 24 hours but decreased to 25 Persoz after two weeks [3]. The hardness values of HBR-1, 2, 3 are close to the values reported in this study. HBR-4 had much higher hardness than the other resins after 14 days. Using two types of fatty acids in the structure has increased the crosslink density and the hardest hyperbranched resin reported in the literature was obtained. All of the resins are aliphatic polymers and since they have no rigid aromatic groups in their structure very high hardness values could not be reached.

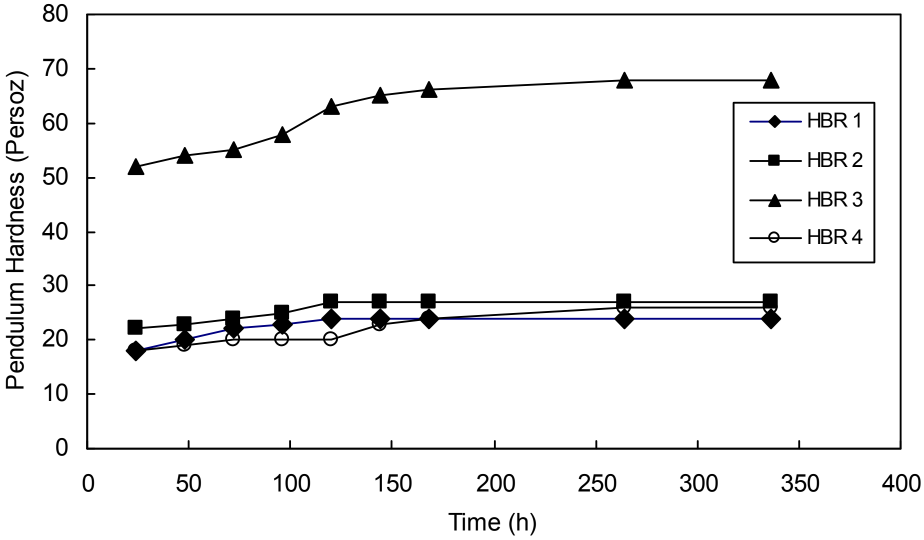


Figure 4.4 Pendulum hardness versus time graph for all resins

4.4.2 Impact Resistance

The maximum potential energy that can be reached by the apparatus is 19.6 Joules which corresponds to dropping of a 2 kg weight from one meter height. All of the samples passed the impact test. No cracks were observed on any of the samples after applying the test. The resins had impact resistance higher than 19.6 Joules. Castor oil fatty acids are usually used as plastifying agents and alkyds of castor oil fatty acids are also used as plastifying alkyds. Though flexibility is a characteristic of alkyd resins, addition of castor oil fatty acids improved the flexibility of the resins.

4.4.3 Bending Resistance

All of the synthesized resins showed excellent flexibility. No cracks were observed after bending the specimens over the conical mandrel. This property provides ease of formability to the coated specimens. The resins could withstand elongation owing to the improved flexibility which may come from castor oil fatty acids.

4.4.4 Abrasion Resistance

All coatings are subject to abrasive forces after being applied to a surface. The synthesized resins were found to be quite resistant to abrasion. This indicates that the synthesized resins were tough and durable. The abrasion resistance values were measured as 11.8 l/μm, 19.4 l/μm, 16.7 l/μm, and 17.4 l/μm for HBR-1, HBR-2, HBR-3, and HBR-4, respectively. HBR-1 had lowest abrasion resistance. This may be due to its slightly tacky surface (i.e. higher coefficient of friction). Abrasive adhered on the surface causing a greater abrasion. On the other hand the abrasive may have encountered a more rubbery surface on HBR-2 and 4. HBR-2 had a higher abrasion resistance than HBR-3 although the latter is harder. Since the crosslink density is high in HBR-3 and the abrasive effect is more pronounced on hard surfaces. This phenomenon can be visualized by the abrasion of a rubber tyre and a steel surface.

4.4.5 Adhesion

A coating must adhere well in order to protect the surface of the substrate and to be used for a long time. The adhesion of the resins on both glass and metal substrates were found to be very strong and the adhesion ratings were found to be the highest 5B. No flakings or ribboning occurred after making cuts and applying the adhesive tape. The hydroxyl groups in the structure of the resins improved the adhesion to the substrates.

4.4.6 Specular Gloss

The specular gloss values of the resins applied both on glass and metal substrates were measured at three different angles of incidence. The results are tabulated in Table 4.1. If the gloss value of a coating measured at 60° is higher than 70, it is said to be in high gloss range. Therefore, it can be said that all of the resins showed high gloss property. The gloss values of the resins on metal substrates came out to be less than the gloss values on glass substrates since glass substrates reflect the diffracted light yielding higher gloss. All of the resins had very high gloss values (between 103.8 and 126) on both substrates at 60°. At 20° the gloss values on glass substrate were much higher than metal substrate. The gloss values at 85° were between 83 and 95.6 for glass substrates and 75.8 and 89.9 for metal substrates. The gloss values measured at 60° were higher than the values at 20° and 85°.

Table 4.1 Specular gloss values of the resins at different angles of incidence and on different substrates.

Resin	Substrate/Angle	20°	60°	85°
HBR-1	Glass	108.3	120.8	89.1
	Metal	76.4	109.8	89.9
HBR-2	Glass	94.3	109.6	95.6
	Metal	63.8	103.8	89.7
HBR-3	Glass	113.8	126.0	83.0
	Metal	88.0	116.2	77.2
HBR-4	Glass	96.2	111.9	84.8
	Metal	69.0	108.8	75.8

4.4.7 Viscosity Measurements

Measurements were made at 23 °C for five minutes until the shear rate reached up to 200 s^{-1} and ten data were collected. Another ten data were collected for two minutes at 200 s^{-1} constant shear rate. The average of five measurements was given for each resin. The viscosity versus shear rate graph is given in Figure 4.5. The viscosity of the resins decreased as the shear rate increased up to 200 s^{-1}. This behavior was more pronounced for

HBR-3 and HBR-4. This may be due to the disappearance of entanglements of longer chains in HBR-3 and of phenyl-phenyl interactions in HBR-4. HBR-1 and 4 had higher viscosities compared to HBR-2 and 3. When 200 s^{-1} shear rate was reached the viscosities of the resins were measured as 17.3, 9.7, 5.8, and 17.5 Pa·s for HBR-1, 2, 3, and 4, respectively. Phenyl-phenyl interaction in HBR-4 was responsible for the increase in viscosity and hydrogen bonding was the main factor of high viscosity in HBR-1. The viscosity of a conventional high solids alkyd resin and commercial conventional resin are given in the literature as 26 Pa·s and 1000 Pa·s, respectively [3]. The viscosities measured for the hyperbranched resins are lower than 5 Pa·s [3,19]. HBR-2 and 3 have much lower viscosities than the conventional alkyd resins while they have higher viscosities compared to hyperbranched resins. Hydrogen bonding due to hydroxyl groups was mainly responsible for this increase in viscosity. On the other hand these groups provide superior adhesion. HBR-1 and 4 had viscosities lower than conventional resins but much higher than hyperbranched resins due to above mentioned reasons. The viscosity versus time graph at a constant shear rate of 200 s^{-1} is given in Figure 4.6. The viscosities of the resins slightly fell from 17.3 to 16.9 Pa·s, 9.7 to 9.6 Pa·s, 5.8 to 5.7 Pa·s, and 17.5 to 16.7 Pa·s for HBR-1, 2, 3, and 4, respectively at the end of two minutes. The viscosity of a coating should decrease at constant shear rate with time to provide ease of application. The applicability of the resins can be improved by the addition of the other components (solvents, pigments, additives).

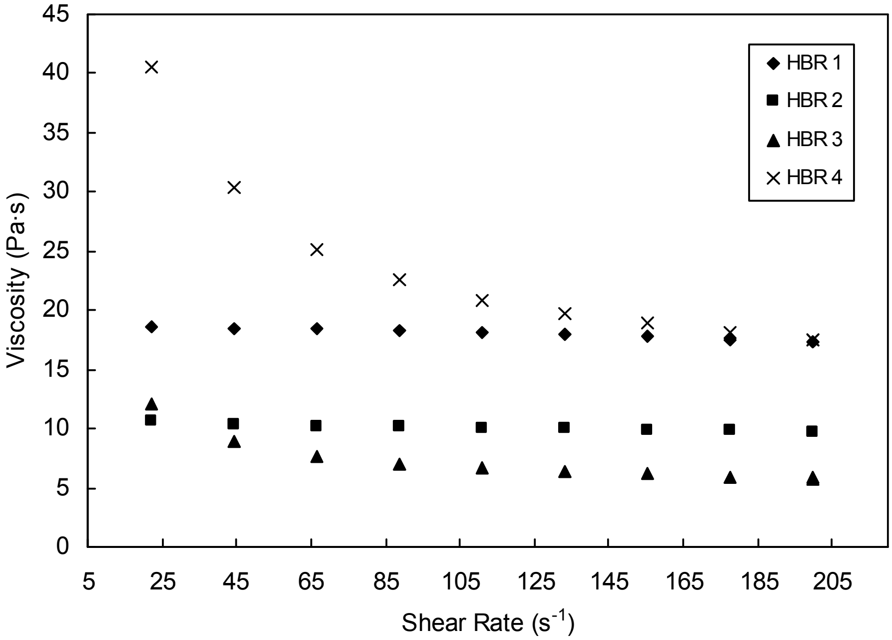


Figure 4.5 Viscosity versus shear rate graph (T= 23 °C)

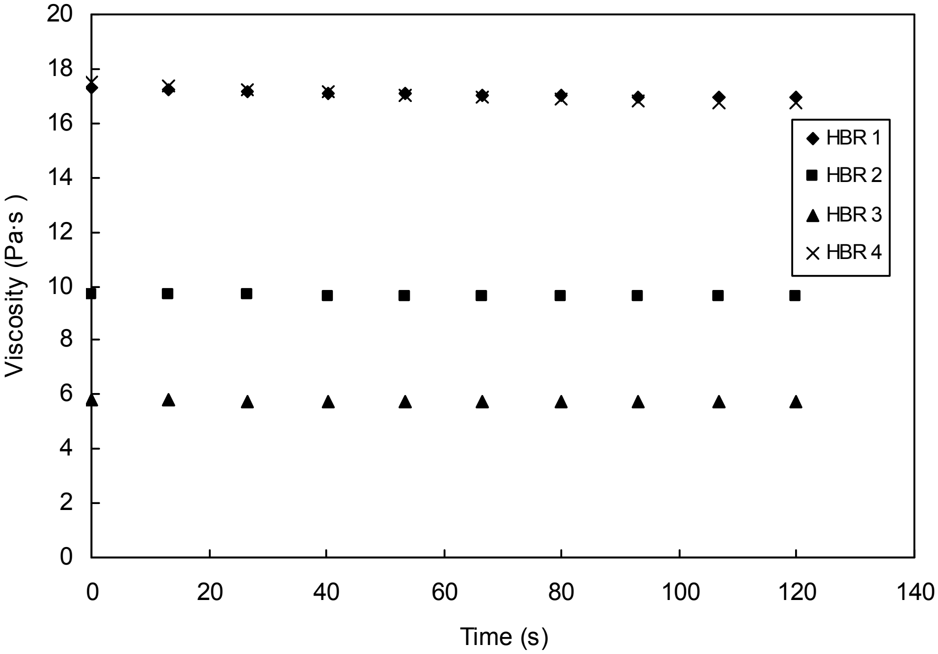


Figure 4.6 Viscosity versus time graph (T= 23 °C)

CHAPTER 5

CONCLUSIONS

1. The acid value of the system should be carefully monitored because the increase in reaction time leads to etherification and gelation.

2. All of the resins are thermally stable up to 300 °C. Complete degradation temperature of HBR-1 is the highest among four resins due to its shorter branches.

3. The hardness of the resins were between low to moderate range compared to other oil based resins but were high compared to hyperbranched resins.

4. The hardness values of the resins increased with time and reached a plateau.

5. The hardness values of the resins increased as the amount of fatty acids (unsaturation) present in the system increased. The hardness value for HBR-1 is 24 Persoz while for HBR-3 it is 68 Persoz. The addition of benzoic acid did not have any significant effect on hardness.

6. Impact and bending resistance tests have shown that the resins are very flexible and easily formable.

7. The resins showed good resistance to abrasion and adhered well on metal and glass substrates.

8. The specular gloss values were excellent for all of the resins. The gloss values at 60° were measured above 70 for all of the resins on both substrates indicating that the resins are in high gloss range.

9. HBR-1 and 4 had high viscosities compared to hyperbranched resins. HBR-2 and 3 also had high viscosities compared to hyperbranched resins given in the literature but much lower viscosities compared to conventional resins.

10. The viscosity of the resins having more linseed FA in their structure had lower viscosities because of the decrease in hydrogen bonding. The addition of benzoic acid introduced phenyl-phenyl interactions which increased the viscosity of the resin.

11. At constant shear rate there was only a little decrease in the viscosity of the resins with time. The applicability of the coating should be improved by the addition of other components (solvents, pigments, additives etc.)

CHAPTER 6

RECOMMENDATIONS

1. Different core molecules can be used instead of dipentaerythritol. For instance; trimethylol propane, pentaerythritol or more rigid cores such as carefully controlled phenol formaldehyde resin can be used.

2. The hydroxyl groups of HBR-1 can be modified with epichlorohydrin to obtain epoxy. The process condition should be carefully set in order not to break ester linkages.

3. The hydroxyl groups of HBR-1 can be modified with a diisocyanate to produce air drying polyurethanes.

4. The resins can be blended with epoxy resins in order to increase their toughness.

5. Acrylic and methacrylic groups can be incorporated into the structure of the resins to obtain UV-curable resins.

6. Especially HBR-3 can be produced in large scale and blended with other resins such as epoxies or melamine formaldehyde resins. Other three resins can also be produced as plastifying resins.

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APPENDIX

VISCOSITY MEASUREMENT DATA

Table A.1 Viscosity and shear rate data for HBR-1

Shear Rate (s^{-1})	**Viscosity (Pa·s)**	**Time (s)**	**σ* (Pa·s)**
21.9	18.65	33.0	0.27
44.3	18.44	66.6	0.29
66.5	18.37	100.2	0.27
88.8	18.24	133.2	0.24
110.9	18.12	166.2	0.24
133.2	17.95	199.8	0.23
155.4	17.73	233.4	0.22
177.6	17.52	266.4	0.22
199.8	17.26	300.0	0.21

* σ : standard deviation

Table A.2 Viscosity and time data for HBR-1 at 200 s^{-1}

Shear Rate (s^{-1})	Viscosity (Pa·s)	Time (s)	σ (Pa·s)
200.0	17.27	0.0	0.21
200.0	17.21	13.2	0.21
200.0	17.16	26.4	0.19
200.0	17.12	40.2	0.20
200.0	17.08	53.4	0.19
200.0	17.05	66.6	0.20
200.0	17.01	79.8	0.18
200.0	16.98	93.0	0.18
200.0	16.95	106.8	0.18
200.0	16.92	120.0	0.19

Table A.3 Viscosity and shear rate data for HBR-2

Shear Rate (s^{-1})	**Viscosity (Pa·s)**	**Time (s)**	**σ (Pa·s)**
22.0	10.65	33.0	0.25
44.3	10.37	66.6	0.25
66.5	10.23	100.2	0.23
88.8	10.12	133.2	0.21
110.9	10.04	166.2	0.20
133.2	9.96	199.8	0.20
155.4	9.88	233.4	0.19
177.6	9.80	266.4	0.19
199.9	9.71	300.0	0.18

Table A.4 Viscosity and time data for HBR-2 at 200 s^{-1}

Shear Rate (s^{-1})	Viscosity (Pa·s)	Time (s)	σ (Pa·s)
200.0	9.70	0.0	0.18
200.0	9.68	13.2	0.19
200.0	9.67	26.4	0.18
200.0	9.65	40.2	0.18
200.0	9.64	53.4	0.18
200.0	9.63	66.6	0.18
200.0	9.62	79.8	0.18
200.0	9.60	93.0	0.18
200.0	9.59	106.8	0.17
200.0	9.59	120.0	0.18

Table A.5 Viscosity and shear rate data for HBR-3

Shear Rate (s^{-1})	Viscosity (Pa·s)	Time (s)	σ (Pa·s)
22.1	12.01	33.0	0.73
44.2	8.84	66.6	0.25
66.5	7.67	100.2	0.13
88.7	7.06	133.2	0.08
110.9	6.66	166.2	0.06
133.1	6.35	199.8	0.05
155.4	6.13	233.4	0.03
177.6	5.94	266.4	0.04
199.8	5.80	300.0	0.04

Table A.6 Viscosity and time data for HBR-3 at 200 s^{-1}

Shear Rate (s^{-1})	Viscosity (Pa·s)	Time (s)	σ (Pa·s)
200.0	5.81	0.0	0.04
200.0	5.78	13.2	0.04
200.0	5.77	26.4	0.04
200.0	5.76	40.2	0.04
200.0	5.76	53.4	0.04
200.0	5.75	66.6	0.04
200.0	5.75	79.8	0.04
200.0	5.74	93.0	0.05
200.0	5.73	106.8	0.05
200.0	5.73	120.0	0.05

Table A.7 Viscosity and shear rate data for HBR-4

Shear Rate (s^{-1})	**Viscosity (Pa·s)**	**Time (s)**	**σ (Pa·s)**
22.0	40.48	33.0	6.85
44.3	30.45	66.6	3.46
66.4	25.13	100.2	2.81
88.6	22.54	133.2	2.40
110.9	20.91	166.2	2.31
133.1	19.73	199.8	2.27
155.4	18.85	233.4	2.16
177.6	18.12	266.4	2.06
199.8	17.50	300.0	1.98

Table A.8 Viscosity and time data for HBR-4 at 200 s^{-1}

Shear Rate (s^{-1})	**Viscosity (Pa·s)**	**Time (s)**	**σ (Pa·s)**
200.0	17.50	0.0	1.97
200.0	17.35	13.2	1.95
200.0	17.24	26.4	1.94
200.0	17.14	40.2	1.93
200.0	17.05	53.4	1.91
200.0	16.98	66.6	1.90
200.0	16.90	79.8	1.90
200.0	16.84	93.0	1.87
200.0	16.78	106.8	1.87
200.0	16.73	120.0	1.86