

SYNTHESIS AND CHARACTERIZATION OF SOLVENT FREE ALKYD RESIN WITH  
HYPERBRANCHED MELAMINE CORE

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NAGEHAN KESKİN

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WITH HYPERBRANCHED MELAMINE CORE**

Submitted by **NAGEHAN KESKİN** in partial fulfillment of the requirements for the degree of **Master of Science in Department of Chemical Engineering, Middle East Technical University** by,

Prof. Dr. Canan Özgen  
Dean, Graduate School of **Natural and Applied Sciences**

\_\_\_\_\_

Prof. Dr. Deniz Üner  
Head of Department, **Chemical Engineering**

\_\_\_\_\_

Prof. Dr. Güngör Gündüz  
Supervisor, **Chemical Engineering Dept., METU**

\_\_\_\_\_

Prof. Dr. Üner Çolak  
Co-advisor, **Nuclear Engineering Dept., Hacettepe U.**

\_\_\_\_\_

**Examining Committee Members:**

Prof. Dr. Göknur Bayram  
Chemical Engineering Dept., METU

\_\_\_\_\_

Prof. Dr. Güngör Gündüz  
Chemical Engineering Dept., METU

\_\_\_\_\_

Assoc. Prof. Dr. Naime Aslı Sezgi  
Chemical Engineering Dept., METU

\_\_\_\_\_

Prof. Dr. Erdal Bayramlı  
Chemistry Dept., METU

\_\_\_\_\_

Prof. Dr. Zühal Küçükyavuz  
Chemistry Dept., METU

\_\_\_\_\_

**Date:** 03.02.2011

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Name, Last name : Nagehan KESKİN

Signature :

## **ABSTRACT**

### **SYNTHESIS AND CHARACTERIZATION OF SOLVENT FREE ALKYD RESIN WITH HYPERBRANCHED MELAMINE CORE**

Keskin, Nagehan

M.Sc., Department of Chemical Engineering

Supervisor : Prof. Dr. Güngör Gündüz

Co-Supervisor : Prof Dr. Üner Çolak

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The use of volatile organic compounds (VOC) in coating materials has adverse effects on both human health and the environment. Due to concern over these problems, coating industry has attempted to decrease the solvent contents of coating materials for the last three decades by developing water dispersed and powder paints. A recently developed method to make solvent free paint is to use highly branched polymers in high solid alkyd resins. Highly branched polymers help to achieve resins with viscosity much lower than its linear counterparts.

In this study, a new alkyd based resin was formulated using long oil alkyd and melamine based hyperbranched polymer having 24 functional groups on its structure. The long oil alkyd was synthesized by using an oil mixture (40% linseed + 60% sunflower). Melamine was preferred as core molecule due to its excellent properties such as greater hardness, alkali and solvent resistance with thermal stability. The resin produced has low viscosity because its hyperbranched structure; therefore, it needs no solvent for its application. The chemical characterization of the resins with different compositions was performed using Fourier Transform

Infrared Spectroscopy and thermal properties were determined by Differential Scanning Calorimetry. Physical and mechanical tests were conducted to determine hardness, flexibility, impact resistance, abrasion resistance, adhesion power, and gloss property of the samples. The viscosity of the resins decreased from 148 Pa.s to 8.84 Pa.s as the hyperbranched polymer to long oil alkyd ratio was increased from 1:3 to 1:24. On the other hand, the hardness values of the resins decreased from 198 Persoz to 43 Persoz. All resins showed excellent flexibility, formability, adhesion, and gloss.

**Keywords:** Paint, Hyperbranched polymer, Melamine, Alkyd, Air drying, Solvent free

## ÖZ

### MELAMİN KÖKENLİ, AŞIRI DALLI VE ÇÖZÜCÜ İÇERMİYEN ALKİT REÇİNE SENTEZİ VE ÖZELLİKLERİNİN BELİRLENMESİ

Keskin, Nagehan

Yüksek Lisans, Kimya Mühendisliği

Tez Yöneticisi : Prof. Dr. Güngör Gündüz

Ortak Tez Yöneticisi : Prof. Dr. Üner Çolak

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Kaplama malzemelerinde uçucu organik bileşen (VOC) kullanımının insan sağlığına ve çevreye olumsuz etkileri vardır. Bu etkilerden dolayı, boya sanayisi son otuz yıldır çözücü miktarını azaltabilmek için su bazlı ve toz boyalar geliştirerek girişimlerde bulunmaktadır. Çözücü içermeyen boya üretmek amacıyla aşırı dallı polimerlerin alkit boya üretiminde kullanılması son zamanlarda geliştirilen bir yöntemdir. Aşırı dallı polimerler reçinenin doğrusal polimerlere göre daha düşük viskoziteye sahip olmasına yardımcı olur.

Bu çalışmada, uzun yağlı alkit ve melamin kökenli, 24 fonksiyonel gruba sahip aşırı dallı polimer kullanılarak yeni bir alkit reçine üretilmiştir. Uzun yağlı alkitler %40 keten ve %60 ayçiçeği yağından sentezlenmiştir. Sertlik, kimyasal malzemelere karşı dayanıklılık ve ısıya karşı kararlılık gibi sahip olduğu üstün özelliklerden dolayı çekirdek molekül olarak melamin tercih edilmiştir. Üretilen reçine aşırı dallı yapının etkisiyle düşük viskoziteye sahiptir; böylece yüzeye uygulama esnasında çözücüye

gereksinim yoktur. Değişik oranlarda üretilen reçinelerin kimyasal özellikleri Fourier Dönüşümlü Kızılötesi Spektroskopisi analizi ile, ısı özellikleri ise Diferansiyel Taramalı Kalorimetre ile belirlenmiştir. Sertlik, esneklik, çarpma dayanımı, aşınma dayanımı, yapışma kuvveti ve parlaklık özelliklerinin belirlenmesi amacıyla fiziksel ve mekanik testler uygulanmıştır. Aşırı dallı polimer ile uzun yağlı alkit oranı 1:3'ten 1:24'e arttıkça reçinenin viskozitesi 148 Pa.s'dan 8.84 Pa.s'a düşmüştür. Öte yandan, reçinenin sertliği 198 Persoz'dan 43 Persoz'a düşmüştür. Tüm reçineler mükemmel derecede esneklik, şekillendirilebilirlik, yapışma ve parlaklık göstermiştir.

**Anahtar Sözcükler:** Boya, Aşırı dallı polimer, Melamin, Alkit, Havada kuruyan, Çözücü içermeyen

To My Family and Şevki

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## NOMENCLATURE

DMPA	Dimethylol proponic acid
HMM	Hexamethylol melamine
HBP	Hyperbranched polymer with melamine core
HBR	Hyperbranched resin
HBR-0	Hyperbranched resin-0 HBP:Alkyd ratio 1:2
HBR-1	Hyperbranched resin-1 HBP:Alkyd ratio 1:3
HBR-2	Hyperbranched resin-2 HBP:Alkyd ratio 1:6
HBR-3	Hyperbranched resin-3 HBP:Alkyd ratio 1:8
HBR-4	Hyperbranched resin-4 HBP:Alkyd ratio 1:12
HBR-5	Hyperbranched resin-5 HBP:Alkyd ratio 1:24
p-TSA	Para toluene sulfonic acid
VOC	Volatile organic compound
w/o	Weight percent

## **CHAPTER 1**

### **INTRODUCTION**

Lately, the use of volatile organic compounds (VOC) as solvents in coating industry has been increasingly considered to be a serious problem. These solvents are normally used to provide formability of the paint by decreasing the viscosity to an optimum value. However, these have negative effects on both environment and human health [1, 2]. Human beings who are subjected to VOC for extended periods are under the risk of contracting Organo Psycho Syndrome (OPS), psycho-neurological disease [2].

Governments have brought about some regulations and restrictions to decrease the use of solvents in coatings because of their negative effects on both the environment and human health [3]. Research conducted to find ways to decrease the need for VOC have produced various solutions [1]:

- Water-based acrylics
- Water-based alkyd emulsions
- Powder coating
- Air-drying, high solid alkyds.

The first two methods are the water-borne coatings, which are preferred because water is an inexpensive and non-toxic solvent. Due to the slow evaporation of water, these methods create some problems such as sagging, shrinking, and popping in coating films. The properties of such types of coatings, therefore, cannot compete with conventional solvent-borne coatings. Still, studies to improve the properties of water borne coatings are being continued [4]. The third method, powder coating, is used only in industry because of difficulties in its application.

The fourth method has focused on the production of air-drying, high solid alkyds. The term 'solid' corresponds here to solvent free portion including resin. The main advantage of this method is that new coatings with low viscosity are produced, which enable these coatings to compete with conventional coatings. The motivation of this research work comes from the use of high solid alkyds because of their excellent properties in making new coating materials. There are different routes to synthesize high solid alkyd resins with low viscosity such as increasing oil length and using narrow molecular weight distributions. The easiest way of producing low viscosity alkyd is increasing oil length which lowers the molecular weight of resin and also introduces more unsaturated groups to the structure. This leads the reduction of the inter-molecular attractions. However, the resins produced need more chemical drying to form a network. This results in slow drying and poor mechanical properties. A useful solution apart from lowering the molecular weight of resins is the increase of their molecular branching. It provides to have a narrower molecular weight distribution to improve film properties [1, 5, 6]. Recent studies have been conducted to produce low viscosity high solid alkyd resins having strong physical and mechanical properties. A new trend in coating industry is to use highly branched polymers with low viscosity so that it can flow like oils [3]. Highly branched chains are more suitable because forming a network is easier with little chemical drying. This provides alkyd resins lower viscosity at the same molecular weight compared to their linear counterparts [6].

Flory et al. theoretically studied highly branched polymers from condensation reactions of AB<sub>x</sub> monomers [7-9]. Dendrimers were introduced at the end of the 1970s by Vögtle and coworkers; however, highly branched polymers were synthesized first by Kim and Webster years later in 1988 [8, 10]. This type of polymers is used in many areas because of their lack of entanglements, globular shape, and a large number of functional groups [8]. One of the areas is the synthesis of hyperbranched alkyd resins. They are synthesized by an esterification reaction of polyester polyols and unsaturated fatty acids obtained from triglyceride oils. Triglyceride oils are considered as an important biodegradable and cheap raw material used in the production of alkyd resins [11].

There are different studies in the literature based on producing low viscosity resin to reduce solvent content in coating materials. Bat et al. synthesized hyperbranched resins [6]. Dipentaerythritol used as the core molecule was twice esterified with dimethylol propionic acid and then esterified with castor oil fatty acids. The hydroxyl groups present in the ricinoleic acid were then reacted with linseed oil fatty acids and benzoic acids. They showed that an increase in the amount of the linseed oil fatty acids increased the hardness and decreased the viscosity of the resins. Another similar study was done by Karakaya et al. [12]. Core molecule, dipentaerythritol, was transesterified with castor oil and a mixture of castor and linseed oil. The hydroxyl groups were then esterified with dimethylol propionic acid. The hyperbranched resin produced was mixed with melamine-formaldehyde resin to improve its properties. They showed that hyperbranched resins mixed with melamine-formaldehyde had higher hardness values but lower gloss, adhesion, and bending [12].

In the light of these studies, a new recipe was developed in current study to synthesize low viscosity resin to attain high hardness values while keeping gloss, adhesion, and bending properties at high performance. Hexamethylol melamine core was twice esterified with dimethylol propionic acid to produce hyperbranched polymer, and then, it was esterified with long oil alkyds to synthesize low viscosity hyperbranched alkyd resin. This work was divided into three parts. The first part was the synthesis of hyperbranched polymer with melamine core. Melamine was selected as core molecule due to its s-triazine ring in the structure; this structure provided it to have excellent hardness and chemical resistance properties. It is mostly used as crosslinkers in coating to improve strength of the film [13]. Hyperbranched polyester was synthesized by pseudo-one step esterification reaction of hexamethylol melamine and dimethylol propionic acid with acid catalyzed reaction. The second part was the synthesis of long oil alkyds from linseed and sunflower oil mixture. Long oil alkyds were synthesized by monoglyceride method by using glycerol and phthalic anhydride as reactants at 170°C. The molecular weight was controlled by determining the acid number during

reaction. The third and final part was the synthesis of solvent free hyperbranched alkyd resin. This resin was produced by an esterification reaction of long oil alkyds and melamine based hyperbranched polymers at 170°C.

The produced resin was applied onto a glass or metal plate by a film applicator at 100 µm wet thickness, and cured in oven at 120°C for 24 hours. The crucial point is that the resin contains no solvent in application while other studied hyperbranched alkyd resins in the literature contain some amount of solvent. Chemical characterization of the resins was performed using Fourier Transform Infrared Spectroscopy and thermal properties were determined by Differential Scanning Calorimetry. After the film formation, physical and mechanical tests were conducted to determine hardness, flexibility, impact resistance, abrasion resistance, adhesion power, and gloss property of the samples.

## **CHAPTER 2**

### **LITERATURE SURVEY**

#### **2.1 Surface Coating**

Surface coating is a process where a solid or liquid material is spread over a surface and forms a thin film. It is used for protection, aesthetic attraction, and some other functional purposes like self-healing in case of damage [14]. The protection of coatings is mainly based on resistance to water and chemicals with improvement of mechanical properties such as hardness, flexural strength, impact and abrasion resistance. The aesthetic consideration deals with color and gloss of finished surface [15, 16].

##### **2.1.1 Composition of Coatings**

###### **2.1.1.1 Resins or Binders**

The main part of the coating is resin which is the film forming agent of the coating material. It adheres to the substrate to form the continuous film on the surface [17]. Resins mainly determine the application method, drying and hardening behavior, adhesion to the substrate, mechanical properties, and chemical resistance [18]. There are two types of resins, namely natural and synthetic resins [16]. In paint industry, most of the resins used are synthetic resins such as alkyds, acrylics, and epoxy resins [18].

### **2.1.1.2 Pigments**

Pigments are finely milled, solid, and insoluble materials which remain suspended in the resin after the film formation [18]. Primary purpose of pigments is to provide color and opacity of the coating film, and also, coating power of the paint is directly related to pigments [16].

### **2.1.1.3 Additives**

Even though additives are used in small amounts, they help to improve properties of the coating material. They are classified according to their functions such as leveling agents, film formation promoters, wetting agents, dispersants, anti-foaming agents, catalyzing agents, anti-floating and anti-flooding agents, anti-skinning agents, matting agents, neutralizing agents, thickening agents, preserving agents, and corrosion inhibitors [18].

### **2.1.1.4 Solvents**

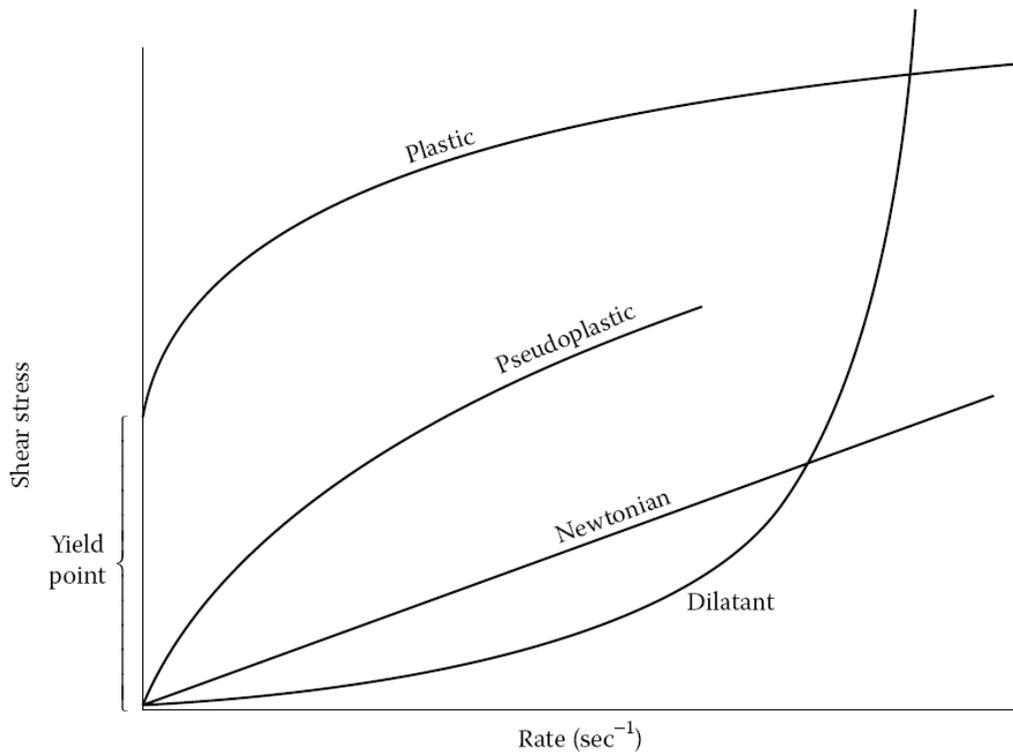
Solvents are used for providing easy application of the coating by lowering the viscosity. After the application, solvent evaporates and a thin film forms on the surface [16].

In coating industry, commonly used solvents are aromatic hydrocarbons, aliphatic hydrocarbons, esters, ethers, and ketones. Since most of them are highly toxic and volatile at room temperature, they are harmful for both human and environment [18]. Moreover, they are highly flammable, and special care is required for storage and handling to prevent explosion. These factors designate the scope of this study as production of solvent free coating material with having good properties (rheology, adhesion, hardness etc.) which meet the requirements of coating industry.

## **2.1.2 Properties of Coating**

### **2.1.2.1 Rheology**

Science of polymer rheology deals with both flow and deformation properties of polymeric materials. Among these properties, the most important one is viscosity ( $\eta$ ) which is the ratio of shear stress to shear rate. Applying force to the coating material results in different changes for different coating materials. If the ratio of shear stress to shear rate of a fluid is constant, then, it is said to be Newtonian fluid. The viscosity of a Newtonian fluid is independent of shear rate (or shear stress). The ratio of shear stress to shear rate of some fluids are not constant. These fluids are called non-Newtonian fluids. In general, polymer solutions, colloids, dispersions and suspensions show non-Newtonian behavior. Shear thinning fluids are a kind of non-Newtonian fluids. Materials in which the viscosity falls with increasing shear rate designate shear thinning (pseudoplastic). Viscosity rising with increasing rate of shear is called shear thickening. The term dilatancy is often applied to shear thickening behavior. In some cases, no detectable flow occurs unless a minimum shear stress is exceeded. Viscosity behavior of different coatings is shown in Figure 2.1 [15, 17].



**Figure 2.1** Variation of shear stress with shear rate for different coatings [17].

After the application, viscosity of the coating causes formation of various deformations such as sagging, slumping, and leveling [17]. Therefore, in order to make a good coating material, its rheology should be deeply considered to have adequate viscosity with good wetting and leveling properties without any sagging [19].

### 2.1.2.2 Hardness

The property of hardness is explained by resistance to deformation when a force is applied. The deformation term is used from indentation, scratching, cutting, and bending. Hardness measurements are applied for quality control of materials. There are three types of hardness tests. First type is scratch hardness, and it measures the resistance of a specimen to fracture deformation made by a sharp material.

Second type is indentation hardness, and it measures the load needed to produce a penetration with a determined depth, or measures the depth of the indentation made by a tool with fixed load. The last one is pendulum hardness, and it measures the number of swings of a pendulum which freely swings on a coated test panel. When the pendulum swings, kinetic energy is absorbed by the film and pendulum loses energy. The softer the coating, the greater it absorbs energy, and the smaller the number of swings [20].

### **2.1.2.3 Adhesion**

In order to form a film on the surface, the coating material should establish strong adhesion with the surface of the substrate. Adhesion force depends on the physical and chemical interactions between the paint and the substrate. Surface roughness is considered as the most important physical interaction since it provides mechanical connection between paint and interface. On the other hand, presence of functional groups both in coating material and substrate surface develops chemical interactions by the formation of chemical bonds at the interface [17].

### **2.1.3 Film Formation**

Film formation is a crucial property for coatings which transforms liquid material into a solid film that adheres tightly to the surface. After the application of the paint film formation occurs by two different drying processes known as physical and chemical drying. Physical film formation process is due to evaporation of the solvent from the paint to form a solid. Chemical film formation process occurs by the oxidation reaction [21]. In this process atmospheric oxygen reacts with resin to transform sticky and liquid film into a solid film. In some film formation processes physical and chemical drying is observed simultaneously. First stage is evaporation of solvents and the next one is oxidation process [18].

## **2.2 Conventional Coatings**

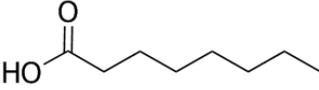
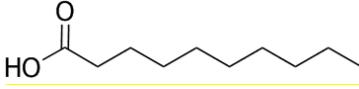
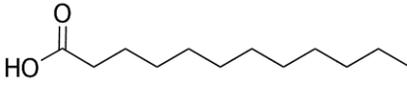
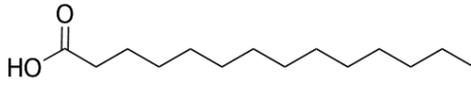
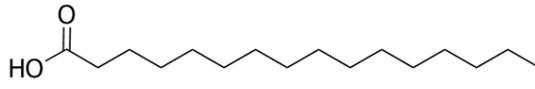
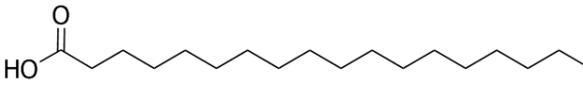
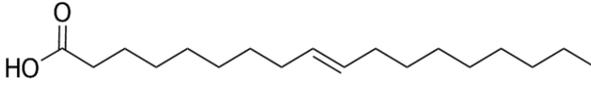
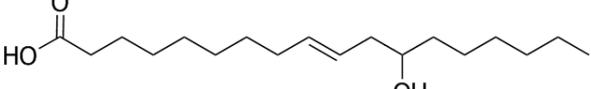
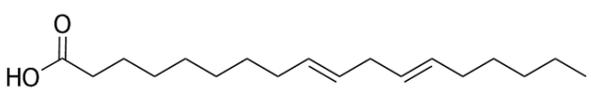
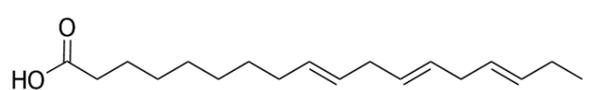
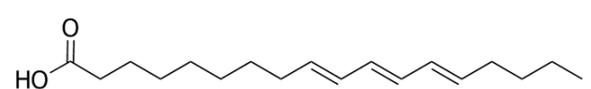
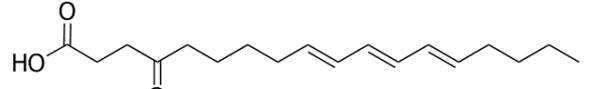
Conventional coatings consist of combinations of resin, pigment, additives, and solvent which is also known as 'solvent borne' coatings in the industry. Resins produced from triglyceride oils have known as the oldest organic coating materials for more than 2000 years [18].

Oil based resins, mostly known as alkyd resins, have dominated in coating industry due to their excellent properties [16]. Their properties mostly depend on type of triglyceride oil and the acid used in the synthesis. In this respect; properties of triglyceride oils and alkyd resins will be explained in detail in the next section.

### **2.2.1 Triglyceride Oils**

Triglyceride oils which are generally known as vegetable oils are not only used for food, but also for surface coatings, printing inks, soaps, cosmetics, pharmaceuticals, lubricants, emulsifiers, multi-purpose additives, bio-diesel, plasticizer, etc. In recent years, renewable resources are favored in the production of surface coatings over petroleum products due to their biodegradable properties [2, 21, 38]. Triglyceride oils are composed of three moles of fatty acid with one mole of glycerol [11, 23]. There are different types of fatty acids summarized in Table 2.1 and types of fatty acids designate the characteristics of the oil. The degree of unsaturation determined by the number of double bonds (C=C), the degree of conjugation related to the positions of the double bonds, and the presence of functional groups like hydroxyl are important characteristics of oils that affect the properties of the resin produced [20, 23, 24]. Studies showed that most commonly used triglyceride oils in coating materials are sunflower, soybean, linseed, castor, safflower, canola, palm, tall, and rapeseed oils [11, 23].

**Table 2.1** Types of fatty acids [20].

	<b># of C atoms</b>	<b># of double bonds</b>	<b>Formula</b>
<b>Saturated Fatty Acids</b>			
Caprylic	8	-	
Capric	10	-	
Lauric	12	-	
Myristic	14	-	
Palmitic	16	-	
Stearic	18	-	
<b>Unsaturated Fatty Acids</b>			
Oleic	18	1	
Ricinoleic	18	1	
Linoleic	18	2	
Linolenic	18	3	
Eleostearic	18	3	
Licanic	18	3	

### 2.2.1.1 Properties of Triglyceride Oils

Degree of unsaturation is the most important parameter to determine the properties of glyceride oils. It is measured by the amount of iodine (in mg) to react completely with double bonds in 100 g of sample [11]. The phase of the oil is determined by degree of unsaturation; oils having high degree of unsaturation are liquid whereas oils with low degree of unsaturation are solid at room temperature. In addition to that, degree of unsaturation also determines the drying properties of oils [20].

Triglyceride oils are classified as drying, semi-drying, and non-drying oils. This classification is done by using both iodine and drying index values (Eq. 2.1). Drying oils have drying index higher than 70 and iodine value higher than 130 [11, 20]. The fatty acid composition of oils is given in Table 2.2.

$$\text{Drying Index} = (\% \text{ Linoleic acid} + 2 \times \% \text{ Linolenic acid}) \quad \text{Eq. (2.1)}$$

Sailer et al. examined linseed and sunflower oil based resins to determine the effect of fatty acid content on drying property [24]. Linseed oil dries faster and forms more cross-link than sunflower oil. Consequently, existence of linolenic and linoleic acids verifies the drying index of the oils because linolenic acid has three and linoleic acid has two double bonds as seen from Table 2.1 [24].

**Table 2.2** Fatty acids compositions of oils [20].

<b>Fatty Acid %</b>	<b>Coconut Oil</b>	<b>Castor Oil</b>	<b>Grape Seed Oil</b>	<b>Linseed Oil</b>	<b>Palm Oil</b>	<b>Safflower Oil</b>	<b>Sunflower Oil</b>	<b>Soya Bean Oil</b>	<b>Tung Oil</b>
<b>Caprylic</b>	6								
<b>Capric</b>	6								
<b>Lauric</b>	44								
<b>Myristic</b>	18				1				
<b>Palmitic</b>	11	2	9	6	48	8	11	11	4
<b>Stearic</b>	6	1	4	4	4	3	6	4	1
<b>Oleic</b>	7	7	20	22	38	13	29	25	8
<b>Ricinoleic</b>		87							
<b>Linoleic</b>	2	3	67	16	9	75	52	51	4
<b>Linolenic</b>				52		1	2	9	3
<b>Eleostearic</b>									80
<b>Licanic</b>									
<b>Iodine Value</b>	7.5-10.5	81-91	130-140	155-205	44-54	140-150	125-136	120-141	160-175

## **2.3 Alkyd Resins**

In this study, solvent free coating material was synthesized by using alkyd resins. The 'alkyd' term is first coined by Kienle and Ferguson at 1927 from the condensation reaction of alcohol and acid [25, 26]. Alkyd resins are known as the polyesters connected with unsaturated fatty acids [5, 14]. They were very important paints in the past because of their strong strength, high film hardness, and gloss retention [18]. Another advantage of this type of resin is the usage of inexpensive and natural raw materials [11, 26].

Alkyd resins are classified as long, medium, and short oil resins depending on the weight percentage of fatty acids involved in the resin. Alkyds which have fatty acid content higher than 55% are considered as long oil alkyds; between 45-55% medium oil alkyds, and lower than 45% short oil alkyds. In addition to percentage of fatty acid, the types of fatty acids also affect the properties of alkyds. Drying property of the resin is determined by the degree of unsaturation values of fatty acids contained [16, 25]. Therefore, film properties are mostly determined by the type of fatty acids or oils used in the production of alkyd resins [27].

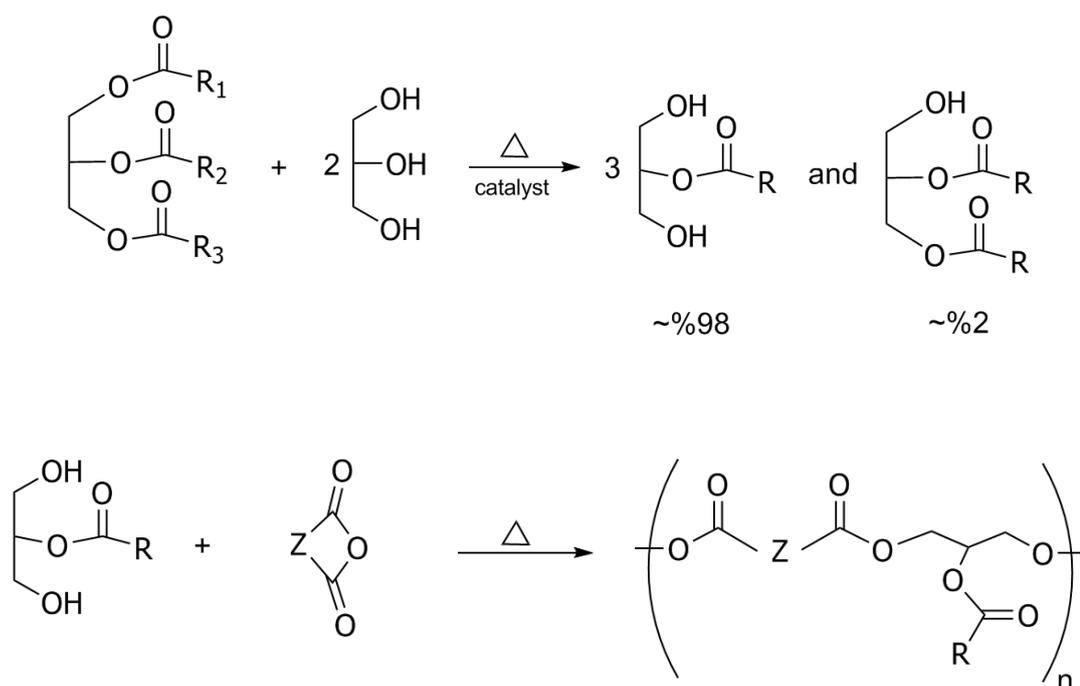
### **2.3.1 Production of Alkyds**

Most common methods for the production of alkyd resins are alcoholysis and fatty acid methods.

#### **2.3.1.1 Alcoholysis Method**

Alcoholysis method which is also known as monoglyceride method has two steps at temperatures of 240-260°C. The reactions are carried out under inert atmosphere to prevent penetration of air which results in darkening of the products. The first step is transesterification reaction conducted by triglyceride oils and polyalcohols (glycerol). This reaction is speeded up using catalysts like NaOH, KOH, etc. The product of this reaction is partial glycerides composed of monoglycerides as 97-

98% and diglycerides as 2-3%. The reaction is controlled by methanol test by dissolving one volume of sample into three volumes of methanol. The produced monoglycerides are soluble in methanol, whereas oil does not dissolve in it. Therefore, reaction continues until one volume of sample totally dissolves in methanol. Produced partial glycerides are esterified with a polyacid. Most commonly used polyacids are phthalic, maleic, glutaric, and succinic anhydrides. Esterification reaction is controlled by acid number and the reaction is stopped when it reaches the desired value. The reactions are given in Figure 2.2 [11, 24, 27, 28].



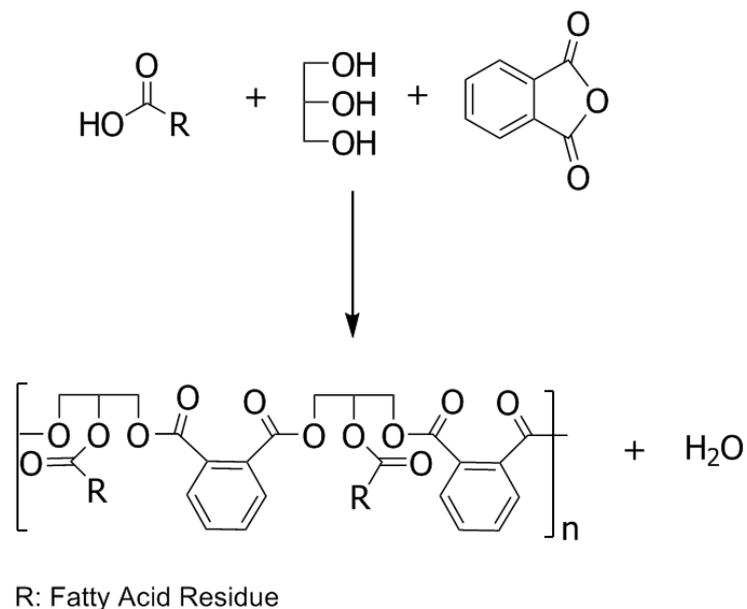
R: Fatty acid residue ( $R_1$ ,  $R_2$ , or  $R_3$ )  
Z: where,  $-(\text{CH}_2)_3-$  for glutaric acid  
 $-\text{CH}=\text{CH}-$  for maleic anhydride  
 $-(\text{CH}_2)_2-$  for succinic anhydride  
benzene ring for phthalic anhydride

**Figure 2.2** Synthesis of oil based alkyd using monoglyceride method [29].

Dutta et al. reported that the use of high temperature for oils exposes some difficulties, because they may be involved in some other reactions like Diels-Alder reaction, oxidative polymerization, ester interchange, cyclization, etc. [22]. These reactions cause high molecular growth and consequently high viscosity. They conducted a study about resin produced from non-heated and heated oils at 250-315°C; and showed that high temperature accelerates the oxidative reaction which initiates thermal degradation. The degradation resulted in the formation of products like ketones, aldehydes, free acids, hydroxyl compounds, etc [22].

### **2.3.1.2 Fatty Acid Method**

Fatty acid method is a one-step process taking place by the addition of fatty acid, polyalcohol, and polyacid simultaneously into the reactor. The complete reaction is given in Figure 2.3 [11]. This method gives the opportunity of higher control of fatty acids in the alkyd to obtain alkyd resins having desirable molecular weight distributions [24, 25]. The advantage of the fatty acid method over the monoglyceride method is a better control of molecular weight and its distribution. Higher quality and higher performance alkyds are produced using the fatty acid method. However, monoglyceride method is better than the fatty acid method from the cost point of view [30].

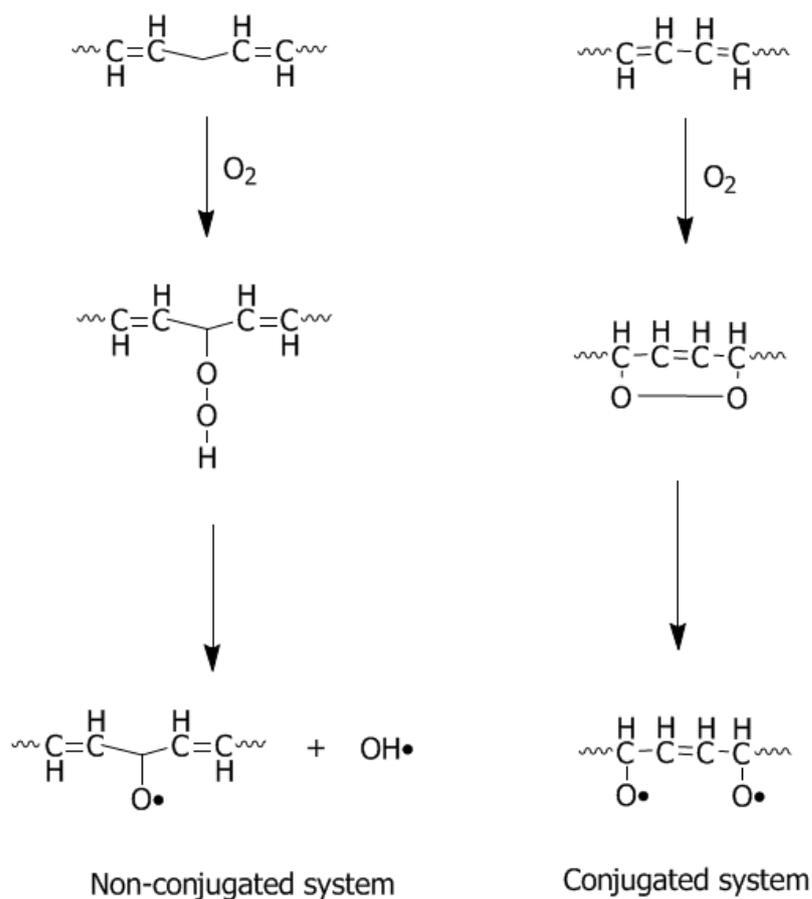


**Figure 2.3** Esterification reaction [30].

### 2.3.2 Drying Process of Alkyd Resins

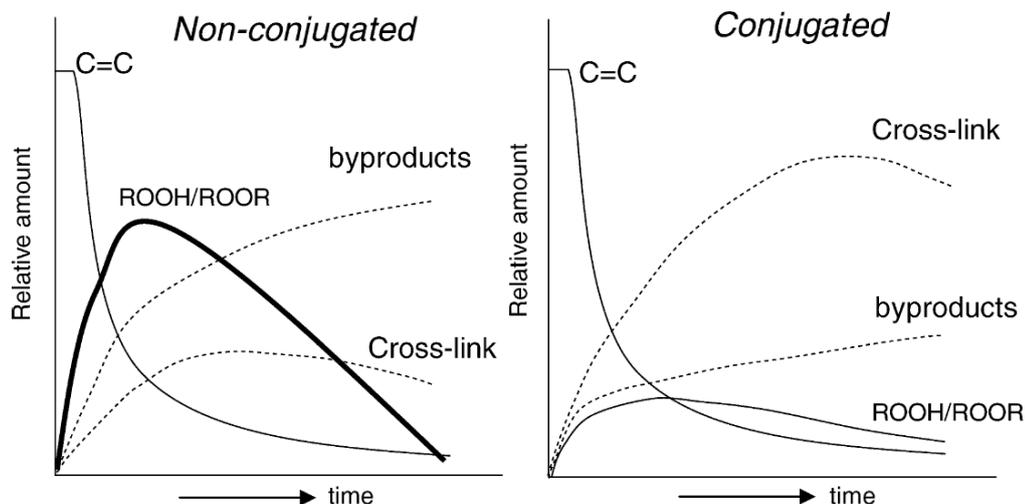
Film formation process is an important part for coating. Alkyd resins are used for production of air-drying coating materials. Drying process of alkyd resin is based on the reaction between oxygen and double bonds of unsaturated fatty acids [31]. The process starts with the formation of a hydroperoxide by the reaction of atmospheric oxygen and carbon-carbon double bond. Produced hydroperoxides decompose to create alkoxy and peroxy free radicals and these free radicals react with each other to form cross-links [15, 16, 20, 21, 24, 31, 32].

Non-conjugated and conjugated unsaturated fatty acids depict somehow different drying mechanisms as shown in Figure 2.4 [16].



**Figure 2.4** Free radical formations of non-conjugated and conjugated systems [16].

The differences in the degree of conjugation and unsaturation of fatty acid molecule lead to differences in the formation of free radicals and cross-links as well [23]. Oyman et al. conducted a study on the differences of oxidation behavior in non-conjugated and conjugated double bonds by using linseed oil (non-conjugated) and tung oil (conjugated). The results of their experiments are summarized in Figure 2.5. Conjugated double bonds form more cross-links than non-conjugated ones; therefore they have shorter drying times than non-conjugated double bonds [32].



**Figure 2.5** Oxidation of non-conjugated and conjugated double bonds [32].

Atimuttigul et al. did a research on the properties of coating materials where different types of oils are used (corn oil, rice oil, sunflower oil, soya bean oil, and dehydrated castor oil) for the production of alkyd resins by monoglyceride method [27]. Dehydrated castor oil has 83% of linoleic acid and it depicts the highest viscosity and shortest drying times due to high rate of cross-link formation. Rice oil, having the fewest double bonds, shows the longest drying times. Fatty acids and double bonds affect certain properties of resins such as drying times and viscosity. In addition, an increase in the reaction temperature only had an influence in darkening the alkyd color and decreasing the drying times of coating films [27].

Oxidation reaction of the resins is accelerated by the addition of driers known as metal complexes. Metal driers are used for decomposition of produced hydroperoxides to form free radicals [18,33]. Driers containing transition metals with several oxidation states are called primary driers. They act as catalysts of hydroperoxide decomposition in a redox reaction. Studies showed that activation energy required to decompose two moles of hydroperoxides is decreased from 90-170 to 40-50 kJ in the presence of metal catalyst. Metallic salts with one oxidation state are classified as secondary driers which favor the primary drier action [34].

These metal driers are classified as top and auxiliary according to their functions. Top driers are used for supporting cross-link formation at the surface of the film, whereas auxiliary driers function on the whole film [24]. Manganese and cobalt metals promote the rapid surface drying of the film; on the other hand, zinc, calcium, lead, and barium metals are used as auxiliary driers [20, 9, 2].

## **2.4 New Trends in Coating Industry**

In addition to demands of improvements in coating properties, environmental and health problems have been a driving force for the coating industry to study new coating systems. The trend is to keep the amount of solvent low while improving the physical and mechanical properties. There are three major types of new coating systems; water-borne coatings, powder coatings, and high solid coatings [19].

Water-borne coating system has gained popularity due to the environmental regulations of VOC. Although water is an inexpensive and environmentally friendly solvent slow evaporation rate of water creates some defects such as popping, shrinking, and sagging. It therefore yields poor chemical and physical properties when compared with the conventional solvent-borne coatings [4]. Powder coating is applied to a surface by high voltage electrostatic spraying or dipping and cured in high temperature ovens. It represents environmental friendly technology with strong physical properties but it is not applicable to use at home; this technique is only used in small scale industrial applications [35]. High solid coatings are conventional coatings including greater than 60% of solids including resin by weight. VOC content is therefore decreased while keeping the properties same as the conventional one. The resin synthesized in this research work is also high solid resins.

### **2.4.1 High Solid Alkyd Resins**

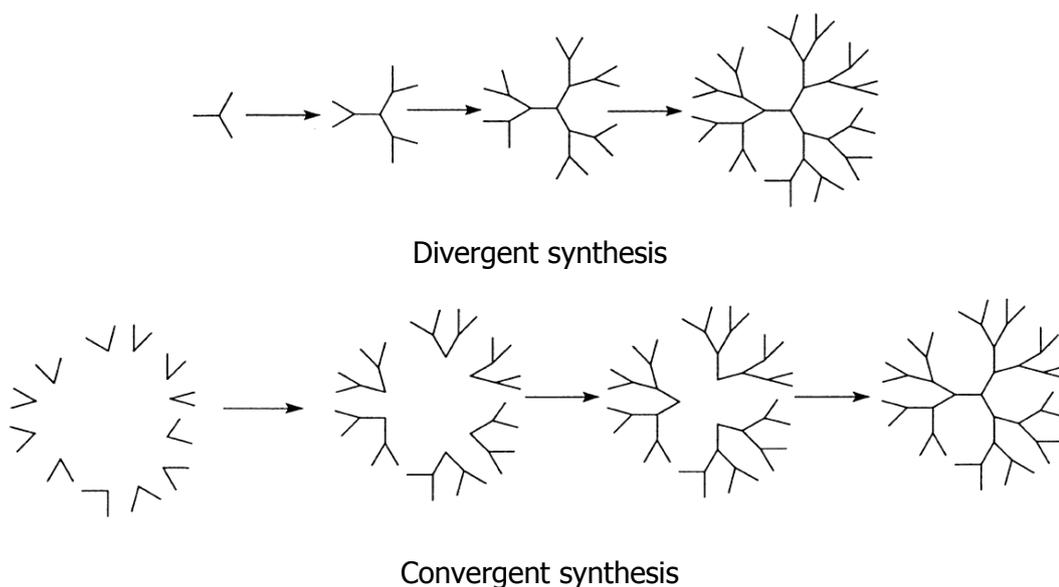
The simplest route to synthesizing high solid alkyd resins is increasing the fatty acid content or OH/COOH content in order to decrease the molecular weight of

oligomers. However, high solid alkyd resins synthesized by these methods have poor properties such as slow drying and poor mechanical performance. In order to overcome these problems, they increased fatty acid branching on the backbone [5].

## 2.5 Highly Branched Polymers in Coating

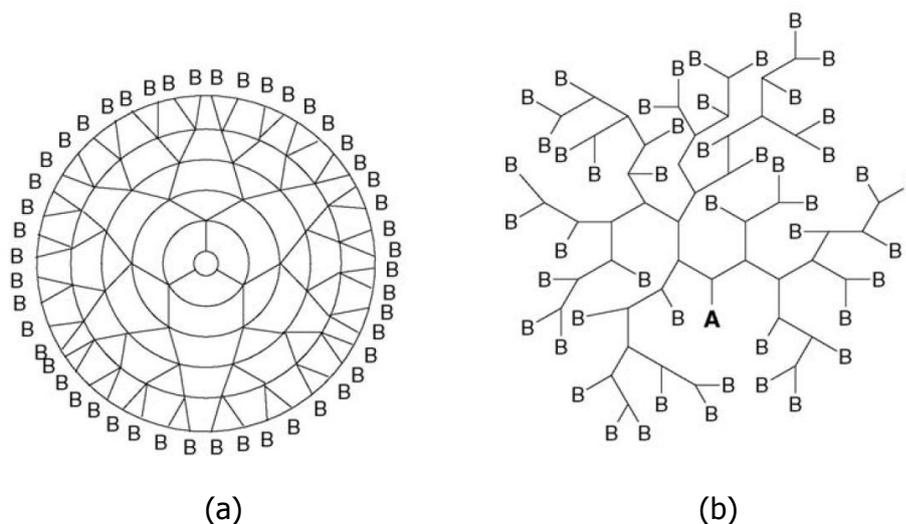
Dendritic and highly branched polymers were firstly theoretically introduced by Flory in 1952 by using the term 'three-dimensional polycondensations'. Dendrimers are defined as uniform polymers having globular shape with many functional groups [7-9].

Dendritic polymers are synthesized by two methods; convergent and divergent methods (Figure 2.6). Convergent method is an outside-to-inside procedure which combines preformed dendrons with a desired core molecule. On the other hand, divergent method is an inside-to-outside procedure which starts with the core molecule and branches are attached to it as a stepwise addition [36, 37].



**Figure 2.6** Two different synthetic routes [38].

There are two different types of dendritic polymers; dendrimers and hyperbranched polymers. Dendrimers are symmetrical, perfectly branched polymers; whereas, hyperbranched polymers are unsymmetrical polymers having random branching as shown in Figure 2.7 [8, 38].



**Figure 2.7** Representation of (a) dendrimer and (b) hyperbranched polymers [8].

## 2.5.1 Properties of Dendritic Polymers

### 2.5.1.1 Thermal Properties

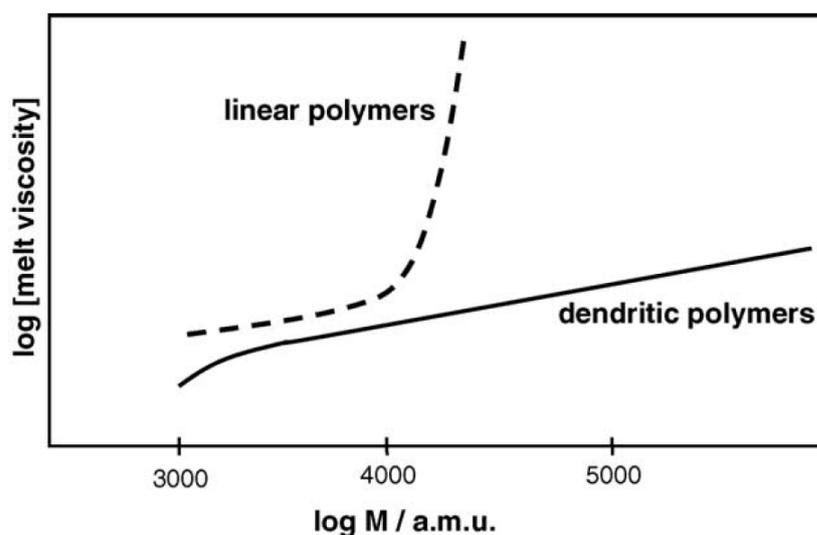
Glass transition temperature ( $T_g$ ) is considered as one of the most important characteristics of dendritic polymers. It is based on their amorphous structure which results in highly branched geometry and polarity of the end-groups [8, 19]. Crosslinking density and presence of a rigid functional group such as an aromatic group increase the  $T_g$  of the polymer [19, 23]. Several researchers reported  $T_g$  behavior of a dendritic polymer up to 100°C [19].

### 2.5.1.2 The Mechanical and Rheological Properties

Large number of branches and globular shape of dendritic polymers cause lack of entanglement. Non-entangled state causes poor mechanical properties like brittle polymers which do not have common usage as thermoplastics [8].

Johansson et al. has studied rheological behavior of hyperbranched polyesters and found out that polyesters having small end-groups exhibit a Newtonian behavior, whereas hydroxyl groups bring in a shear thinning behavior due to hydrogen bonding [19]. Newtonian behavior is explained by the structure of the resin due to the lack of entanglement [39].

Viscosity of dendritic polymers is highly different from linear polymers. For linear polymers, increasing the molar mass above a critical value causes high entanglements between chains. This causes a sharp increase in melt viscosity. On the other hand, for dendritic polymers, increasing the molar mass does not cause entanglement due to the globular shape; therefore, melt viscosity does not exhibit a sharp increase. This situation is illustrated in Figure 2.8 [8].



**Figure 2.8** Melt viscosity vs. molar mass of linear and dendritic polymers [8].

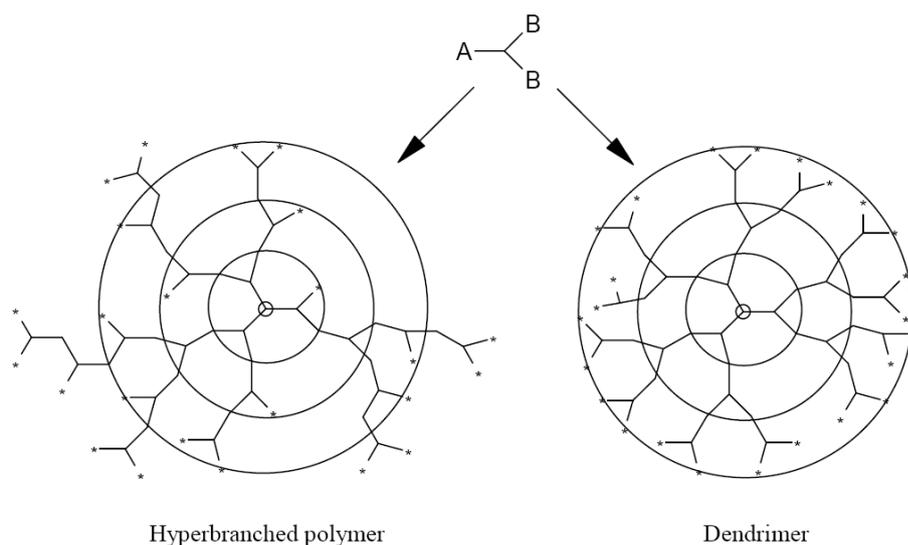
### **2.5.1.3 Solution Behavior**

The lack of chain entanglement and the presence of functional groups also affect the solution behavior of the hyperbranched polymers. They have high solubility in different solvents [19].

### **2.5.2 Hyperbranched Polymers**

In this study, hyperbranched polymers were selected to produce solvent-free high solid alkyd resin. Hyperbranched polymers were first introduced by Kim and Webster in 1988 with the synthesis of hyperbranched polyphenylene. Due to their physical and chemical properties and potential applications in various fields, interest in hyperbranched polymers is growing rapidly [10]. Properties like lack of chain entanglements, spherical shape, and presence of a large number of functional groups in the structure are the advantages that determine new application areas of hyperbranched polymers [8, 37, 40]. Particularly, functional groups on the structure determine the physical and chemical properties such as aggregation, reactivity, stability, and solubility [38].

The synthesis of hyperbranched polymers has advantages over dendrimers. The synthesis of dendrimer has protection, deprotection, and purification steps which make it difficult and time consuming in large scale synthesis. On the other hand, synthesis of hyperbranched polymers has one-step procedure and no purification steps [8, 19, 39]. The procedure of the synthesis has been reported by Malmström and Hult as a pseudo-one-step esterification reaction at 140°C conducted with an acid catalyst in the bulk [36]. Johansson et al. illustrated the schematic representation of the unsymmetrical synthesis route of hyperbranched and symmetrical synthesis route of dendrimer polymers as shown in Figure 2.9 [19].

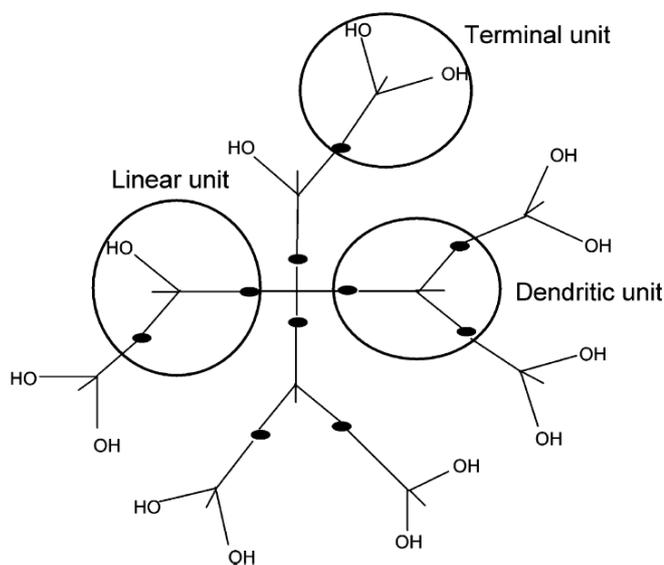


**Figure 2.9** Synthesis route of hyperbranched and dendrimer polymers [19].

### 2.5.2.1 Applications of Highly Branched Polymers

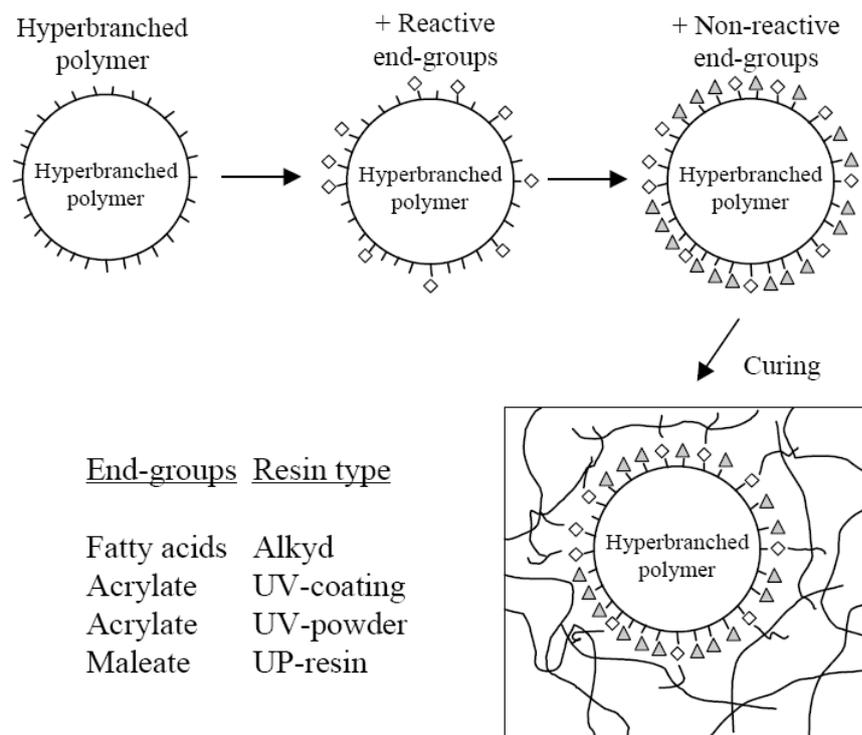
Highly branched polymers offer high functionality, broad variety of functional groups, high solubility, and special rheological behavior which offer them wide industrial application areas. [3]. In coating industry, hyperbranched polymers are used in powder coatings, high solid coatings, flame retardant coatings, and barrier coatings [10].

In hydroxylated hyperbranched polymers (Figure 2.10), extended number of polar side chains exists. They provide excellent adhesion with different substrates such as glass, metal, synthetic fabrics, etc. [41]. These polymers have been synthesized by using different core molecules. Malmström [36] and Manczyk [5] used trimethylol propane; Murillo [40] used pentaerythritol; and Zagar [42] used pentaerythritol as core molecule to synthesize hydroxylated hyperbranched polymers. The choice of monomer structure directly affects the properties of produced polymer. For instance polymers produced from aromatic monomers are resistant to high temperatures; polymers containing halogens exhibit non-flammable property, and polymers containing fluorine have high resistance to water and solvents [11].



**Figure 2.10** Representation of hydroxylated hyperbranched polyester [39].

Hydroxyl ended hyperbranched polymers can be functionalized by different end groups. Therefore, different types of the coating materials can be made depending on the types of end groups. Johansson et al. have synthesized hydroxyl ended hyperbranched polymer [19]. In their study, synthesized polymer was reacted with different end groups to illustrate the principle of synthesizing different types of resins (Figure 2.11). Cross-link density of the final network can be adjusted by using different fractions of non-reactive/reactive end groups. Different types of end groups produce different resins ranging from alkyds to UV-curable resins and powder coatings. For example a hyperbranched polymer reacts with fatty acid to form an alkyd resin; whereas, it reacts with maleate to form an unsaturated polyester resin (UP-resin). Hydroxyl end groups can be functionalized either by reactive groups which serve in forming cross-links; or by non-reactive groups which modify the polarity of the resin [19].

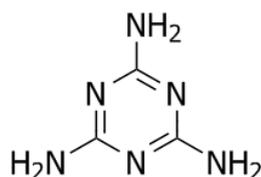


**Figure 2.11** Synthesis of different resins based on hyperbranched polymers [19].

In our study, melamine based hydroxyl ended hyperbranched polymer was synthesized. This new molecule was then reacted with long oil alkyds to produce hyperbranched alkyd resins.

## 2.6 Use of Melamine Core in Coating Material

Melamine has s-triazine ring (1, 3, 5-triazine) in the structure (Figure 2.12) which provides greater hardness, alkali and solvent resistance with thermal stability [43]. Due to these properties, it is an important industrial chemical used for producing thermosetting polymers, crosslinkers in coating, and ingredient in flame retardants etc. [13].



**Figure 2.12** Structure of melamine.

In coating industry, melamine is used for the production of coil coating. It is used for protecting metal surfaces from environmental factors and hardness improvement for scratch resistance. There are different coil coating systems like polyester/melamine, polyvinylidene fluoride, and polyvinyl chloride. However, polyester/melamine system is the most commonly used one due to its superior properties [44].

In addition to coil coating, amino resins are produced by combination of melamine and formaldehyde. The melamine-formaldehyde resin is one of the hardest and stiffest polymeric materials in coating applications [45]. Ahmad et al. has cured hydroxylated linseed oil epoxy resin with butylated melamine formaldehyde resin by changing weight percentages to observe changes on coating properties. The results showed that cured resins exhibited better coating properties in terms of higher scratch hardness, gloss, adhesion, flexibility, chemical and thermal resistance [43].

Karakaya et al. have synthesized oil based hyperbranched resin with dipentaerythritol core and mixed produced resin with melamine-formaldehyde to improve its properties [12]. They showed that incorporating melamine-formaldehyde resin into hyperbranched resin improved hardness. However, it decreased gloss, adhesion, and bending resistance [12].

Van Benthem et al. reported the advantages of using a core molecule with a more dendritic architecture as, further reduction of chain entanglements and globular molecular morphologies, resulting in lower intrinsic viscosities [3].

### **2.6.1 Synthesis of Hyperbranched Polyester with Melamine Core**

In our study, in order to use melamine as a core in hyperbranched polyester, it was first converted into hexamethylol melamine, and then, it was esterified to produce hyperbranched polymer. First reaction product, hexamethylol melamine, is a type of methoxylated melamines which are used at different areas. It was synthesized by Manley in 1972 [46]. The reaction of melamine and formaldehyde at 65-70°C forms prepolymer of methylol melamines; di-, tri-, tetra-, penta-, or hexamethylol melamines. The percentage of major product depends on melamine:formaldehyde ratio. Using 1:3 ratio leads to trimethylol melamine; while 1:6 or 1:8 ratios are necessary for the synthesis of hexamethylol melamine. The produced prepolymer is dissolved in methanol and dried in vacuum at 50°C. Finally, purification is achieved by water, since solubility of hexamethylol melamine in water is lower than other methylol melamines [46, 47].

This synthesis procedure has some difficulties due to easy gelation. In a kinetic study on melamine compound, Dixon et al. stated that rate of prepolymer formation from melamine and formaldehyde compounds were essentially affected by pH of the solution. According to reported studies in the literature, the rate of prepolymer formation is affected by hydrogen ion concentration of melamine and formaldehyde compounds [48]. For this reason, formaldehyde is neutralized before the reaction to adjust the pH of the overall solution to 8.0-9.0 [46, 47, 49]. After the formation of prepolymer, further heating causes high rate of condensation to form crosslinked high molecular weight product [49]. Consequently, in order to prevent gelation for the synthesis of hexamethylol melamine, the pH of the solution and optimum rate of condensation has to be adjusted accordingly.

After the synthesis of hexamethylol melamine compound, esterification reaction was conducted to produce hyperbranched polyester with melamine core. Malmström E. et al. [36] have used a one-step procedure to synthesize hyperbranched polyester using trimethylol propane as core molecule. Their

procedure is an esterification performed in the bulk using acid catalyst with no purification step.

## **2.7 Hyperbranched High Solid Alkyd Resins**

In our study, hyperbranched alkyd resins were synthesized by a classical esterification reaction of hyperbranched polyester and long oil alkyds. Globular shape and lack of entanglement of hyperbranched alkyd resins result in low viscosity resins which do not need solvent for thinning. Perstorp et al. studied air drying resins made of hyperbranched poly(bismethylolpropionic acid) esterified with tall oil fatty acids [3]. They compared viscosity and drying times of hyperbranched alkyd resins with classical high solid alkyd resin. They reported that hyperbranched alkyd resins have lower viscosity and shortened drying times. However, a drawback was also reported as high oil length alkyds caused low film hardness in hyperbranched alkyd resins [3]. Manczyk et al. studied the drying properties of hyperbranched alkyd resins and they concluded that the globular structure provides some advantages to the resins. Highly branched resins have a globular shape, and therefore, fatty acids residues being located on the surface of the structure are easily accessible to reactive oxygen [5].

Atimuttigul et al. studied the effects of the type of oil on the properties of alkyd resins [27]. The color of the resin depends on both the temperature and type of fatty acids. Particularly the presence of linolenic acid results in darkness. They showed that alkyd resins produced from soya bean oil, which has 5-11% linolenic acid had the dark color whereas alkyd resins produced from corn oil which has 0-2% linolenic acid had light color, both produced at the same reaction temperature [27]. This is the reason why linseed oil is not much preferred in resin production even though it imparts excellent drying property by having high linolenic fatty acid content; it gives dark color resins [50]. Furthermore, high reaction temperature also gives darker color than lower reaction temperatures. At higher temperatures more oxidation occurs in double bonds [27]. High oxidation rate is partially prevented by introducing an oxygen free inert gas to the reactor [26, 27].

In recent years, researchers have studied the synthesis of hyperbranched alkyd resins in order to lower the use of solvent. However, there is still addition of solvent to the produced resin in order to apply it easily to the surface.

Manczyk et al. synthesized star and hyperbranched alkyd resins and compared their chemical and mechanical properties with conventional alkyd resins. They have prepared thin films by dissolving produced resins in 20% solvent. They showed that increasing the degree of branching of the resins decreased the viscosity, and therefore, the need for the use of solvent also decreased. Increasing branching accelerated the drying time of the resin. Another difference is the elasticity of the resins in which highly branched resins have lower elasticity than conventional ones. Most of the other properties are almost same as the conventional alkyd resins [5].

Bat et al. synthesized air-drying hyperbranched fatty acid based resins with dipentaerythritol core [6]. They studied the effects of changing linseed oil fatty acid content on coating properties. The viscosities of produced resins were measured as 5.8 to 17.5 Pa.s. They showed that the increase in the amount of linseed oil fatty acids increased hardness and decreased viscosity of the resins [6].

Haseebuddin et al. studied hydroxylated hyperbranched resins from dipentaerythritol and a mixture of soya oil and dehydrated castor oil fatty acids [50]. They found that increasing branching and dipentaerythritol content in the resin provided better flow, leveling, film hardness, and gloss [50].

Murillo et al. synthesized hyperbranched alkyd resins from fourth generation hydroxylated hyperbranched polyester and tall oil fatty acid [39]. They dissolved the resins in 50% solvent. The produced high solid alkyd resins presented high stability, good adhesion, flexibility, short drying time, high gloss, and chemical resistance [39].

In our study, main concern is to eliminate the use of solvent completely while preserving properties of the coating material high.

## CHAPTER 3

### EXPERIMENTAL

In this chapter the materials used in the experiments and the procedure for producing hyperbranched alkyd resin were described in detail. Moreover, information about physical and chemical test instruments was given.

#### 3.1 Raw Materials

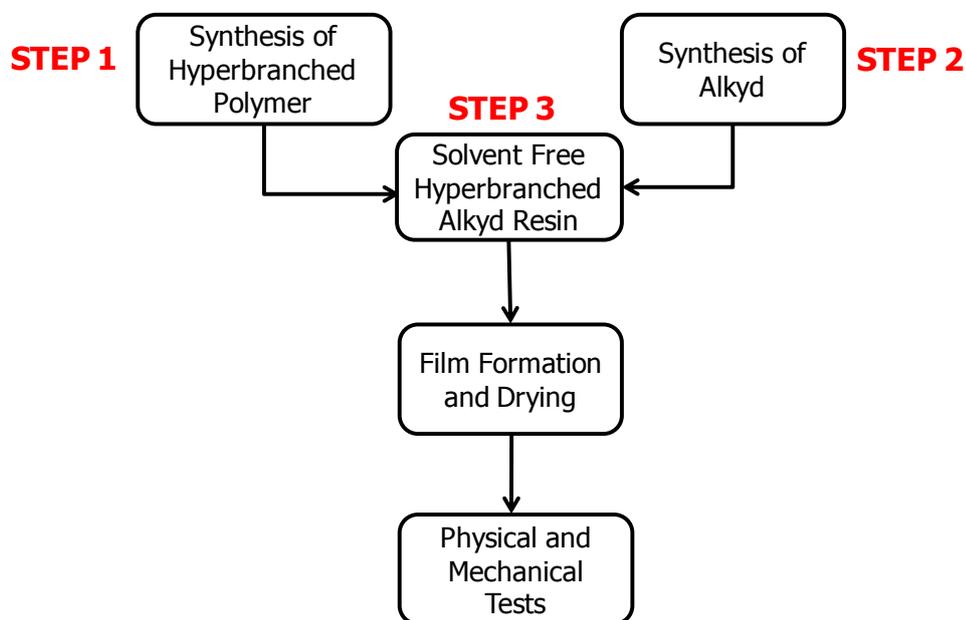
1. Refined linseed oil (Betek Boya)
2. Sunflower oil
3. Sodium hydroxide (NaOH), (Merck A. G.)
4. Sodium chloride (NaCl), (Technical Grade)
5. Sulfuric acid (95-98 %), ( $H_2SO_4$ ), (Sigma Aldrich)
6. Phthalic anhydride (Merck A. G.)
7. Ethyl alcohol (Technical grade)
8. Dimethylol propionic acid (DMPA), (Perstorp AB, Sweden)
9. Melamine (Sigma Aldrich)
10. Formaldehyde (Merck A. G.)
11. Methanol (Merck A. G.)
12. Para-toluene sulfonic acid (p-TSA), (Merck A. G.)
13. Toluene (Merck A. G.)
14. Sodium carbonate
15. Isopropyl alcohol (Merck A. G.)
16. Cobalt naphthenate (Volkan Boya)
17. Lead naphthenate (Volkan Boya)
18. Nitrogen gas (Oksan)
19. Glycerol

### 3.1.1 Dehydration of Raw Materials

The esterification catalyst p-toluene sulfonic acid (p-TSA) was dehydrated at 85°C for about 2 hours in an oven.

### 3.2 Procedure

In this study, the main objective is to synthesize and characterize solvent free alkyd resin by using hyperbrached melamine core. The procedure followed for this study was summarized in the Figure 3.1. First step was the synthesis of melamine based hyperbranched polymer which is not used in coating industry before. Second step, known in literature, was synthesis of oil based alkyd. Third step was the synthesis of solvent free hyperbranched alkyd resin. After the production, the resin was applied to the surface with constant thickness and dried. Finally, physical and mechanical tests were conducted to the produced samples.



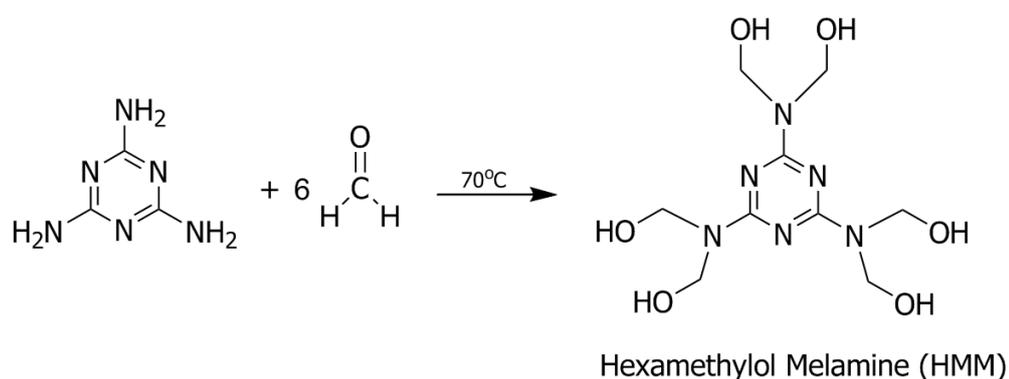
**Figure 3.1** Overall procedure.

### 3.3 Synthesis of Hyperbranched Polymer

Hexamethylol melamine was synthesized first in order to produce hyperbranched resin. After this step, hexamethylol melamine was esterified by dimethylol propionic acid (DMPA) to produce twenty-four hydroxyl ended and globular shaped hyperbranched polymer.

#### 3.3.1 Synthesis of Hexamethylol Melamine

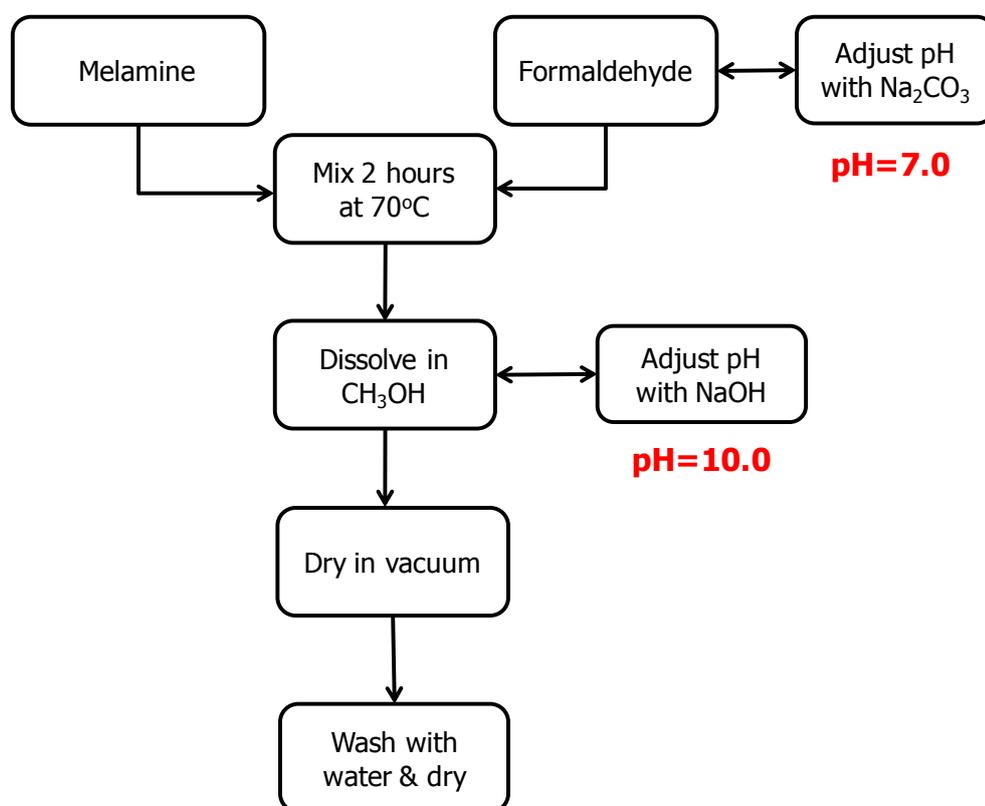
Melamine which has s-triazine ring is expected to impart high mechanical properties when used as core molecule. It was first converted to hexamethylol melamine according to the reaction given in Figure 3.2.



**Figure 3.2** Synthesis of hexamethylol melamine (HMM).

The procedure for the synthesis of hexamethylol melamine was given by Konar [47] and Manley [46]. However, some changes were made in their procedures in order to prevent gelation. The reaction was carried out in a three-necked reactor equipped with a reflux condenser, and a thermometer. A magnetic stirrer was used to agitate the substances. The flow chart of the procedure was given in Figure 3.3. Before mixing, formaline (37% formaldehyde) was neutralized with a few drops of

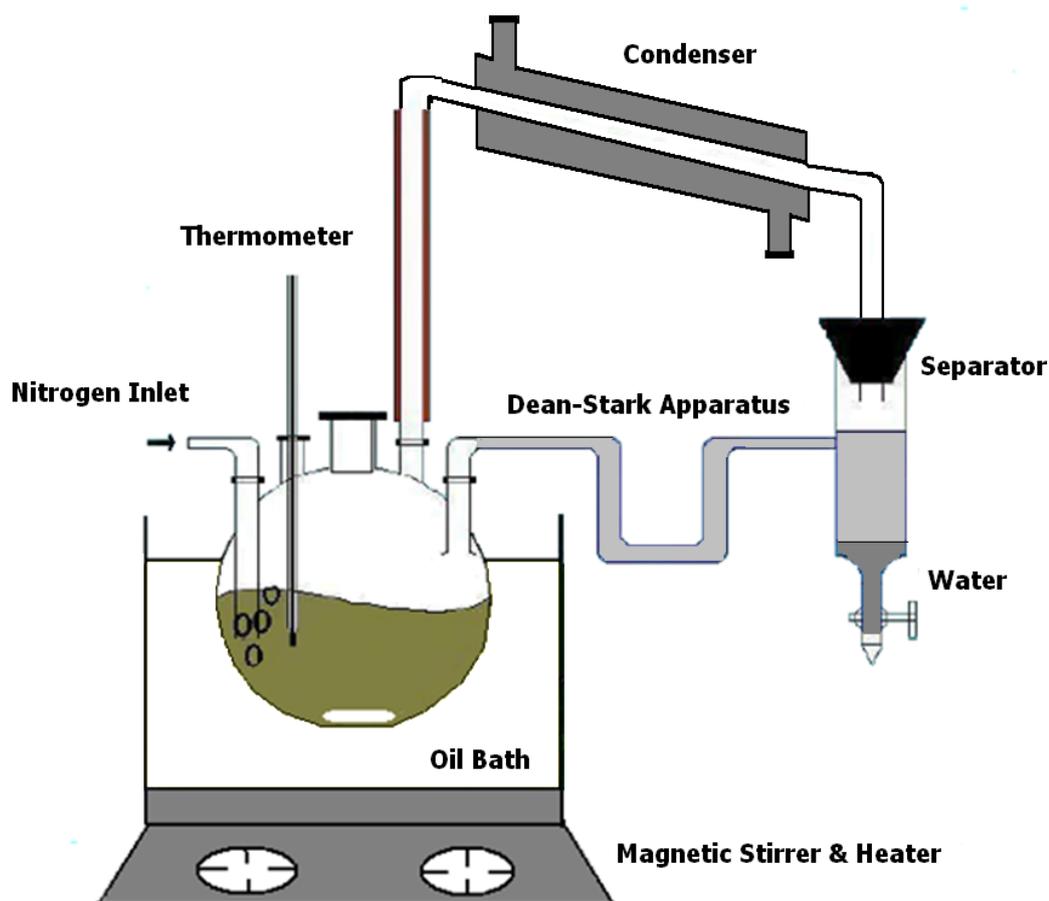
$\text{Na}_2\text{CO}_3$  to adjust the pH of the solution to 8.0-9.0. The melamine and the neutralized formaldehyde were mixed at 1:8 molar ratios, in excess formaldehyde to be able to produce hexamethylol melamine as major product. The solution was heated at  $70^\circ\text{C}$  for 2 hours under continuous stirring. Palanikkumaran et al. indicated that the transparent color of the mixture specifies the formation of prepolymer [49]. It was cooled after the completion of reaction, and it turned into white on cooling. It became milky on addition of methanol. The solution was made alkaline using 10%  $\text{NaOH}(\text{aq})$  in order to prevent gelation in the course of drying. It was dried in a vacuum drier overnight at  $50^\circ\text{C}$  and 400 mmHg. The resulting white solid product was washed with water to remove other methoxylated melamine derivatives (di-, tri-, tetra-, pentamethylol melamine). The solubility of hexamethylol melamine is lower than other derivatives. After filtration, the residual part was dried at  $50^\circ\text{C}$ .



**Figure 3.3** Flowchart for HMM synthesis.

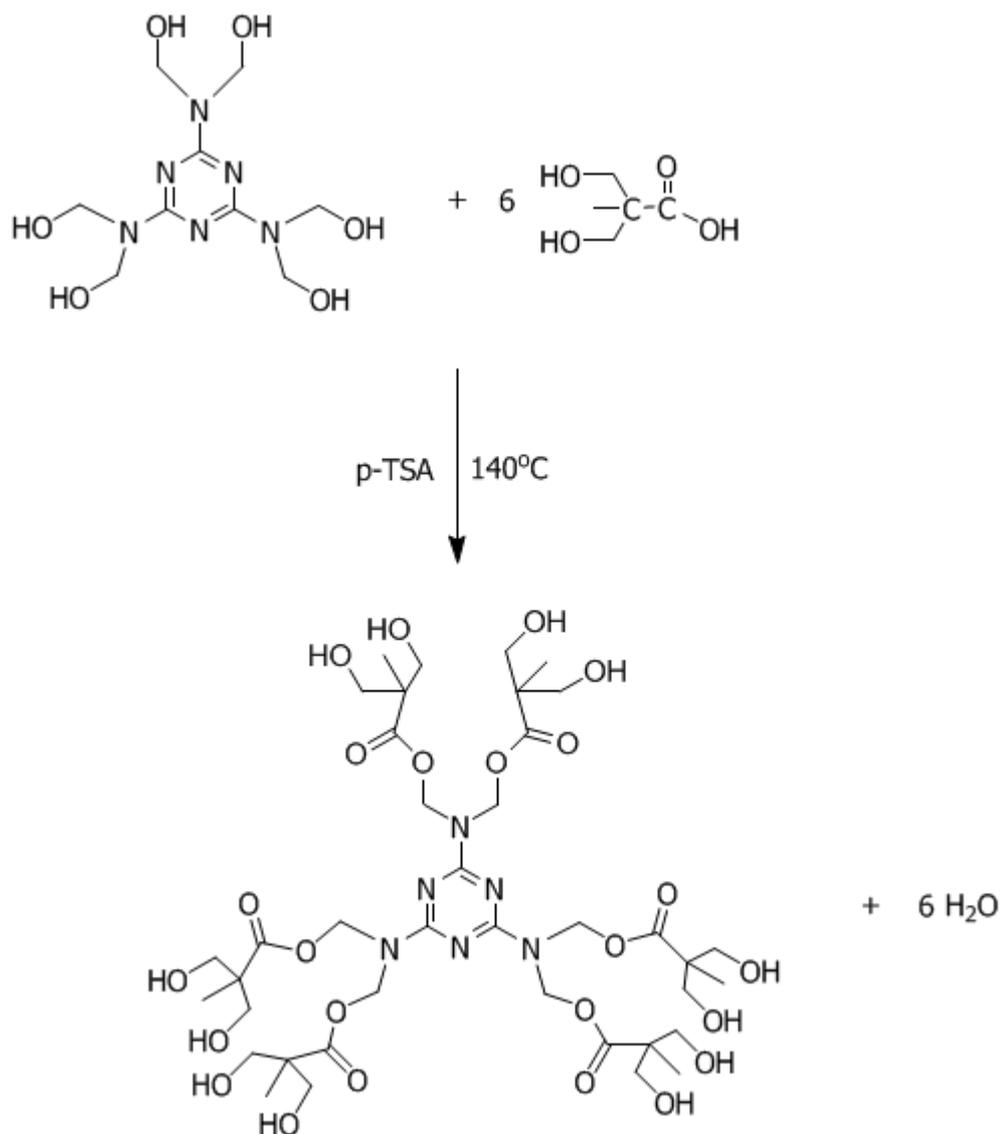
### **3.3.2 Esterification of Hexamethylol Melamine**

Melamine based hyperbranched polymer was synthesized to be used as the main component for the production of solvent free alkyd paint. Hexamethylol melamine was used as the core molecule, and DMPA was used for hydroxyl functionalization. The synthesized HMM was esterified with DMPA twice in acid-catalyzed esterification reaction. The pseudo-one-step procedure was performed in a five necked reactor (Figure 3.4) equipped with a thermometer, an inlet for the nitrogen gas, a condenser combined with a Dean-Stark apparatus. It is agitated by a magnetic stirrer. Toluene was used as only in the synthesis parts for removing of the produced water from esterification reaction. Toluene makes an azeotrope with water and the azeotropic mixture boils at 84.1°C. This is an effective method to remove even residual amounts of water formed in the reaction. The Dean-Stark apparatus was used to feed back toluene removed from the reactor in the form of an azeotropic mixture with water. Water and toluene were separated out from each other in the separator.



**Figure 3.4** Experimental set-up.

The pseudo-one-step procedure of hyperbranched polyester from trimethylol propane and DMPA given by Malmström et al. was followed in our synthesis [36]. The reactor was placed in an oil bath, and heated to 140°C. Previously produced HMM (0.1 mol, 30.57 g) and DMPA (0.6 mol, 80.32 g) were fed into the reactor with a ratio of 1:6 at perfect stoichiometry. The catalyst p-toluene sulfonic acid (p-TSA) was added at 0.4 w/o of DMPA. Toluene was added at 2-6 w/o of the total fed. Nitrogen was also used to accelerate the removal of water. Water removal is important for the effective completion of esterification reaction. After 12 hours reaction time, first generation (Figure 3.5) was completed.



**Figure 3.5** First generation reaction.

For the second generation, the required amount of DMPA (1.2 mol, 160.64 g) and p-TSA were added into the reactor and the same reaction conditions were held as in the first generation. The reaction of second generation for hyperbranched polymer is given in Figure 3.6. The final product was obtained after 12 hours of reaction time and it was assumed to have expected twenty-four branches.



### 3.4 Synthesis of Alkyd

The types of oils used highly affect the properties of alkyds produced. Especially, the unsaturation contents of oils are of extreme importance as drying is concerned.

#### 3.4.1 Selection of Oil Content

Sunflower and linseed oils are most commonly used triglyceride oils in coating industry. Their fatty acid contents were given in Table 3.1. The main properties affected by the types of fatty acids are drying time, yellowing, and hardness of the resin produced.

**Table 3.1** Compositions of fatty acids [20].

Fatty Acid	Unsaturation	Linseed oil w/o	Sunflower oil w/o
Palmitic	-	6	11
Stearic	-	4	6
Oleic	1	22	29
Linoleic	2	16	52
Linolenic	3	52	2

Drying properties of different oils were determined by using drying index equation given below.

$$\text{Drying Index} = [\% \text{ Linoleic Acid} + 2 \times \% \text{ Linolenic Acid}]$$

Oils having drying index higher than 70 are considered as drying oils. In order to produce air drying alkyd resin the drying index must be maintained higher than 70. Yellowing property, on the other hand, is an important structural defect of alkyd resins due to use of high percentage of linolenic acid which makes the main contribution to drying index.

In order to select proper oil content two different formulations were prepared to compare their properties. In the first case, 100% linseed oil unsaturated fatty acids (oleic, linoleic, linolenic acids) were obtained and resin was synthesized by using these fatty acids. The synthesis was carried by fatty acid method. In the second case, 40% linseed oil and 60% sunflower oil mixture were used for the synthesis of alkyd resin by using monoglyceride method. Drying index properties of two cases were given in Table 3.2.

**Table 3.2** Drying index property.

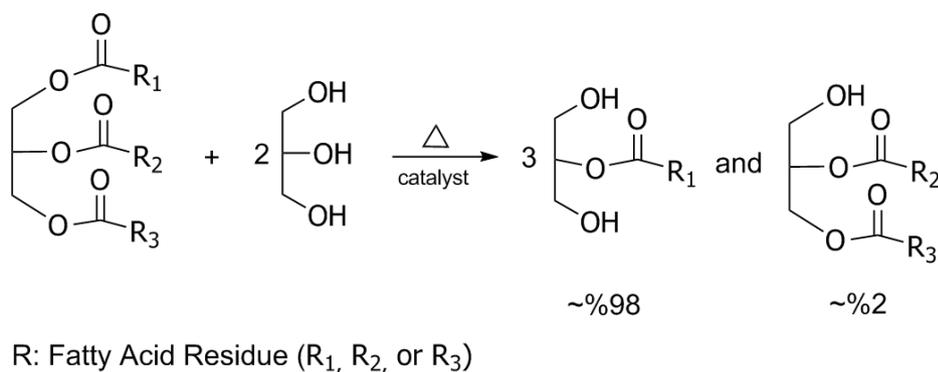
	<b>Case 1</b>	<b>Case 2</b>
<b>Property</b>	100% Linseed oil unsaturated fatty acids*	40% Linseed oil + 60% Sunflower oil
<b>Drying Index</b>	133.4	81.6

\*Based on unsaturated fatty acid content

The selection of the oil content was based on smooth appearance of the resin produced. The surface of dried resin in case 2 was much better than case 1; this is why case 2 was selected as the composition of oil.

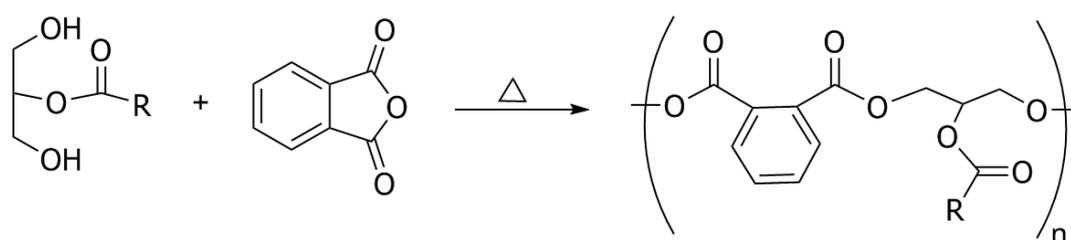
### 3.4.2 Synthesis of Long Oil Alkyd with Oil Mixture

After the selection of oil content as a mixture of 40% linseed oil and 60% sunflower oil, synthesis of long oil alkyd by using monoglyceride method was conducted. This synthesis was performed in a five-necked reactor (Figure 3.4) used in hyperbranched polymer synthesis. The first step of procedure, transesterification reaction, is the production of monoglycerides from linseed and sunflower oils (Figure 3.7). In the first reaction, linseed oil (60 g) and sunflower oil (90 g) mixture was heated to 150°C under nitrogen atmosphere. Glycerol (38.43 g) and NaOH which is used as a catalyst in 0.2 w/o of total fed were added into the reactor. The reaction temperature was increased to 170°C. In the literature, the temperature of this reaction was reported as 240-260°C [24, 29, 51]. However, in order to prevent dark color and high cross-link density, temperature was kept lower than reported ones. The reaction time of the reaction was reported as 0.5-1 hours at 230-250°C [24, 29]. The product is a mixture of mostly monoglyceride with small amounts of diglyceride and triglyceride. The completion of the reaction was monitored by methanol test. Oil does not dissolve in methanol, whereas, monoglyceride is soluble in it. When one volume of sample totally dissolves in three volumes of methanol the transesterification reaction is completed. Decreasing the reaction temperature increased the time of the reaction to 5-6 hours at 170°C.



**Figure 3.7** Transesterification reaction.

In the next step, phthalic anhydride (0.42 mol, 61.86 g) was added to synthesize long oil alkyd by polyesterification reaction (Figure 3.8). The temperature was kept at 170°C. Previously added NaOH was still in the reactor and it also catalyzed the alkyd production. Toluene was added at 2-6 w/o of total fed to remove water. The reaction was followed up by determining acid value. Its determination is given in Appendix A. To obtain low viscosity long oil alkyds, the reaction was stopped at acid number of 30-35 mg KOH/g of alkyd.



R: Fatty acid residue ( $R_1$ ,  $R_2$ , or  $R_3$ )  
n: Number of repeating unit

**Figure 3.8** Production of long oil alkyd.

The overall formulation of synthesized long oil alkyd (60% oil) is given in Table 3.3.

**Table 3.3** Formulation of long oil alkyd.

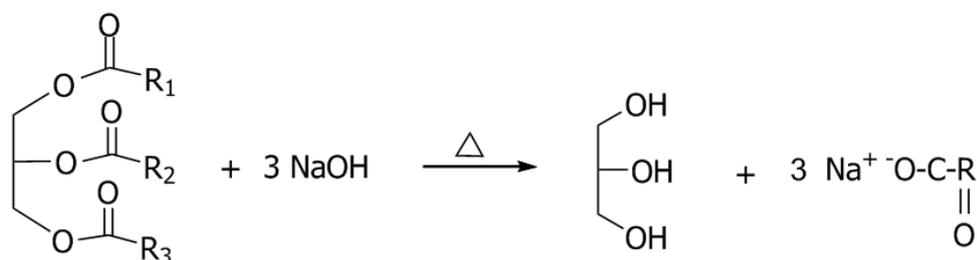
Ingredients	Weight (g)	Composition (w/o)
Oil mixture	150	60
Linseed oil	60	
Sunflower oil	90	
Glycerol	38.43	15
Phthalic anhydride	61.86	25

### 3.5 Production of Hyperbranched Resin

Hyperbranched resin was synthesized by using two different methods as mentioned below.

#### 3.5.1 Method I: Using Fatty Acids

Before the resin, linseed oil fatty acids were produced first. In order to saponify the linseed oil, a solution of sodium hydroxide in 1:1 ethanol-distilled water and stoichiometric amount of linseed oil were reacted at 80°C under reflux condition for 1-2 hours. Saponification reaction of oils with NaOH is shown in Figure 3.9. After then phase separation was accomplished by using saturated NaCl solution. The soap was collected in the upper layer, and glycerol goes to aqueous phase in the lower layer. The soap produced was filtered out by means of a vacuum filter to remove the aqueous phase. The residue is dissolved in water, and then reacted with stoichiometric amount of sulfuric acid (20 w/o) at room temperature. The neutralization reaction is seen in Figure 3.10. Fatty acids produced collects at the upper layer. It is then separated by the help of a separatory funnel. The separated part is washed out several times with water to remove water soluble impurities, and then centrifuged at 5000 rpm for 10 minutes to get rid of remaining water. Then, linseed oil unsaturated fatty acids, namely oleic, linoleic and linolenic fatty acids, were obtained.



R: Fatty acid residue ( $R_1$ ,  $R_2$ , or  $R_3$ )

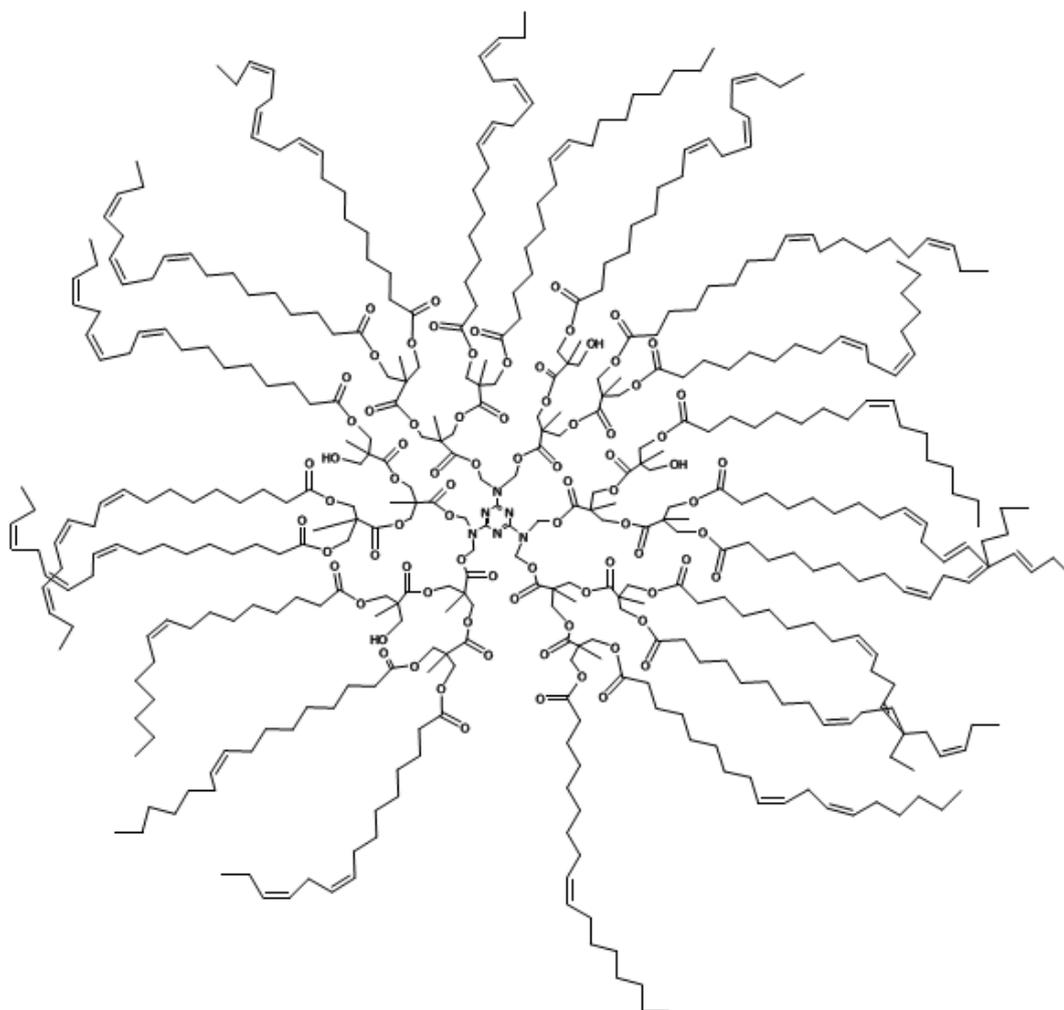
**Figure 3.9** Saponification reaction of the oil.



R: Fatty acid residue (R<sub>1</sub>, R<sub>2</sub>, or R<sub>3</sub>)

**Figure 3.10** Reaction of soap and sulfuric acid.

The produced fatty acids and melamine based hyperbranched polyester having twenty four hydroxyl groups were reacted to form hyperbranched resin. The synthesis was performed in the previously used five necked reactor (Figure 3.4). Hyperbranched polyester/fatty acids molar ratio was taken to be 1:24. Toluene and nitrogen gas were both used as before to remove reaction water from esterification reaction. The reactor was placed in an oil bath at a temperature of 160°C. The reaction was followed up by monitoring the acid number. As the reaction proceeds, the acid value decreases regularly. The reaction was stopped when the acid number decreased to 20-25 mg KOH/g resin. The suggested structure of the final product for the perfect generation is shown in Figure 3.11.

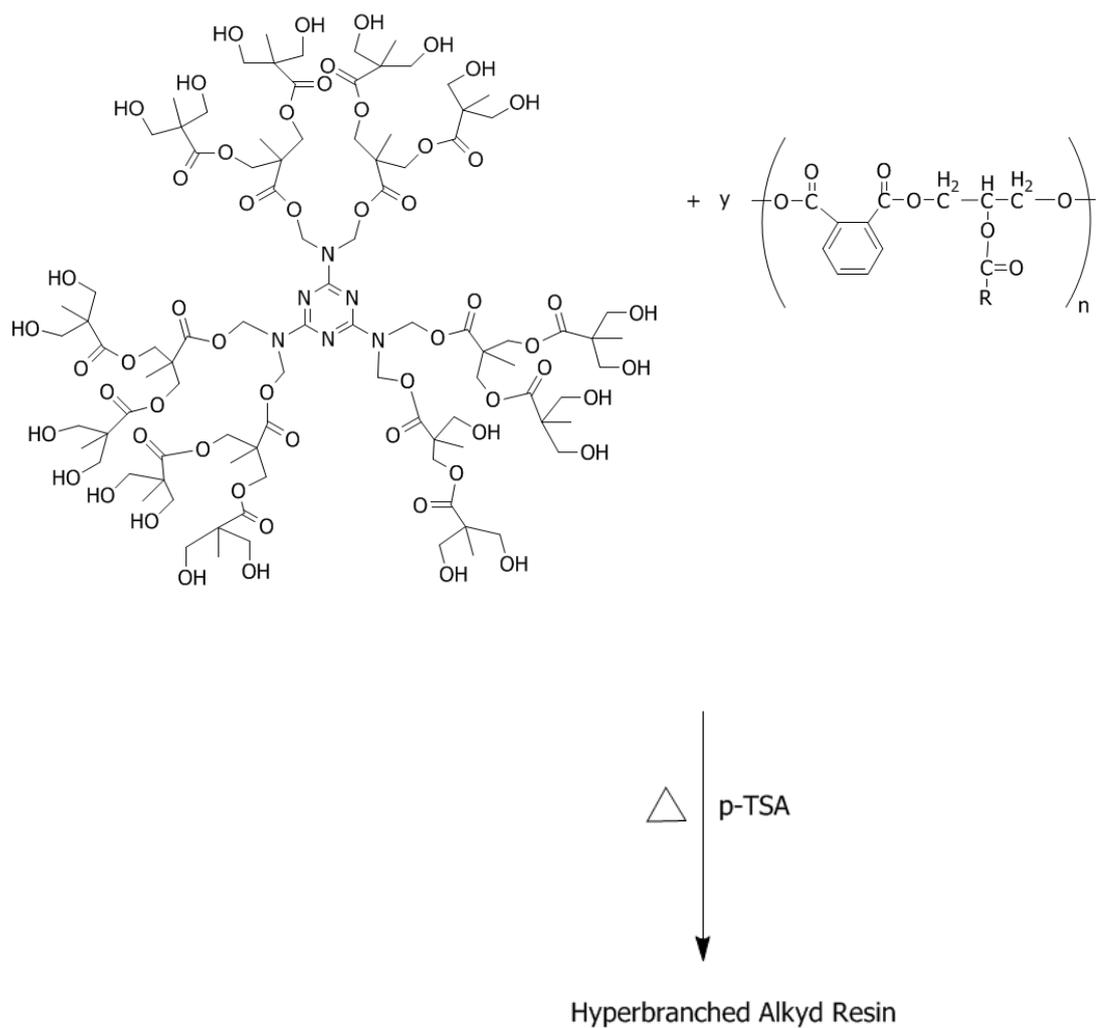


**Figure 3.11** Hyperbranched resin with 1:24 ratio by using fatty acid method.

### **3.5.2 Method II: Using Long Oil Alkyds**

The synthesized long oil alkyd molecules had hydroxyl group on one end and carboxylic acid group on the other end. So hyperbranched polymer/long oil alkyd molar ratio was set to be 1:24 which is the stoichiometric proportion for maximum level of esterification. Toluene was added at 6 w/o of the total feed, and p-TSA was added at 0.4 w/o of long oil alkyd. All reactants were introduced into a five-necked reactor (Figure 3.4) immersed in an oil bath. The reaction was carried out at 160°C

under nitrogen atmosphere. The reaction was followed up by monitoring the acid number as mentioned before. The reaction was stopped when the acid number was less than 15 mg KOH/g alkyd. The reaction scheme of the final resin production is given in Figure 3.12. It is now hyperbranched alkyd resin.

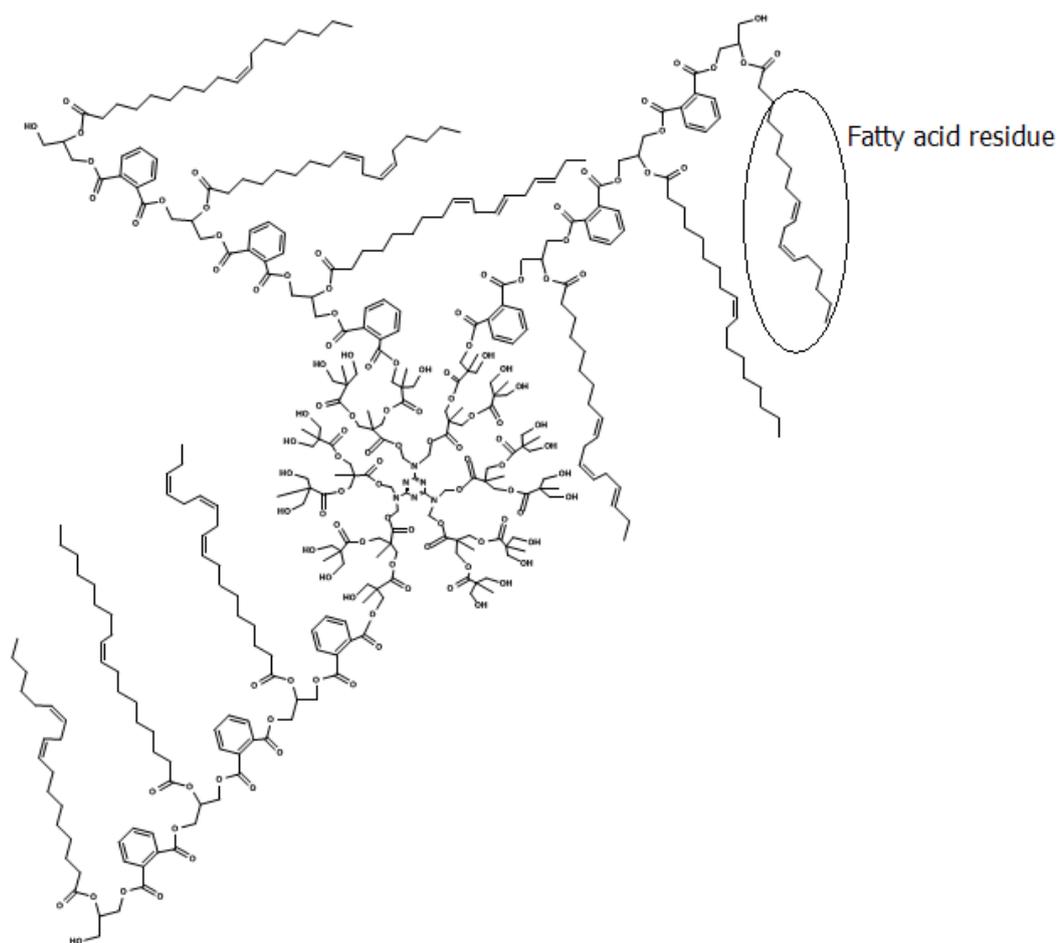


**Figure 3.12** The reaction scheme of resin synthesis.

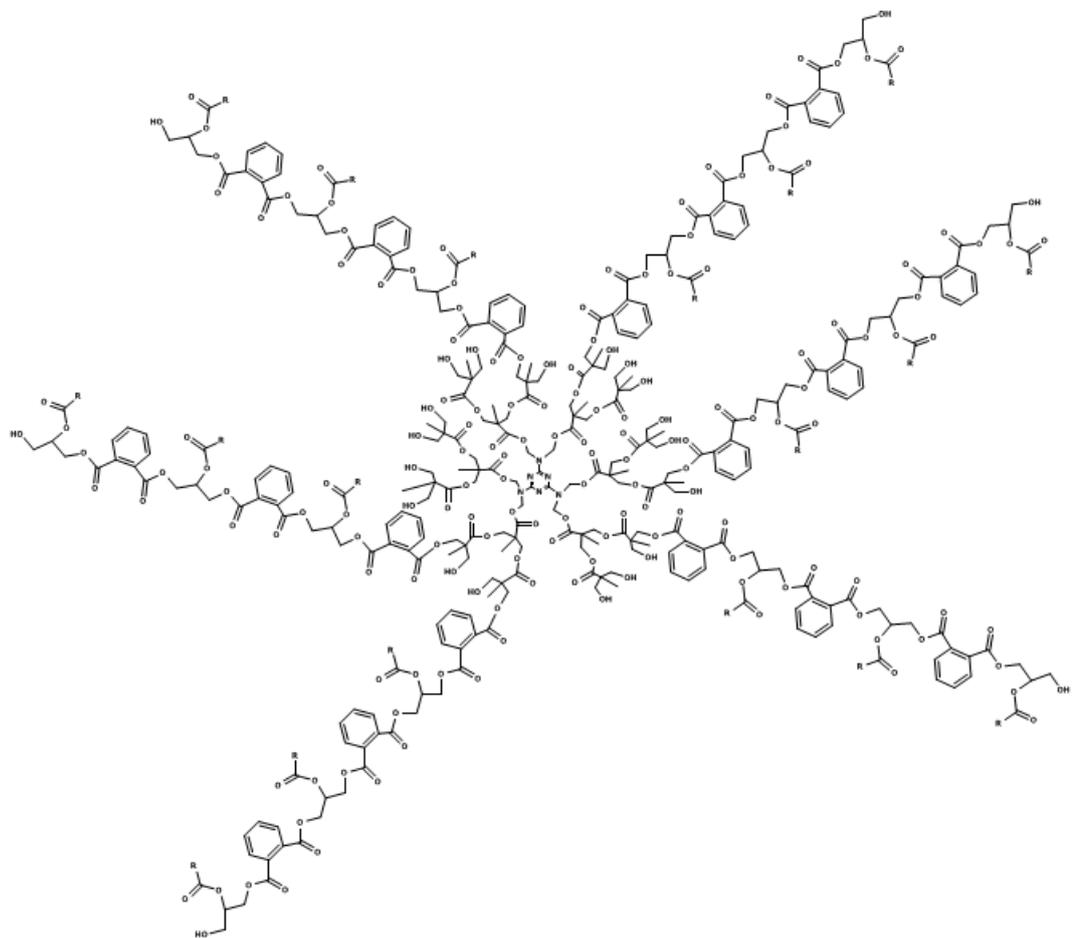
In order to understand the effect of HBP:alkyd ratio on the properties of resin, different ratios were used for the synthesis of hyperbranched alkyd resin. The ratios for resin production were changed as given in Table 3.4. All resins were synthesized by the same procedure. The fifth resin (HBR-5) can be considered to have maximum number of fatty acid residues since all 24 hydroxyl groups were assumed to be esterified by long oil alkyds. In other resins, the amount of alkyd steadily increased as the ratio changed from 1:2 to 1:24. This situation, consequently, increases the branching unit of the resin. The schematic representations of produced resins are given in Figure 3.13-17. First trial, HBR-0 was failed due to high cross-link density. Its viscosity was very high to use as a solvent free alkyd resin.

**Table 3.4** Resin production with different ratios.

<b>Resin</b>	<b>HBP:Alkyd Ratio</b>	<b>HBP (g)</b>	<b>Long Oil Alkyd (g)</b>
HBR-0	1:2	5.44	6.7
HBR-1	1:3	5.44	10.0
HBR-2	1:6	5.44	20.0
HBR-3	1:8	5.44	26.7
HBR-4	1:12	5.44	40.0
HBR-5	1:24	5.44	80.0

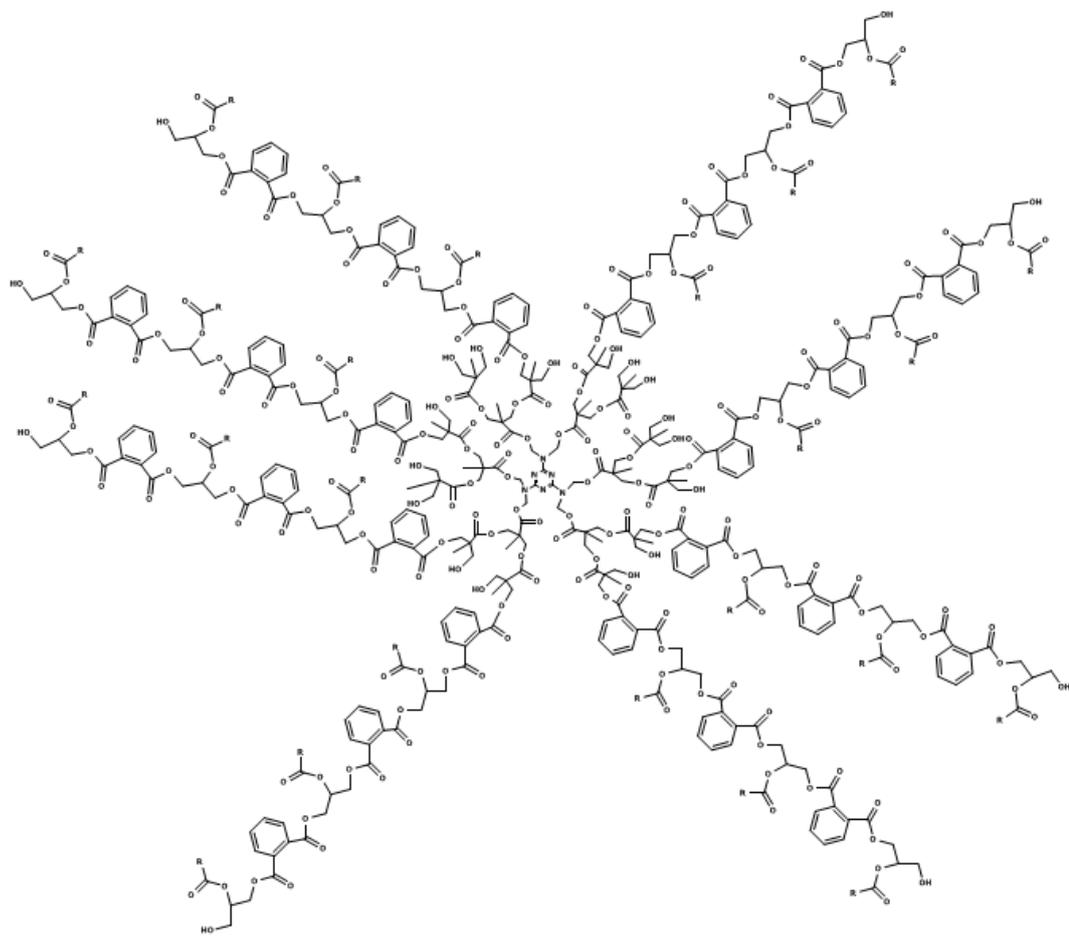


**Figure 3.13** The schematic representation of HBR-1.



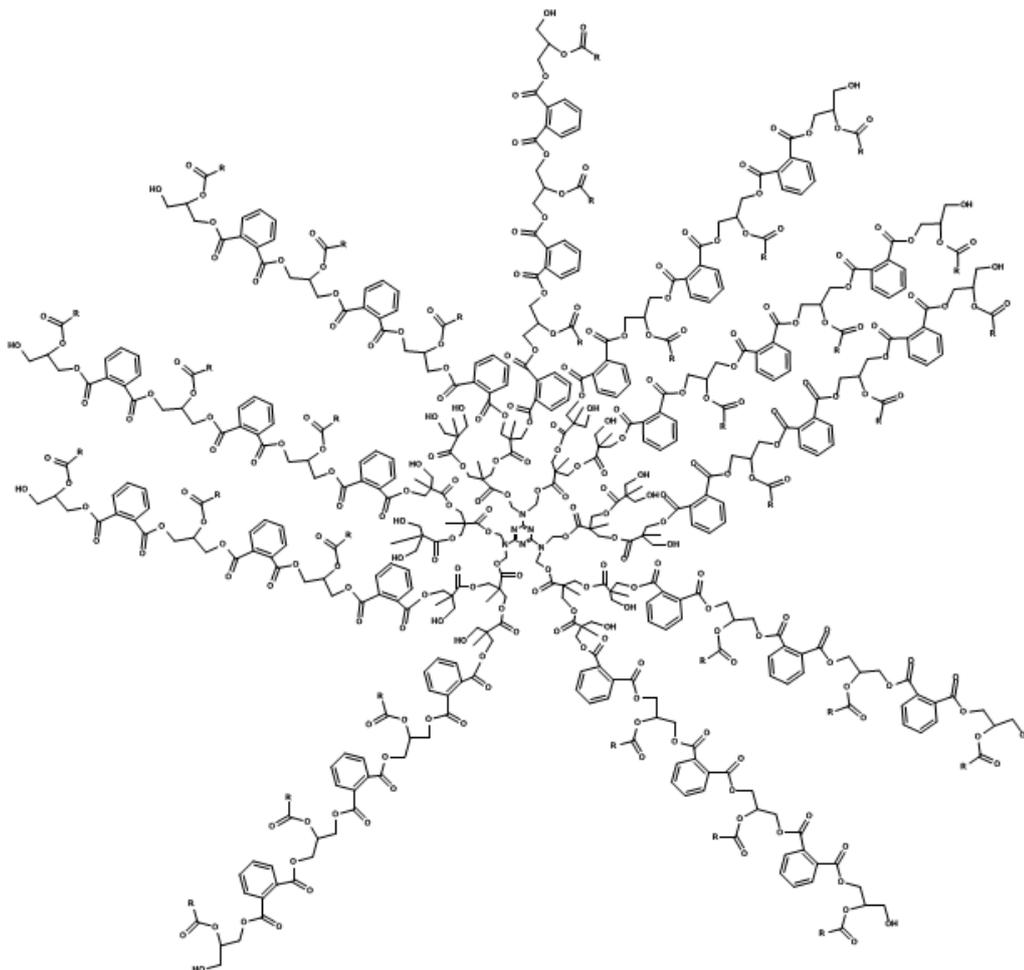
R: Fatty acid residue

**Figure 3.14** The schematic representation of HBR-2.



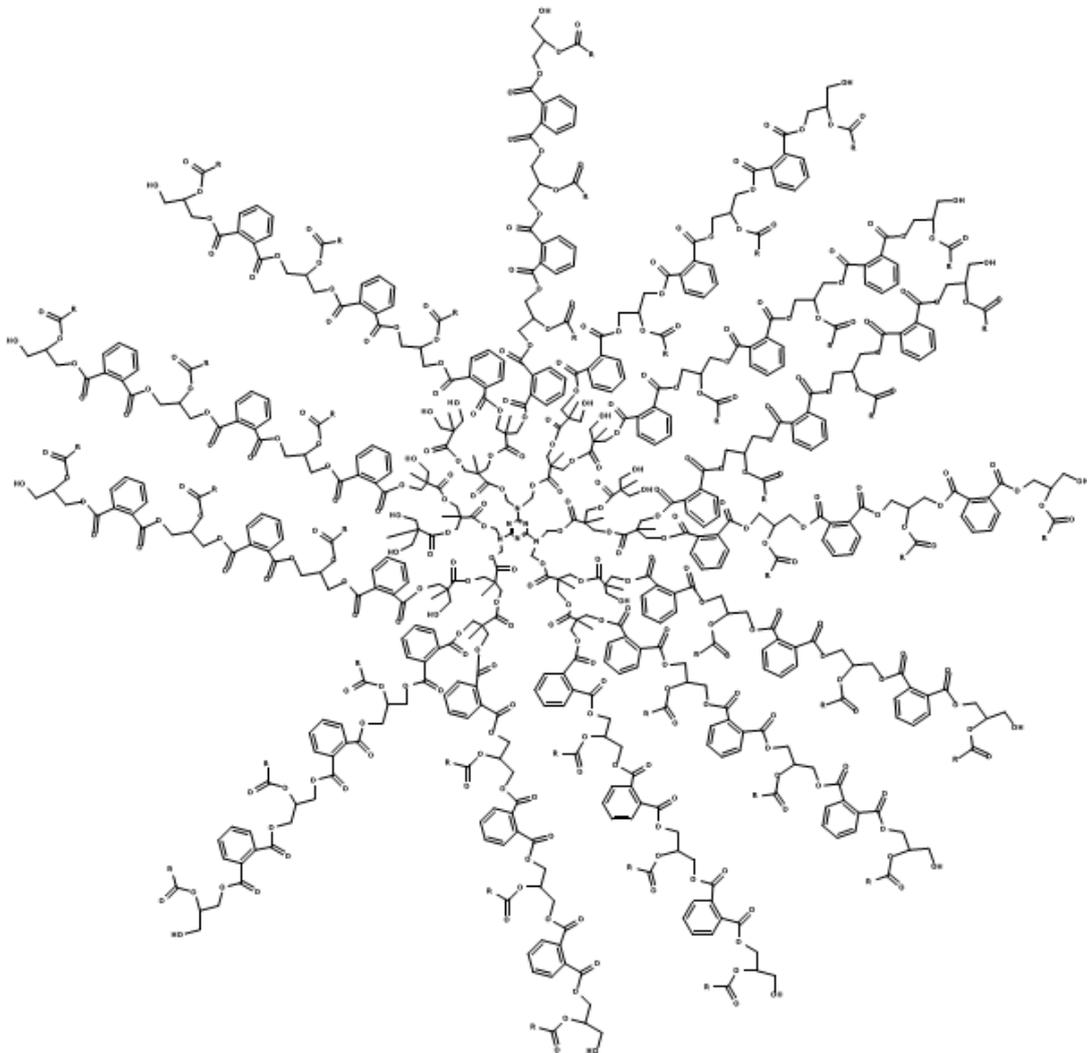
R: Fatty acid residue

**Figure 3.15** The schematic representation of HBR-3.



R: Fatty acid residue

**Figure 3.16** The schematic representation of HBR-4.



R: Fatty acid residue

**Figure 3.17** The schematic representation of HBR-5.

### **3.6 Chemical Characterization**

#### **3.6.1 Fourier Transform Infrared (FTIR) Spectroscopy**

Shimadzu (Prestige-21) FT-IR Spectroscopy was used to characterize hyperbranched polymers and resins. The solid specimens were prepared by using KBr. On the other hand, liquid specimens were prepared by capturing a drop of liquid sample between prepared two thin KBr pellets.

### **3.7 Thermal Characterization**

#### **3.7.1 Differential Scanning Calorimetry (DSC)**

Thermal properties of samples were determined using Dupont (Model TA 910 S) differential scanning calorimeter. Specimens (2-3 mg) were placed in stainless steel pans and heated at a rate of 10°C/min. A flowing inert gas, nitrogen, was used for removal of moisture and oxygen which may accumulate and damage the cell over time. Use of nitrogen gas also provides more efficient heat transfer between the disc and the sample pan, resulting in more sensitive and faster response time.

### **3.8 Viscosity Measurement**

Viscosity was measured using two different methods. In the first method AND SV-10 Vibro Viscometer Instrument was used. The working principle of the instrument depends on measuring the resonant frequency of a probe which is vibrating at a constant frequency of 30 Hz. In the second method Gardner Bubble viscometer (ASTM D154) was used. This measurement is based on comparing the viscosity of the sample with Gardner standards. Sample and the standards have an air bubble in the tube and the test is based on determination of the standard tube in which air bubble rises with the same speed of the bubble in the sample tube. The Gardner standard viscosities are given at 25°C; therefore, water bath was used for temperature adjustment.

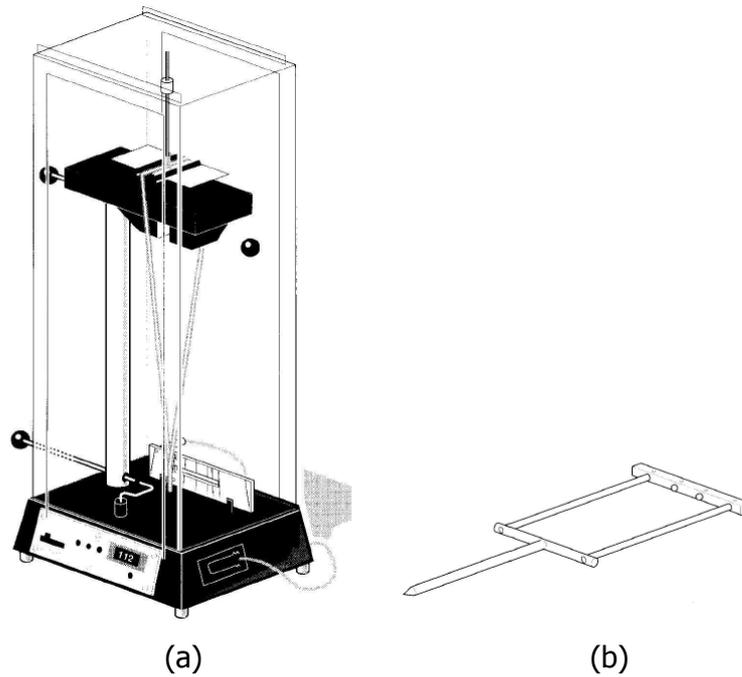
### **3.9 Physical and Mechanical Tests**

#### **3.9.1 Preparation of Test Panels**

The resins containing no solvent were applied on glass and metal plates using a Braive Instrument casting knife film applicator at 100  $\mu\text{m}$  wet thickness. Metal plates made of iron were used for impact, mandrel, and abrasion tests. Glass plates were used for pendulum hardness test. Gloss and adhesion tests were performed using both metal and glass panels. These samples were dried in an oven at 120<sup>o</sup>C for 24 hours. The tests were carried out a week later.

#### **3.9.2 Pendulum Hardness Test**

Pendulum Hardness Test was performed using a Braive Instruments hardness tester (Model 3034) equipped using Persoz pendulum within the specified limits of amplitude (decrease from 12<sup>o</sup> to 4<sup>o</sup> for Persoz pendulum) determined by accurately positioned photo sensors as shown in Figure 3.18. This tester works with the principle of measuring the damping time of the viscoelastic behavior of the coating by a pendulum based (ASTM D 4366). The softer the surface of the sample, the faster the oscillation of pendulum stops. The hardness is reported in terms of the number of oscillations recorded by a sensor.



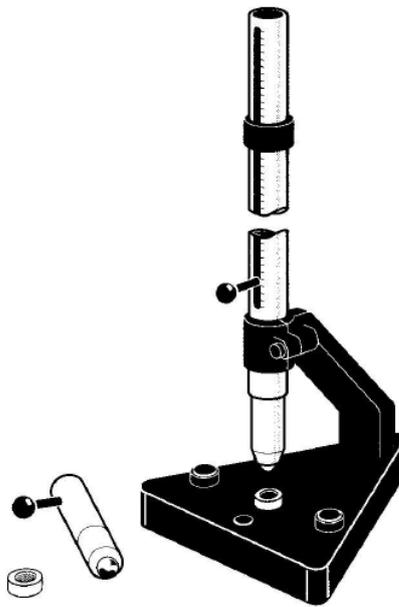
**Figure 3.18** (a) Pendulum hardness tester and (b) Persoz pendulum [20].

### 3.9.3 Impact Resistance Test

Impact test is used to establish the stone-chip resistance of coatings [17]. For this test a Gardner Impact Tester (Model 5524) was used as shown in Figure 3.19. The principle of test depends on the determination of potential energy obtained by drop weight (1+0.9 kg) from a specified height to form cracks on the surface. Impact resistance is determined when cracks first appear on the coating (ASTM D 2794). The impact energy is simply found from the potential energy by measuring the height according to equation given below.

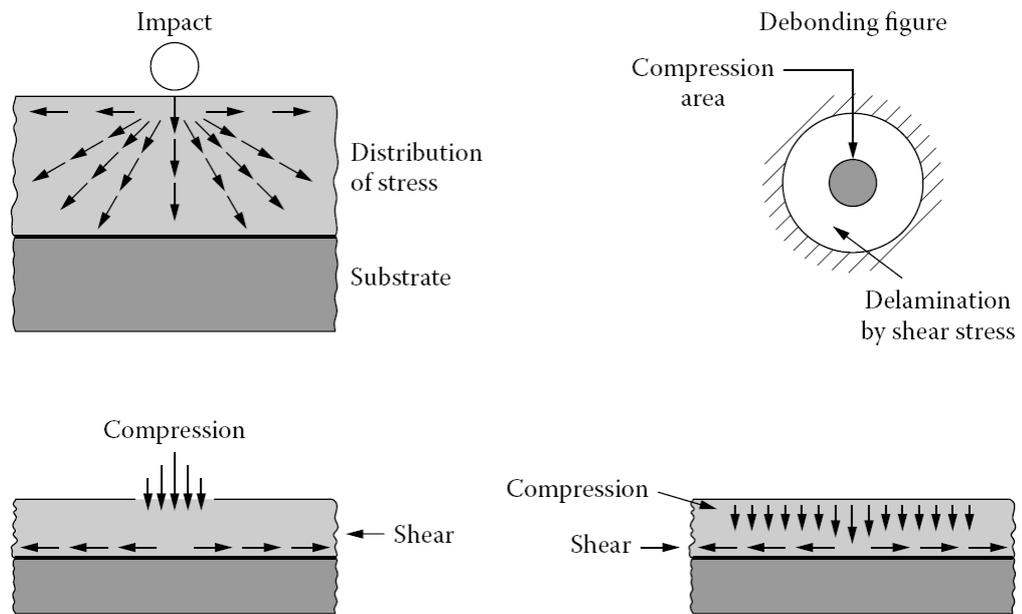
$$\text{Impact Energy (J)} = m.g.h$$

where;  $m$  = weight of the dropweight (kg)  
 $g$  = gravitational acceleration of the earth ( $m/sec^2$ )  
 $h$  = height of dropweight (m)



**Figure 3.19** Impact resistance tester [20].

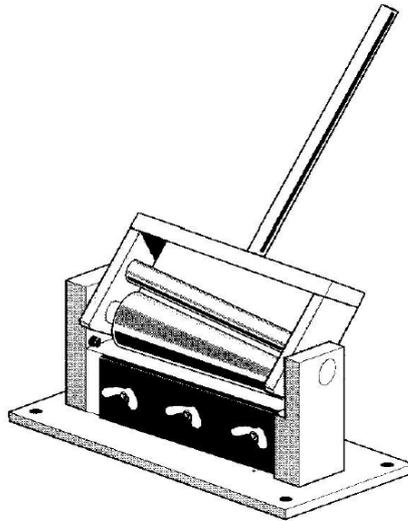
The mechanism of impact is simply shown in Figure 3.20. Transfer of impact force through the film and the resulting damage is shown in this figure. In debonding area, compression stress is present in the middle and the shear stress is in the annular region. Therefore, debonding area illustrates the measure of the adhesion with a negative relation. The larger the debonding area, the lower the adhesion level of the coating [17].



**Figure 3.20** Effect of impact [17].

### 3.9.4 Mandrel Bending Test

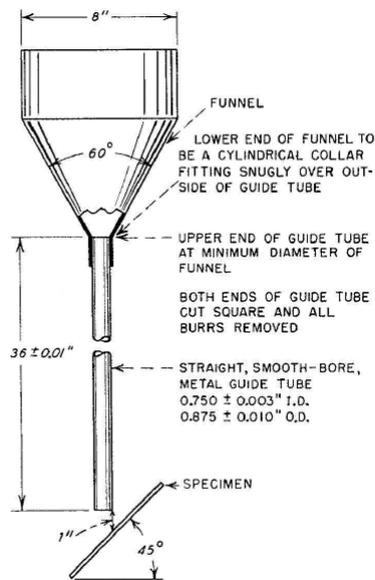
This test was performed using a Braive Instrument (Model 1510) conical mandrel bending tester as shown in Figure 3.21. The principle of the test depends on measuring the properties of flexibility and adhesion of coating material by applying a bending stress on the plate. Metal plates are used for the test and the length of cracks is measured after the bending is over (ASTM D 522).



**Figure 3.21** Conical mandrel bending tester [20].

### **3.9.5 Abrasion Resistance Test**

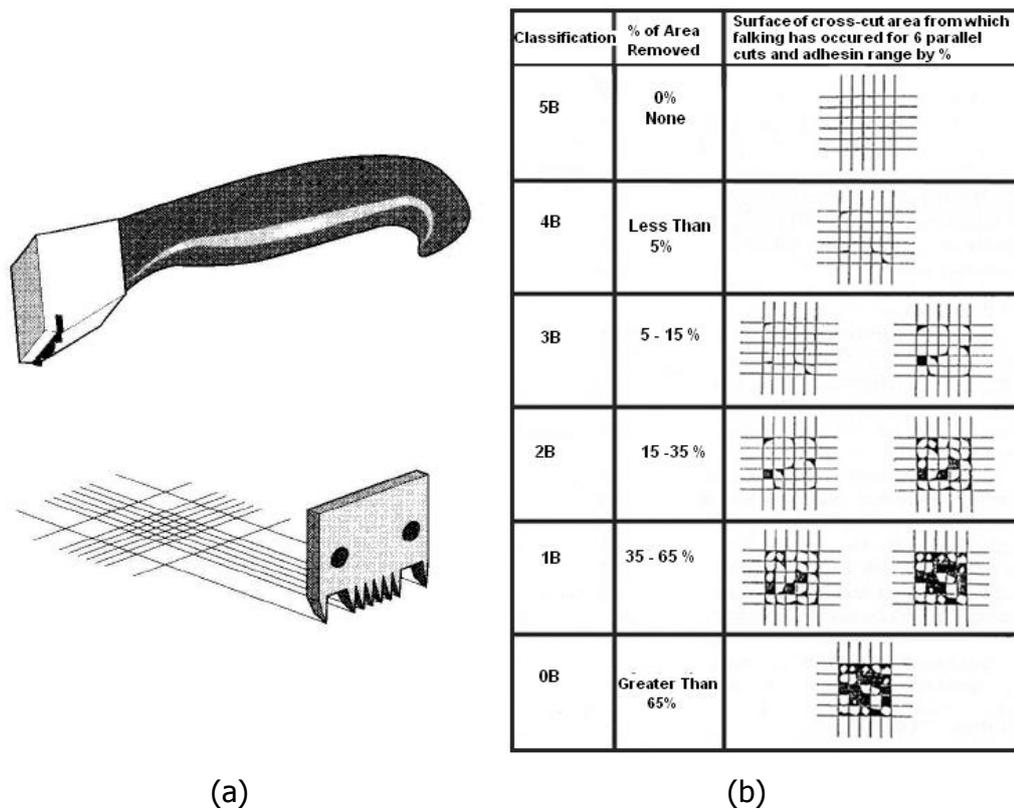
This test was performed to measure the resistance of coating films against abrasion caused by an abrasive falling from a specified height through a guide tube onto a coated metal (ASTM D 968). Silica sand was used as the abrasive agent. It was poured onto the coated metal until some scratching was detected. The volume of sand which changes the thickness of the film by certain extent determines the abrasion resistance. The abrasion is given in terms of 'ℓ per micrometer'. The instrument is shown in Figure 3.22.



**Figure 3.22** Abrasion resistance tester [20].

### 3.9.6 Adhesion Test

This test was performed to measure the strength of the bonds formed between the coating material and the applied surface. Cross-cut test (ASTM D 3359) is the most commonly used adhesion test and the equipment is shown in Figure 3.23. The classification is based on the percentage of paint flakes peeled off from the surface, and the levels are shown in the same figure [17].



**Figure 3.23** (a) Cross-hatch cutter and (b) levels for the classification of film [17].

### 3.9.7 Specular Gloss

A Rhopoint glossmeter was used for measuring the gloss values of films on glass and metal plates. The principle of this test depends on measuring the ability of the coating material to reflect incident light from its surface. The instrument measures the intensity of the light reflected from coated plates at three different incidence angles (ASTM D 523).

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Preliminary Experiments

A series of experiments was performed to synthesize hexamethylol melamine. Acid content in the solution was very important parameter for this reaction. In order to prevent gelation the pH of the medium was carefully adjusted.

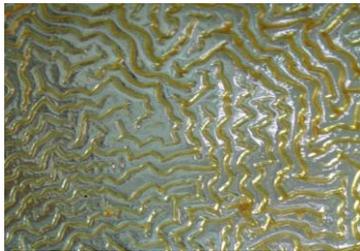
Some experiments were also performed to optimize the reaction temperature of alkyd synthesis. High reaction temperature produced high viscosity and dark colored resins because of linseed oil fatty acids. Some trials were done above 200°C and the produced alkyd had dark color and high viscosity. Darkening and high viscosity could be decreased by lowering the reaction temperature, but then, the reaction took longer time.

##### 4.1.1 Selection of Oil Composition

For selection of oil composition two different experiments were done, and two different hyperbranched alkyd resins were produced. The compositions and the appearances of the resins produced are given in Table 4.1. Both samples were cured at the same conditions (120°C, 24 hours). In case 1, drying index was higher than case 2 due to high amount of linolenic acid. It resulted in highly wrinkled surface. It should be due to high cross-link density and the presence of soft segments on the back bone. In case 2, drying index was lower than case 1, but still in the range of 'drying oils'. As mentioned earlier drying oils have drying index higher than 70. The appearance was much better than the first one, and it did not have any wrinkles. Linseed oil, having high percentage of linolenic acid has high

drying index, but yellows in time. So it is usually blended with other oils in industrial applications. By the same token the oil mixture 'Case 2' in Table 4.1 was used in alkyd production in this research work.

**Table 4.1** Effect of oil content on the appearance of final resin.

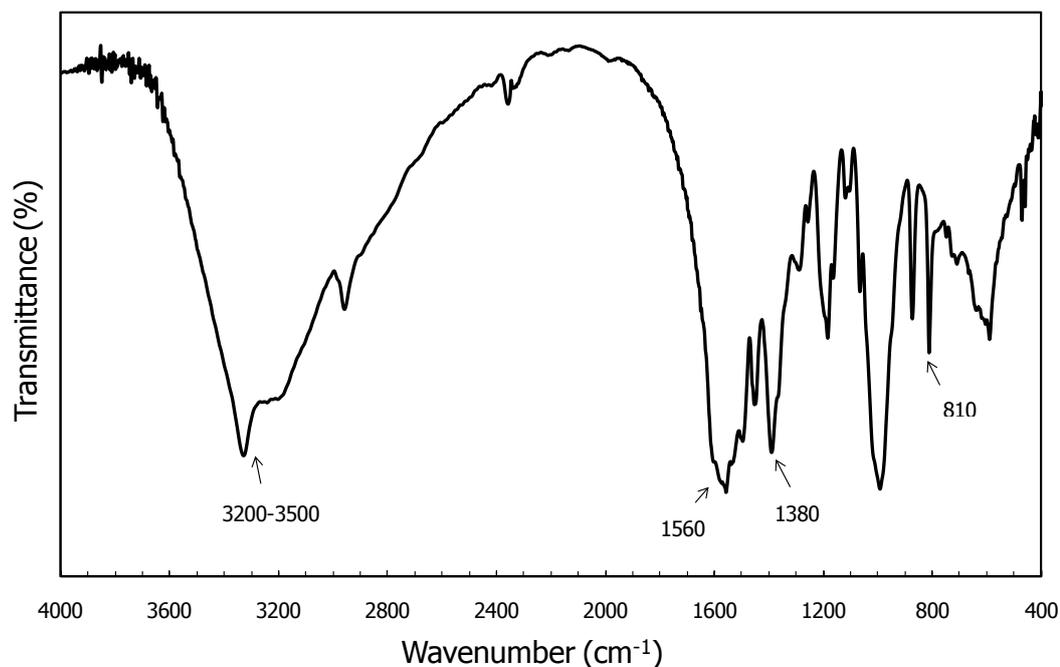
	<b>Case 1</b>	<b>Case 2</b>
<b>Property</b>	100% Linseed oil unsaturated fatty acids	40% Linseed oil + 60% Sunflower oil
<b>Drying Index</b>	133.4	81.6
<b>Appearance</b>		

## 4.2 Chemical Characterization

### 4.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

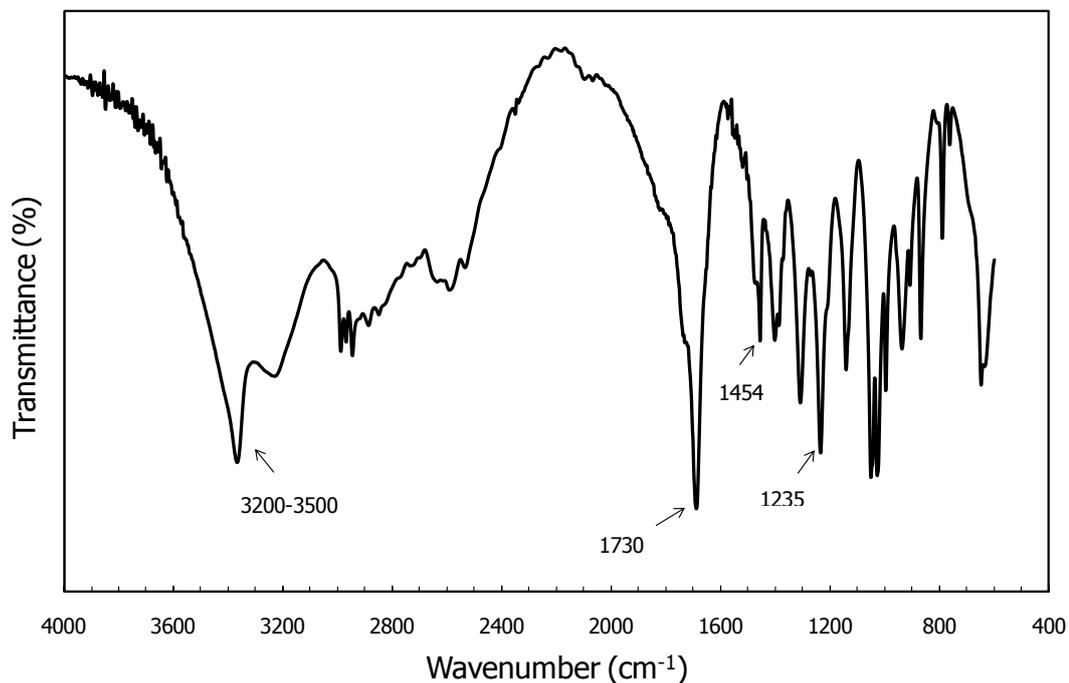
FTIR spectrum of produced hexamethylol melamine (HMM) is given in Figure 4.1. The broad peak in the range of 3200-3500  $\text{cm}^{-1}$  corresponds to characteristics hydroxyl groups (-OH) formed. In-plane and out-of-plane vibrations of triazine ring in melamine core were observed at 810 and 1560  $\text{cm}^{-1}$ . Strong hydrogen bonding in

the structure causes broad peaks in the spectrum. The peak at  $1380\text{ cm}^{-1}$  indicates methylene bending ( $-\text{CH}_2-$ ).



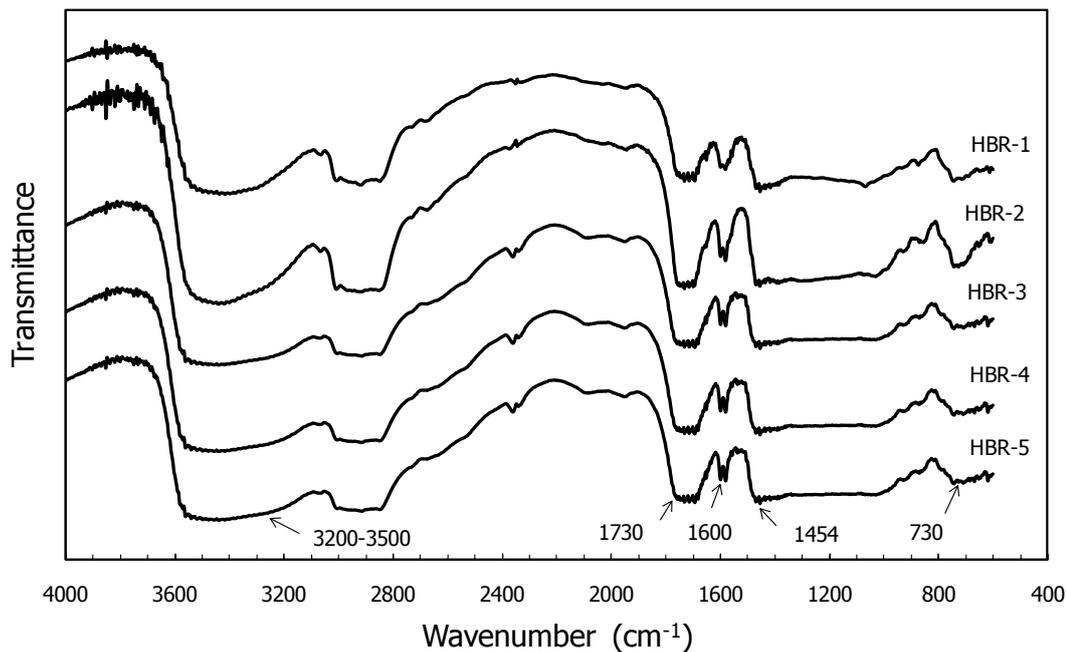
**Figure 4.1** FTIR spectrum of hexamethylol melamine (HMM).

FTIR spectrum of twice esterified hexamethylol melamine is given in Figure 4.2. The broad peak in the range of  $3200\text{--}3500\text{ cm}^{-1}$  corresponds to hydroxyl ( $-\text{OH}$ ) groups formed due in the reaction. It has common peaks with hexamethylol melamine compound because both of them have similar structures. Characteristic difference is the ester structure formed in esterification reaction. Carbonyl group ( $\text{C}=\text{O}$ ) of the characteristic ester group is observed at  $1730\text{ cm}^{-1}$  and it is the evidence for the transformation of hydroxyl groups in ester groups. Bending of methylene ( $\text{C-H}$ ) groups gives peak at  $1454\text{ cm}^{-1}$ . The peak at  $1235\text{ cm}^{-1}$  indicates aliphatic polyester ( $\text{O}=\text{C-O-C}$ ) stretching.



**Figure 4.2** FTIR spectrum of double esterified hexamethylol melamine.

FTIR spectrum of HBR-1, 2, 3, 4, and 5 were given in Figure 4.3. All spectra have common peaks because the structures of all resins are very similar. The broad peak in the range of 3200-3500 cm<sup>-1</sup> corresponds to hydroxyl groups (-OH). The small peak from olefinic =C-H stretching due to fatty acids is seen at about 3010 cm<sup>-1</sup> in all resins. Bending of methylene (C-H) groups gives peak at 1454 cm<sup>-1</sup>. Typical ester group (-COO) is observed at 1730 cm<sup>-1</sup>. The band at 1600 cm<sup>-1</sup> is due to C=C stretching vibration of vinyl group. The peak at about 730 cm<sup>-1</sup> corresponds to rocking of multiple (>4) methylene groups of fatty acids in HBR.

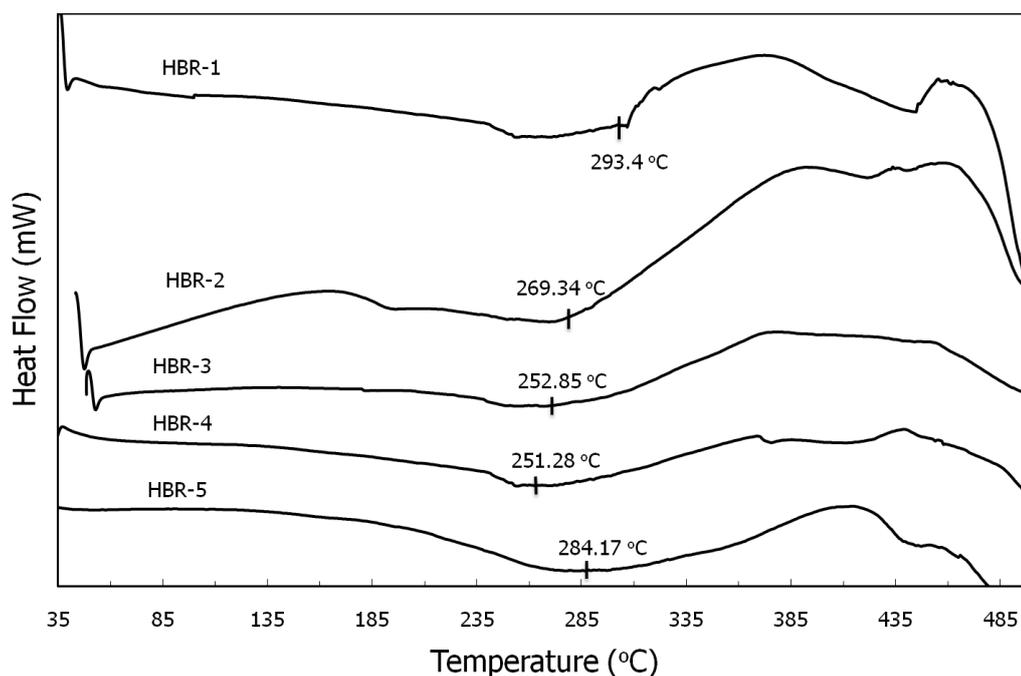


**Figure 4.3** FTIR spectra of resins.

## 4.3 Thermal Properties

### 4.3.1 Differential Scanning Calorimetry (DSC)

The DSC spectra of produced resins (HBR-1, 2, 3, 4, 5) are given in Figure 4.4. Since high temperature curing yields highly cross-linked resins thermal analysis gives degradation temperatures of resins. All the resins were found to be thermally stable up to 250°C. Thermal degradation of all resins occurred between 250°C to 300°C. Aromatic groups in the structure imparted rigidity of the resin which cause increase in thermal stability.



**Figure 4.4** DSC spectra of resins.

#### 4.4 Viscosity Measurements

Two different viscosity measurement methods were used. First method was AND SV-10 Vibro viscometer. Second method is Gardner bubble viscometer which was based on comparing sample with standards as mentioned earlier. In order to make comparison between two methods all measurements were done at 25°C. Vibro viscometer has a range up to 100 Pa.s, therefore, HBR-1 and HBR-2 could not be measured using this instrument; they had very high viscosities. The viscosities measured using two different methods are given in Table 4.3.

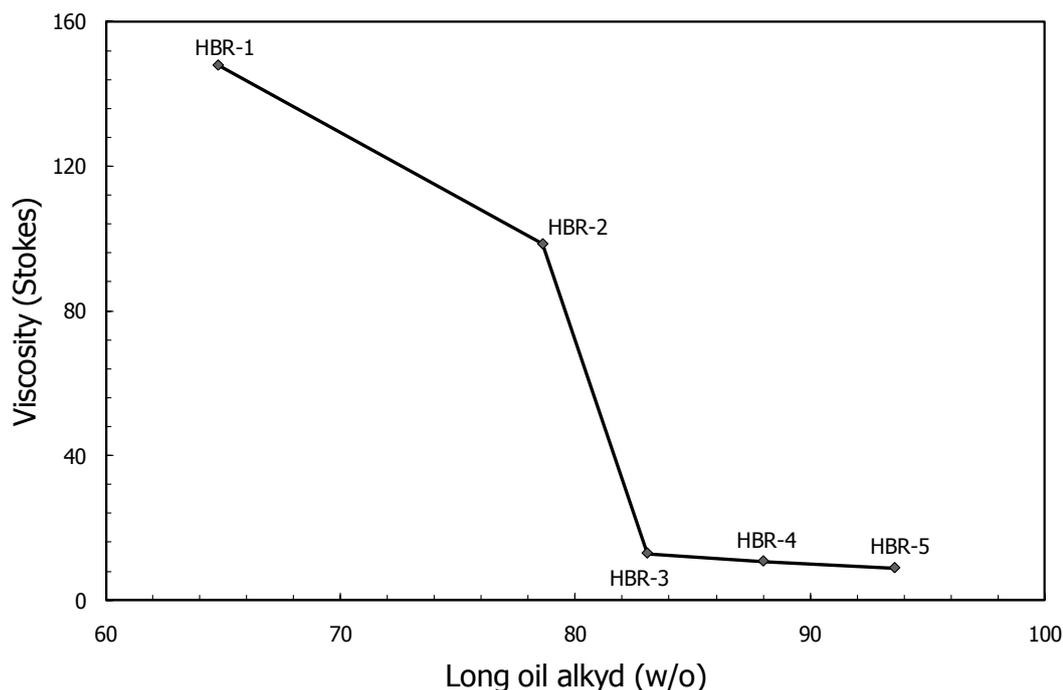
**Table 4.2** Viscosity values of produced resins.

<b>Resin</b>	<b>HBP:Alkyd Ratio</b>	<b>Viscosity* (Pa.s)</b>	<b>Viscosity** (Stokes)</b>
HBR-1	1:3	High	148.00
HBR-2	1:6	High	98.50
HBR-3	1:8	10.24	12.90
HBR-4	1:12	7.49	10.70
HBR-5	1:24	5.89	8.84

\* Measured by AND SV-10 Vibro viscometer at 25°C

\*\* Measured by Gardner bubble viscometer at 25°C

A conventional high solid alkyd resin has a viscosity of 26 Pa.s (26 Stokes) [5]. On the other hand, HBR-3, HBR-4 and HBR-5 have lower viscosities than that for the conventional one, because the conventional alkyd resins have higher molecular weights and thus higher viscosities. Lower molecular weight alkyd resin was produced in this research on purpose. A decrease in viscosity was observed due to increase in the percentage of long oil alkyd in resins as shown in Figure 4.5 (Data used in graph is given in Appendix B).



**Figure 4.5** Variation of viscosity with fatty acid content.

#### 4.5 Drying Properties

In the conventional alkyd resins, film formation occurs by oxidative drying. This is accomplished by the oxidation of double bonds of fatty acid residues to form hydroperoxides. The decomposition of hydroperoxides is followed by the formation of cross-links between fatty acid residues. Film formation for hyperbranched alkyd resin is eventuated with almost the same procedure. Only difference is drying time. Drying time for hyperbranched alkyd resins are shorter than conventional resins. This difference is attributed to low viscosity of hyperbranched alkyd resins. Since fatty acids are in the periphery situation, oxygen diffusion is better and consequently oxidation process is easier than conventional alkyd resins [5, 39].

In order to find out the drying behavior of produced resins, two different methods were used. In the first method UV curing was applied with the addition of benzoin

which is used as photo-initiator. In the second method, resins were put into oven heated at 120°C with the addition of metal driers to form oxidative curing, this is actually the conventional drying method. In the UV curing method, the produced films were softer than oxidative curing method. In addition to that there were some thin wrinkles on the surface as seen in Figure 4.6. Oxidative curing method formed smooth, hard films which were used in mechanical property tests.



**Figure 4.6** Film produced by UV curing.

## **4.6 Mechanical Properties**

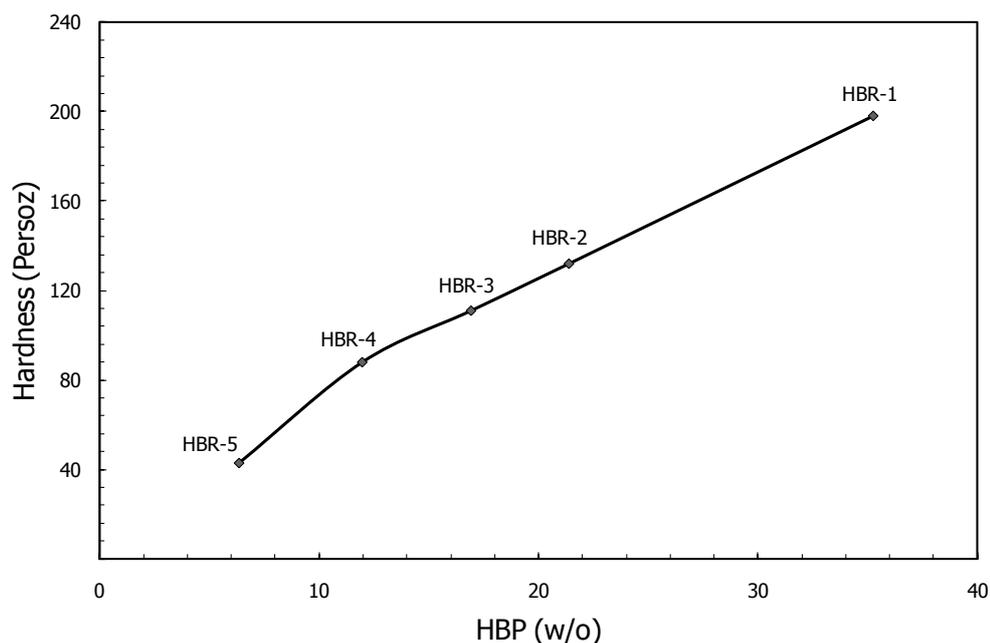
### **4.6.1 Pendulum Hardness**

The hardness values of the resins are given in Table 4.3. The increase in the fraction of melamine based hyperbranched polymer increased the hardness value of the resin due to triazine ring in the melamine core.

**Table 4.3** Hardness values of synthesized resins.

<b>Resin</b>	<b>Hardness (Persoz)</b>
HBR-1	198
HBR-2	132
HBR-3	111
HBR-4	88
HBR-5	43

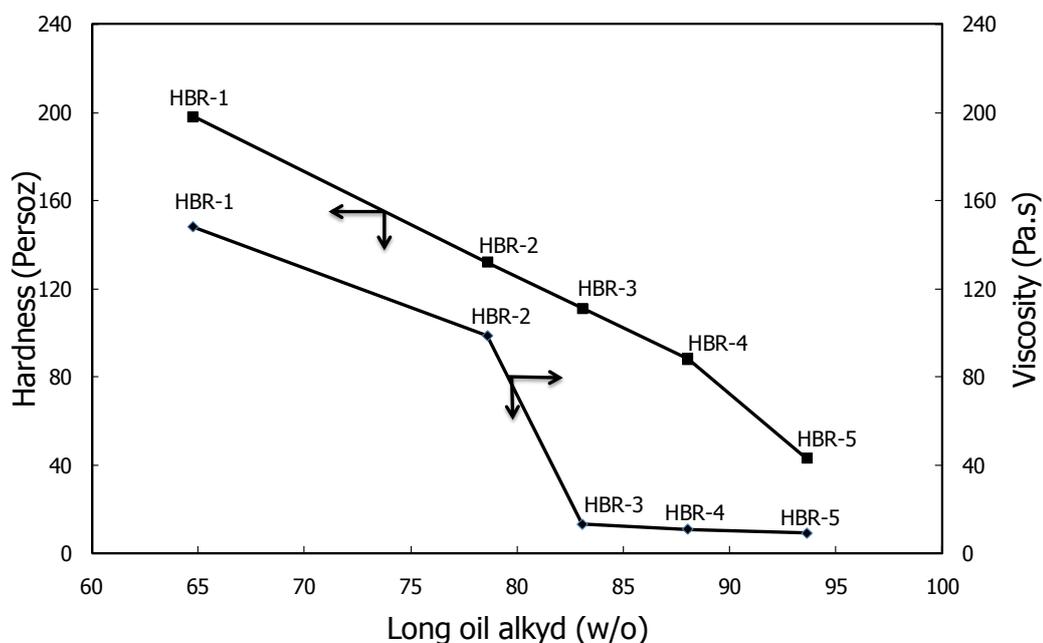
Melamine has more significant effect on the hardness than cross-links formed at unsaturated fatty acids; the increase in the fraction of melamine based hyperbranched polymer causes a high increase in hardness values as seen from Figure 4.7 (Data used in graph is given in Appendix B). While decreasing melamine based hyperbranched polymer content in the resin from 35.2 w/o to 6.4 w/o, hardness values were decreased 78.2%.



**Figure 4.7** Effect of hyperbranched polymer with melamine core content on hardness.

In the alkyd resin formulation the oil content or length of oil is an important variable. The decrease of the oil or fatty acid content correlates proportionally to an increase of the three-dimensional polymer. The reduced level of oil or fatty acid content in the resin produces a polymer with an increased hardness and viscosity [27]. This result was completely achieved by samples and results were given in Figure 4.8 (Data used in graph is given in Appendix B). From HBR-1 to HBR-5 long oil alkyd content was increased therefore, indirectly, oil and fatty acid content was increased. This increase caused a decrease in hardness from 198 Persoz to 43 Persoz; but a decrease of viscosity from 148 Pa.s to 8.84 Pa.s. In this study, low viscosity resin was desired with high hardness property. The results show that HBR-1 has the highest hardness value; however, it has also the highest viscosity value which is not desired. On the contrary, HBR-5 has the lowest viscosity value but it has the lowest hardness property among other samples. In such a case, an optimum sample can be chosen having sufficient hardness value with low enough viscosity to become applicable without any solvent. It seems that HBR-3 has both

high hardness and low viscosity, and can be further studied for commercial application.



**Figure 4.8** Effect of long oil alkyd content to hardness and viscosity.

#### 4.6.2 Impact Resistance

HBR-1, 2, and 3 had an impact resistance of 11, 13, and 17 Joules, respectively. On the other hand, HBR-4 and 5 samples showed no cracking in impact test with 1.9 kg weight and 1 m height. It shows that these samples had an impact resistance higher than 19 J which is the upper limit of the potential energy that can be measurement by this instrument. As expected the increase in aromaticity increases impact strength of the resins.

### **4.6.3 Bending Resistance**

Conical mandrel bending test results showed that all of the synthesized resins had excellent flexibility because there were no cracks occurred on bending. Melamine-formaldehyde resin was known as inflexible due to its rigid structure [12]. It is seen that the long oil alkyds introduced sufficient flexibility in these resins.

### **4.6.4 Abrasion Resistance**

Abrasion resistance test results are given in terms of amount of sand required to remove 1  $\mu\text{m}$  thickness from coating material. The measured results are given in Table 4.4. The abrasion resistance increases with the increase of hardness of resins; HBR-1 has the highest abrasion resistance as seen from Table 4.4.

**Table 4.4** Abrasion resistance values of synthesized resins.

<b>Resin</b>	<b>Abrasion Resistance (<math>\ell/\mu\text{m}</math>)</b>
HBR-1	13.20
HBR-2	11.55
HBR-3	9.90
HBR-4	8.20
HBR-5	6.60

#### **4.6.5 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.

#### **4.6.6 Specular Gloss**

Specular gloss values of the synthesized resins applied both on glass and metal substrate were measured at three different angles of incidence of light as  $20^\circ$ ,  $60^\circ$ , and  $85^\circ$ . The values are given in the Table 4.5. The gloss values of the resins on metal plates were lower than those on glass plates at the same angles, because glass reflects diffracted light more than metal surfaces. Therefore, it has higher gloss values. According to standards, resins which have gloss values higher than 70 at  $60^\circ$  of incident angle are considered as high gloss materials. All the resins were in the high gloss category. It is well known that gloss increases with the oil content

in conventional alkyd paints. This general tendency also shows up in the resins synthesized in this research work. As seen from Table 4.5 gloss values increase while the alkyd content increases.

**Table 4.5** Specular gloss of the resins.

Resin	Angle					
	20°		60°		85°	
	Glass	Metal	Glass	Metal	Glass	Metal
<b>HBR-1</b>	66.3	60.4	100.4	93.2	81.0	81.4
<b>HBR-2</b>	88.5	68.9	100.0	92.4	93.3	83.1
<b>HBR-3</b>	87.5	62.2	99.3	90.2	94.1	80.6
<b>HBR-4</b>	80.0	60.2	97.1	92.1	94.8	84.6
<b>HBR-5</b>	88.4	65.3	96.8	88.0	97.1	88.6

## CHAPTER 5

### CONCLUSIONS

1. This study was based on the synthesis of solvent free and air drying hyperbranched alkyd resin with melamine core. The pH of the solution was an important parameter to prevent gelation while synthesizing hexamethylol melamine.
2. Alkyd resins to be used in such hyperbranched applications should have relatively smaller chain lengths. In this research work the appropriate number of repeating units on the chain was found to be almost 3 corresponding to an acid number of 10-15 ml KOH/mg resin.
3. Increasing long oil alkyd content led to achieving low viscosity resins, therefore corresponding alkyd products contain no volatile organic compounds (VOC).
4. All of the resins were thermally stable up to 250°C.
5. The viscosity of the resins decreased as the content of long oil alkyd increased. HBR-1 with the lowest long oil alkyd content (64.8 w/o) had a viscosity of 148 Pa.s, whereas HBR-5 with the highest long oil alkyd content (93.6 w/o) had a viscosity of 8.84 Pa.s.
6. Increasing melamine based hyperbranched polymer content in the resin gave excellent hardness property to the resins. HBR-1 with 35.2 w/o polymer had the highest hardness value among other resins. Hardness

value for HBR-1 was 198 Persoz while it is 43 Persoz for HBR-5 which had 6.4 w/o polymer content.

7. The lowest viscosity resin, HBR-5 depicted the lowest hardness.
8. Bending tests showed that all resins are flexible; none of them had any cracks in the tests.
9. Impact resistance decreased with the increase of long oil alkyd content.
10. Abrasion resistance values were in agreement with hardness values. The hardest film (HBR-1) gave the highest abrasion resistance value of 13.20  $\ell/\mu\text{m}$ ; while the softest film (HBR-5) gave the lowest abrasion resistance value of 6.60  $\ell/\mu\text{m}$ .
11. Specular gloss values were excellent for all resins. Values at  $60^\circ$  of incidence angle came out to be higher than 95 for all resins. In fact, resins with gloss values higher than 70 are considered to be high gloss resins.
12. HBR-3 has sufficiently high hardness value with low viscosity to become applicable without any solvent. It is an optimum sample for industrial use.

## **CHAPTER 6**

### **RECOMMENDATIONS**

1. Different core molecules of inorganic origin can be used instead of melamine to have low viscosity hyperbranched resin.
2. Oil type can be changed to produce long oil alkyds, such as castor, soya bean oil etc.

## REFERENCES

1. Lindeboom, J., *Air-drying high solids alkyd pants for decorative coatings*. Progress in Organic Coatings, 1997. **34** (1-4): p. 147-151.
2. Van der Walle, G.A.M., et al., *Development of environmentally friendly coatings and paints using medium-chain-length poly(3-hydroxyalkanoates) as the polymer binder*. International Journal of Biological Macromolecules, 1999. **25** (1-3): p. 123-128.
3. Van Benthem, Rolf, A.T.M., *Novel hyperbranched resins for coating applications*. Progress in Organic Coatings, 2000. **40** (1-4): p. 203-214.
4. Bao, C.-L., L.-S. Wang, and A.-Q. Zhang, *Synthesis and properties of waterborne hyperbranched aliphatic polyester clear coats*. Journal of the Taiwan Institute of Chemical Engineers, 2009. **40** (2): p. 174-179.
5. Manczyk, K. and P. Szewczyk, *Highly branched high solids alkyd resins*. Progress in Organic Coatings, 2002. **44** (2): p. 99-109.
6. Bat, E., Gündüz, G., Kısakürek, D., and Akhmedov, I. M., *Synthesis and characterization of hyperbranched and air drying fatty acid based resins*. Progress in Organic Coatings, 2006. **55** (4): p. 330-336.
7. Kricheldorf, H.R., *Hyperbranched cyclic and multicyclic polymers by "a<sub>2</sub>+b<sub>4</sub>" polycondensations*. Journal of Polymer Science Part A: Polymer Chemistry, 2009. **47** (8): p. 1971-1987.

8. Seiler, M., *Hyperbranched polymers: Phase behavior and new applications in the field of chemical engineering*. Fluid Phase Equilibria, 2006. **241** (1-2): p. 155-174.
9. Yates, C.R. and W. Hayes, *Synthesis and applications of hyperbranched polymers*. European Polymer Journal, 2004. **40** (7): p. 1257-1281.
10. Gao, C. and D. Yan, *Hyperbranched polymers: from synthesis to applications*. Progress in Polymer Science, 2004. **29** (3): p. 183-275.
11. Güner, S. F., Yağcı, Y., and Tuncer Erciyes, A., *Polymers from triglyceride oils*. Progress in Polymer Science, 2006. **31** (7): p. 633-670.
12. Karakaya, C., Gündüz, G., Aras, L., and Mecidoğlu, I. A., *Synthesis of oil based hyperbranched resins and their modification with melamine-formaldehyde resin*. Progress in Organic Coatings, 2007. **59** (4): p. 265-273.
13. Mukherjee, S. and J. Ren, *Gas-Phase Acid-Base Properties of Melamine and Cyanuric Acid*. Journal of the American Society for Mass Spectrometry, 2010. **21** (10): p. 1720-1729.
14. Edwards, K.N. and Mislav, H.B., *History of coatings*, in *Applied Polymer Science: 21st Century*, D.C. Clara, E.C. Charles, and Jr, Editors. 2000, Pergamon: Oxford. p. 439-447.

15. Karakaya, C., *Synthesis of Oil Based Hyperbranched Resins and Their Modification with Melamine Formaldehyde Resins*, in *Chemical Engineering* 2005, Middle East Technical University Ankara
16. Gündüz, G., *Boya Bilgisi*. 2005, Ankara: Kimya Mühendisliği Odası.
17. Schweitzer, P.A., *Paint and Coatings: Applications and Corrosion Resistance* ed. P.A. Schweitzer. 2006, New York: CRC.
18. Stoye, D. and Freitag, W., *Paints, Coatings and Solvents*. 2 ed, ed. D. Stoye and W. Freitag. 1998, Germany: Wiley-VCH.
19. Johansson, M., Glauser, T., Jansson, A., Hult, A., Malmström, E., and Claesson, H., *Design of coating resins by changing the macromolecular architecture: solid and liquid coating systems*. *Progress in Organic Coatings*, 2003. **48** (2-4): p. 194-200.
20. Bat, E., *Synthesis and Characterization of Hyperbranched and Air Drying Fatty Acid Based Resins* in *Chemical Engineering* 2005, METU: Ankara
21. Okan Oyman, Z., Ming, W., and Van der Linde, R., *Oxidation of model compound emulsions for alkyd paints under the influence of cobalt drier*. *Progress in Organic Coatings*, 2003. **48** (1): p. 80-91.
22. Dutta, N., Karak, N., and Dolui, S.K., *Structural analysis, rheological behaviour and the performance of films for surface coatings' application of heated and unheated Nahar seed oil*. *Polymer Degradation and Stability*, 2005. **88** (2): p. 317-323.

23. Sharma, V. and Kundu, P.P., *Addition polymers from natural oils--A review*. Progress in Polymer Science, 2006. **31** (11): p. 983-1008.
24. Sailer, R.A., Wegner, J. R., Hurtt, G. J., Janson, J. E., and Soucek, M. D., *Linseed and sunflower oil alkyd ceramers*. Progress in Organic Coatings, 1998. **33** (2): p. 117-125.
25. Tracton, A.A., *Coatings Materials and Surface Coatings* ed. A.A. Tracton. 2006: CRC Press. 528.
26. Williams, R.C., *Advances in alkyd resins*, in *Applied Polymer Science: 21st Century*, D.C. Clara, E.C. Charles, and Jr, Editors. 2000, Pergamon: Oxford. p. 471-481.
27. Atimuttigul, V., S. Damrongsakkul, and W. Tanthapanichakoon, *Effects of oil type on the properties of short oil alkyd coating materials*. Korean Journal of Chemical Engineering, 2006. **23** (4): p. 672-677.
28. Sabin, P., B. Benjelloun-Mlayah, and M. Delmas, *Offset printing inks based on rapeseed and sunflower oil. Part I: Synthesis and characterization of rapeseed oil-and sunflower oil-modified alkyd resins*. Journal of the American Oil Chemists' Society, 1997. **74** (5): p. 481-489.
29. Aydın, S., Akçay, H., Özkan, E., Güner, F. S., and Erciyes, A. T., *The effects of anhydride type and amount on viscosity and film properties of alkyd resin*. Progress in Organic Coatings, 2004. **51** (4): p. 273-279.

30. Chittavanich, P., *Pigmented UV-Curable Alkyd*. 2009, University of Akron.
31. Lazzari, M. and Chiantore, O., *Drying and oxidative degradation of linseed oil*. *Polymer Degradation and Stability*, 1999. **65** (2): p. 303-313.
32. Oyman, Z.O., Ming, W., and Linde, R., *Oxidation of drying oils containing non-conjugated and conjugated double bonds catalyzed by a cobalt catalyst*. *Progress in Organic Coatings*, 2005. **54** (3): p. 198-204.
33. Mirminachi, F., *Improvements of Physical and Mechanical Properties of Styrenated Alkyd Resins by Acrylonitrile*, in *Chemical Engineering* 1992, METU: Ankara
34. Mallégol, J., Lemaire, J., and Gardette, J. L., *Drier influence on the curing of linseed oil*. *Progress in Organic Coatings*, 2000. **39** (2-4): p. 107-113.
35. Weiss, K.D., *Paint and coatings: A mature industry in transition*. *Progress in Polymer Science*, 1997. **22** (2): p. 203-245.
36. Malmström, E., Johansson, M., and Hult, A., *Hyperbranched Aliphatic Polyesters*. *Macromolecules*, 1995. **28** (5): p. 1698-1703.
37. Scholl, M., Kadlecova, Z., and Klok, H.-A., *Dendritic and hyperbranched polyamides*. *Progress in Polymer Science*, 2009. **34** (1): p. 24-61.

38. Froehling, P.E., *Dendrimers and dyes-- a review*. Dyes and Pigments, 2001. **48** (3): p. 187-195.
39. Murillo, E.A., Vallejo, P.P., and López, B.L., *Synthesis and characterization of hyperbranched alkyd resins based on tall oil fatty acids*. Progress in Organic Coatings, 2010. **69** (3): p. 235-240.
40. Murillo, E.A., Vallejo, P. P., Sierra, L., and López, B. L., *Characterization of hyperbranched polyol polyesters based on 2,2-bis (methylol propionic acid) and pentaerythritol*. Journal of Applied Polymer Science, 2009. **112** (1): p. 200-207.
41. Tang, J., Wang, J., He, Y., Tong, Z., Shen, Z., Li, X., and Li, B., *Corrosion protection of galvanized sheet by maleic anhydride-g-liquid polybutadiene environmental friendly coatings*. Progress in Organic Coatings, 2008. **63** (2): p. 195-200.
42. Zagar, E., Zigon, M., and Podzimek, S., *Characterization of commercial aliphatic hyperbranched polyesters*. Polymer, 2006. **47** (1): p. 166-175.
43. Ahmad, S., Ashraf, S. M., Kumar, G. S., Hasnat, A., and Sharmin, E., *Studies on epoxy-butylated melamine formaldehyde-based anticorrosive coatings from a sustainable resource*. Progress in Organic Coatings, 2006. **56** (2-3): p. 207-213.
44. Zhang, W.R., Zhu, T. T., Smith, R., and Lowe, C., *An investigation on the melamine self-condensation in polyester/melamine organic coating*. Progress in Organic Coatings, 2010. **69** (4): p. 376-383.

45. Gindl, W., Zargar-Yaghubi, F., and Wimmer, R., *Impregnation of softwood cell walls with melamine-formaldehyde resin*. *Bioresource Technology*, 2003. **87** (3): p. 325-330.
46. Manley, T.R., *Thermal Stability of Hexamethylolmelamine*. *Polymer Journal*, 1972. **4** (1): p. 111-113.
47. Konar, B.B., *A kinetic and rheometric investigation of hexamethylol melamine derivative on the cure of natural rubber compounds*. *Journal of Applied Polymer Science*, 1997. **63** (2): p. 233-237.
48. Dixon, J.K., Woodberry, N.T., and Costa, G.W., *The dissociation constants of melamine and certain of its compounds*. *Journal of the American Chemical Society*, 1947. **69** (3): p. 599-603.
49. Palanikkumaran, M., Gupta, K. K., Agrawal, A. K., and Jassal, M., *Highly stable hexamethylolmelamine microcapsules containing n-octadecane prepared by in situ encapsulation*. *Journal of Applied Polymer Science*, 2009. **114** (5): p. 2997-3002.
50. Haseebuddin, S., Parmar, R., Wagahoo, G., and Ghosh, S. K., *Study of hexafunctional polyol in high solids air-drying alkyd: Improved film performance*. *Progress in Organic Coatings*, 2009. **64** (4): p. 446-453.
51. Nimbalkar, R. and Athawale, V., *Synthesis and Characterization of Canola Oil Alkyd Resins Based on Novel Acrylic Monomer (ATBS)*. *Journal of the American Oil Chemists' Society*, 2010. **87** (8): p. 947-954.

## APPENDIX A

### ACID NUMBER DETERMINATION

Acid number is the number of milligrams of potassium hydroxide required to neutralize the free acids in one gram of the tested material under test conditions. The acid number of the varnishes or resin solutions should be expressed on the basis of solid components, not on the solution. Usually, the acidity is due to the presence of carboxylic groups from free fatty acids or acids used in polyester production.

Determination of acid number is made by titration of the sample with standardized potassium or sodium hydroxide solution. The solvent in the sample must be removed and the sample in solid basis must be weighed. Then the sample is dissolved in a solvent 1:1 isopropyl alcohol and toluene mixture. Phenolphthalein is used as indicator and a pink coloration indicates the end point. The acid number is calculated from the following equation:

$$\text{Acid number} = \frac{V_{\text{KOH}} \times N_{\text{KOH}} \times \text{Mw}_{\text{KOH}}}{m_{\text{sample}}} \quad (\text{Eq. B1})$$

where;            V is the volume of potassium hydroxide solution consumed, in ml,  
                      N is the normality of the solution,  
                      m is the weight of the sample in gram (solid basis).

## APPENDIX B

### DATA USED IN GRAPHS

**Table B.1** Data used in graphs

	HBP:Alkyd ratio	HBP (g)	Long oil alkyd (g)	HBP w/o	Long oil alkyd w/o	Viscosity (Pa.s)	Hardness (Persoz)
HBR-1	1:3	5.44	10.0	35.2	64.8	148.0	198
HBR-2	1:6	5.44	20.0	21.4	78.6	98.5	132
HBR-3	1:8	5.44	26.7	16.9	83.1	12.9	111
HBR-4	1:12	5.44	40.0	12.0	88.0	10.7	88
HBR-5	1:24	5.44	80.0	6.4	93.6	8.84	43