

SYNTHESIS OF OIL BASED HYPERBRANCHED RESINS AND THEIR
MODIFICATION WITH MELAMINE FORMALDEHYDE RESINS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
THE MIDDLE EAST TECHNICAL UNIVERSITY

BY

CEYLAN KARAKAYA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

AUGUST 2005

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Nurcan Baç
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis and for the degree of Master of Science.

Prof. Dr. Leyla Aras
Co-Supervisor

Prof. Dr. Güngör Gündüz
Supervisor

Examining Committee Members

Prof. Dr. Ülkü Yılmaz (METU, CHE) _____

Prof. Dr. Leyla Aras (METU, CHEM) _____

Prof. Dr. Ali Usanmaz (METU, CHEM) _____

Assoc. Prof. Naime Sezgi (METU, CHE) _____

Prof. Dr. Güngör Gündüz (METU, CHE) _____

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Name, Last name : Ceylan Karakaya

Signature :

ABSTRACT

SYNTHESIS OF OIL BASED HYPERBRANCHED RESINS AND THEIR MODIFICATION WITH MELAMINE FORMALDEHYDE RESINS

Karakaya, Ceylan

M.S., Department of Chemical Engineering

Supervisor: Güngör Gündüz, Prof. Dr.

Co-Supervisor: Leyla Aras, Prof. Dr.

August 2005, 85 pages

In this research hyperbranched resins containing fatty acid residues like alkyds were synthesized. Dipentaerythritol which has six hydroxyl groups was used as the core molecule, and it was transesterified with (i) castor oil, and (ii) a mixture of castor oil and linseed oil at 240°C in the presence of sodium hydroxide as catalyst. The resulting molecule, in either case, was then esterified with dimethylol propionic acid at 140°C in the presence of p-toluene sulfonic acid as catalyst.

Melamine-formaldehyde resin was synthesized to be used with the synthesized hyperbranched resins, and it was successfully modified by all hyperbranched resins at a ratio of 3:1.

FTIR spectroscopy was used to characterize the hyperbranched resins and the thermal properties were determined by DSC. DSC showed that the hyperbranched resins decomposed between 315-345°C. The viscosity of the resin that was synthesized by using only castor oil was 3.0 Pa·s and by using 50% linseed oil it was 1.0 Pa·s. When reacted with dimethylol propionic acid, the former's viscosity increased to 7.0 Pa·s, and the second's viscosity increased to 3.7 Pa·s.

The hyperbranched resins showed excellent adhesion, gloss, flexibility, and formability. The mixture of hyperbranched resin plus melamine-formaldehyde resin samples had higher hardness values but lower gloss, adhesion and bending resistance values than the hyperbranched resins, and they had good impact and abrasion resistances.

Keywords: Hyperbranched, Air drying, Castor oil, Linseed oil, Melamine-formaldehyde

ÖZ

YAĞ ESASLI DALLANIK REÇİNELERİN YAPIMI VE MELAMİN FORMALDEHİD REÇİNELERİYLE HARMANLANMA ÖZELLİKLERİNİN ARAŞTIRILMASI

Karakaya, Ceylan

Yüksek Lisans, Kimya Mühendisliği Bölümü

Danışman: Güngör Gündüz, Prof. Dr.

Yardımcı Danışman: Leyla Aras, Prof. Dr.

Ağustos 2005, 85 sayfa

Bu çalışmada, alkitler gibi yağ asidi içeren dallanık reçineler sentezlenmiştir. Altı hidroksil grubu bulunan dipentaeritritol çekirdek molekül olarak kullanılmıştır ve (i) hint yağı ve (ii) hint yağı ve keten yağı karışımı ile 240°C'de katalizör olarak sodyum hidroksit kullanılarak transesterlenmiştir. Her iki durumda da oluşan moleküller, dimetilol propiyonik asit ile 140°C'de katalizör olarak p-toluen sulfonik asit kullanılarak esterleştirilmiştir.

Sentezlenmiş dallanık reçinelerle birlikte kullanılmak üzere melamin-formaldehid reçinesi sentezlenmiştir ve 3:1 oranında tüm dallanık reçinelerle başarıyla harmanlanmıştır.

FTIR spektroskopisi dallanık reçineleri karakterize etmek için kullanılmıştır ve reçinelerin ısı özellikleri DSC ile belirlenmiştir. DSC bütün dallanık reçinelerin 315°C ile 345°C arasında bozunduğunu göstermiştir. Sadece hint yağı kullanılarak sentezlenen reçinenin viskozitesi 3.0 Pa·s ve %50 keten yağı kullanılarak sentezlenen reçinenin viskozitesi ise 1.0 Pa·s'tır. Dimetilol propiyonik asit ile reaksiyona girdiklerinde birincinin viskozitesi 7.0 Pa·s'a ikincinin viskozitesi 3.7 Pa·s'a yükselmiştir.

Dallanık reçineler mükemmel yapışma, parlaklık, esneklik ve şekillendirilebilirlik göstermiştir. Melamin-formaldehid ve dallanık reçine karışımları dallanık reçinelerden daha yüksek sertlik değerlerine sahip olmakla birlikte parlaklık, yapışma ve esneklik değerleri daha düşüktür. Çarpma ve aşınma değerleri ise oldukça iyidir.

Anahtar Sözcükler: Dallanık, Havada kuruyan, Hint yağı, Keten yağı, Melamin-formaldehid

To My Family
&
Onur

ACKNOWLEDGEMENTS

First of all, I would like to express my deepest appreciation to my supervisor Prof. Dr. Gngr Gndz for his valuable guidance, his humanity and his kindly attitude towards me.

I would also like to thank my co-supervisor Prof. Dr. Leyla Aras, for her suggestions and help. I wish to express my thanks to Assoc. Prof. Gknur Bayram and İlknur akar for their help in viscosity measurements. Also, I would like to thank Perstorp AB Sweden, Akzo Nobel Kemipol, and Betek Boya for supplying some of the chemicals and to the technicians of the machine shop for their help.

My special thanks goes to Mustafa Onur Diri for his help, greatest encouragement and for being with me all the time.

I wish to thank Bařak Kurbanođlu and Nursel İpek zmen for their friendship and motivation. Last but not least, I would like to thank my lab partners Erhan Bat, Umut Barıř Ayhan, Senem Tanrıverdi, Arzu Bykyađcı and Cemil Alkan for their helpful discussions, support, help and friendship.

I would like to present my greatest thanks to my family for their endless love, unlimited support, and care throughout my life. Everything would have been harder without them.

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NOMENCLATURE

Dipenta	Dipentaerythritol
DMPA	Dimethylol propionic acid
HBR	Hyperbranched resin
HBR-1	Hyperbranched resin-1 (Dipenta + Castor Oil)
HBR-2	Hyperbranched resin-2 (Dipenta + (Castor Oil + Linseed Oil))
HBR-3	Hyperbranched resin-3 (Dipenta + Castor Oil + DMPA)
HBR-4	Hyperbranched resin-4 (Dipenta + (Castor Oil + Linseed Oil) + DMPA)
MFR	Melamine-Formaldehyde resin
M_w	Weight average molecular weight
M_n	Number average molecular weight
PET	Poly (ethylene terephthalate)
PP	Polypropylene
p-TSA	Para toluene sulfonic acid
Std. Dev.	Standard deviation
UV	Ultraviolet
VOC	Volatile organic compound

CHAPTER 1

INTRODUCTION

The coatings industry has experienced a strong drive towards new products during the last few decades. New products must allow lower total “system” cost, have better performance and lower impact on the environment. The coatings which contain very high levels of solvents (volatile organic compounds (VOCs)) cause global warming and create photochemical ozone which is toxic to all living things. Also, the used solvents increase the cost of coatings. The increasing costs of solvents as well as the restrictions on solvent emission are forcing coating industry to produce less expensive coatings having very low VOC content or no VOC at all, and also have good properties [1, 2].

Scientists have tried to produce environment friendly coatings and since the last few decades, they developed several coatings having low VOC content such as water-based acrylic dispersions, water-based alkyd emulsions, and air drying, high solids alkyds. But the main problem is to decrease the viscosity while keeping the properties at high level. In order to deal with this problem, highly branched chains were synthesized. They have lower viscosity when compared to linear analogues at the same molecular weight.

The synthesis of branched condensation polymers from multifunctional monomers was first presumed by Flory in 1952. The development of the ‘true dendrimers’ was first presented in the article describing the preparation of

poly-(amidoamine) polymer in 1984 and the term 'dendrimer' was used for the first time in this article [3].

Dendritic polymers have high solubility and lower solution and melt viscosity compared to linear analogues. Their globular shape eliminates the entanglements and they can also be tailored with respect to functionality and polarity to adjust the properties for certain applications.

Dendritic polymers have mainly three sub-classes; (i) dendrimers, (ii) dendrigrafts, and (iii) hyperbranched polymers. Dendrimers are highly uniform, three-dimensional, and monodisperse polymers with a tree-like globular structure. They have good material properties, but the synthesis is often time-consuming, complicated, and costly to produce.

In the early 1990s, Kim and Webster synthesized highly branched polydisperse macromolecules with an imperfect architecture and they named these products 'Hyperbranched Polymers'. Hyperbranched polymers can be produced in large scale at a reasonable cost making them more attractive in several areas [4–7]. The use of hyperbranched polymers in several coating applications have been discussed in the literature [8–12].

Hyperbranched alkyd resins have been studied in order to obtain air drying low viscosity resins [13–15]. In these studies, they modified the hydroxyl groups at the outer periphery of hyperbranched polyesters with different fatty acids.

These works were taken as the beginning point and the aim of this research was to synthesize low viscosity hyperbranched resins having properties close to alkyds and to react the synthesized hyperbranched resins with melamine-formaldehyde resin to obtain new surface coating resins. A hyperbranched polymer was synthesized using dipentaerythritol as the core molecule and transesterified with the castor oil. This resin was not an air

drying resin. Then, a mixture of castor oil and linseed oil was transesterified by dipentaerythritol. Linseed oil was used because the high unsaturation of linseed fatty acids provides easy air drying. The resulting oligomeric molecules in either case were then reacted with dimethylol propionic acid (DMPA).

Amino resins have been widely in use in surface coating systems normally in combination with other resins. Butylated melamine-formaldehyde resin was synthesized to be used with hyperbranched resins. The hyperbranched resins and the hyperbranched resin plus the melamine formaldehyde resin mixture were applied to the surface of glass and metal test panels. The hyperbranched resins and the melamine-formaldehyde resin were mixed by a ratio of 1:3. All hyperbranched resin samples on plates were left for 12 hours in an oven at 90°C to accelerate curing and the hyperbranched resin and melamine formaldehyde resin mixture was cured at 150°C for 1 hour in an oven. Resins were characterized and the mechanical and the physical properties of the samples were tested.

CHAPTER 2

LITERATURE SURVEY

2.1 Coatings

Surface coatings are solid or liquid materials, that can be applied as one or more thin layers to the surface of an object and dry to form well adhering films. Paint and coating terms are often used interchangeably. Usually the term paint is used when the primary consideration is the decorative purposes, on the other hand when the primary consideration is the protection of the materials the term coating is used [16]. Today coatings are used for decoration or protection or some functional purposes or for more than one of these reasons. The decorative effect may be obtained through color, gloss or combinations of these properties. The protective function includes resistance to water and chemicals, together with improved superficial mechanical properties such as greater hardness and abrasion resistance. In certain cases, coatings make the surface either a good or poor electrical conductor, and improve the workability of coated metals in the mechanical processing [16–18].

The origin of paints dates back to prehistoric times when the early inhabitants of the earth recorded their activities in colors on the walls of their caves. Certain objects were colored in order to ensure good fortune in hunting, to hold evil spirits at bay, to propitiate the stern gods or to honor the dead in their graves. These crude paints probably consisted of colored earths or clays suspended in water. The Egyptians, starting very early, developed the art of painting and by 1500 B.C. had a large number and wide

variety of colors. About 1000 B.C. they discovered the varnishes, usually naturally occurring resins or beeswax were the film-forming ingredient. It is only at a higher level of cultural development that the purely artistic motive becomes dominant and it was very late in history with the birth of industrialism that painting came to be used extensively to protect objects and extend their useful lives [16, 19].

2.1.1 Composition of Coatings

Coatings contain three major ingredients together with smaller quantities of additives. The major ingredients are pigments, binders, and solvents [20].

2.1.1.1 Pigments

Pigments are finely divided insoluble solids that are dispersed in the vehicle and remain suspended in the binder after film formation. Generally, the primary purpose of pigments is to provide color and opacity to the coating film [17]. However, there are many other reasons for the incorporation of pigments into the system. Pigments have a considerable influence on the consistency of the paint and hence on its application properties. Pigments are also of importance for the resistance of the film to external attack, in that they are partially responsible for such properties as resistance to abrasion and weathering. They are also added for the durability characteristics and to inhibit the corrosion [16, 21].

Pigments can be inorganic or organic. Inorganic ones are usually metallic oxides, such as lead oxide, chromium oxide, cobalt blue etc. Organic ones are generally not found in nature, and they are synthesized from the coal tar and petroleum distillates.

2.1.1.2 Binders or Resins

Binders are the materials that form the continuous film which adheres to the substrate (the surface being coated), bind together the other substances in the coating to form an adequately hard film on the surface [17]. The binder is the most important one of the components. Many of the properties of coatings, such as their mode of drying, and adhesive and mechanical properties of the films are determined by the nature of the binder.

Resins can be divided into two as natural resins and synthetic resins. Both natural resins and synthetic resins are organic compounds, often with complicated chemical structure and in many cases of high molecular weight. Today, synthetic resins have mostly replaced natural resins because of their advantages. They may be produced to fairly close technical tolerances, while the natural resins show wide variations in quality. Most important advantage of the synthetic resins is that they can be varied in relation to the end use for which they are required; in other words, they can be 'tailor made'. Some examples of natural resins are rosin, amber, mastic etc. and some examples of synthetic resins are alkyd, amino, epoxy, acrylic etc. [16].

2.1.1.3 Solvents

Solvents are used in paints to reduce the viscosity or consistency of the material and so facilitate the application of a uniform coating. After application, the solvent is no longer needed and it should evaporate completely from the film.

Coating solvents, with the exception of water, are volatile organic liquids. The classes of materials used as solvents include aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, esters, ketones and ethers. Water is the solvent in water-borne and emulsion paints [20].

2.1.1.4 Additives

In addition to these three components, modern paints may contain additives of various kinds, such as plasticizers, driers, emulsifiers or other stabilizers.

2.1.2 Film Formation

Most coatings are liquids with a viscosity appropriate for the application method to be used [17]. After the application, the liquid is converted to a solid film. During film formation process, the coating is transformed to a film that adheres tightly to the surface [22]. The conversion of the liquid material into an adherent, durable coating is the process of film formation [18]. There are three general methods by which film-formers change from liquid to solid state [9]:

- i. evaporation of solvents or water.
- ii. oxidation.
- iii. polymerization.

2.1.3 The Drying Process

A differentiation is made between physical and chemical drying according to the way in which film formation occurs.

Physical drying is a process in which film formation occurs solely as a result of the evaporation of the volatile constituents like solvents. Physically dried coating films may be redissolved in solvents. Some physically drying resins are vinyl resins, acrylic resins, and some natural resins like shellac and rosin.

Chemical drying is a process in which the molecules of the binder undergo chemical reaction with each other. The film formed by chemical drying is insoluble in solvents. If the material contains volatile components, which is normally the case where synthetic binders are used, the chemical drying usually occurs only after the greater part of the volatile constituents has

evaporated. Some chemically drying resins are polyurethane resins, epoxide resins, and alkyd resins [16].

2.1.4 Driers

Driers are used in some types of organic coatings to accelerate the conversion of the liquid coating to the dry film. To be effective, driers must be miscible and stable in unpolymerized and polymerized oils and resins, in mixtures of these, and in solvent thinners normally used in coating formulations [18, 23]. Without the use of these catalysts, film formation would be so slow as to be commercially unacceptable but the amounts of driers should be kept to the minimum possible level, since they not only catalyze drying but also catalyze the reactions that cause postdrying embrittlement, discoloration and cleavage. There are three classes of driers [24]:

- i. *The Primary Driers.* These are organic salts (e.g. octoates, tallates and naphthenates) of transition metals, most usually manganese or cobalt. They directly catalyze the oxidation of the oil and are normally employed in amounts varying from 0.005 to 0.1 % metal based on the oil. Their primary function is to promote rapid surface drying of the film.
- ii. *The Secondary Driers.* These are organic salts of zinc, calcium, lead or barium. They do not have any direct effect on the oxidation when used on their own, but when used in conjunction with a primary drier, they act as synergists and considerably increase the rate of oxygen uptake of the oil.
- iii. *The Co-ordination Driers.* These are compounds of usually zirconium or aluminum, which assist in the polymerization process by the formation of co-ordination compounds.

2.1.5 Viscosity

The viscosity of a fluid characterizes its resistance to flow. The viscosities of coatings are mostly important for the ease of application appearance of films. Viscosity ' η ', is defined as the ratio of shear stress ' τ ', to shear rate ' $\dot{\gamma}$ ' [25].

$$\eta \equiv \frac{\tau}{\dot{\gamma}}$$

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 plot of shear rate as a function of shear stress is linear. 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. Such materials are called Bingham plastics. Schematic flow diagrams are shown in Figure 2.1 [17, 25].

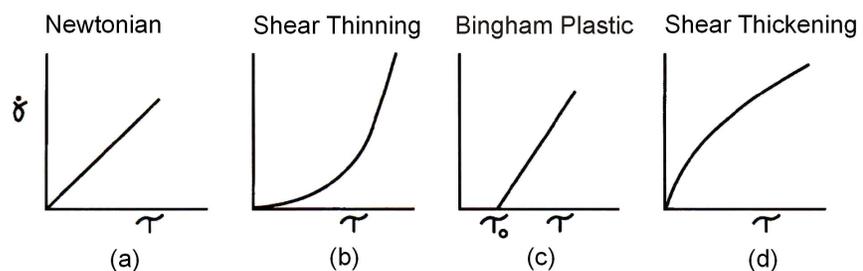


Figure 2.1 Schematic plots of flow of different types of liquids [17].

Time-dependent fluids are those whose viscosity is a function of both shear rate (or shear stress) and time. The most common such behavior

- i. the number of C=C double bonds (degree of unsaturation)
- ii. the relative positions of the double bonds (degree of conjugation)
- iii. the presence (or absence) of polar groups (such as OH or C=O) on the carbon backbone.

Saturated fatty acids have hydrocarbon chains containing no double bonds. Fatty acids with chains containing double bonds are termed unsaturated. They may have one, two, three or more double bonds, whose position in the chain may vary. Two double bonds separated by a single bond are called conjugated.

The double bonds in unsaturated fatty acids are chemically reactive sites. The reaction of oxygen with the oil molecule at the double bond results in drying; usually the greater the unsaturation, the better is the drying. Saturated fatty acids are nondrying. However, in addition to the number of double bonds, the position of the double bond is also important. Conjugated double bonds polymerize and dry more rapidly than isolated double bonds [18].

The variations in properties encountered with the different oils are a function of the variation in fatty acid structure. Since more than one type of fatty acid can be present per oil molecule, the properties of a particular oil can be directly related to the fatty acid composition [24]. Fatty acid compositions and some constants of common oils are given in Table 2.1.

Table 2.1 Fatty acid compositions and some constants of common oils [24]

Acid	Molecular formula	Number of double bonds	Coconut Oil	Castor Oil	Grape Seed Oil	Linseed Oil	Oiticica Oil	Palm Oil	Safflower Oil	Sunflower Oil	Soya Bean Oil	Tung Oil
Caprylic	C ₈ H ₁₆ O ₂	0	6				Contains 4% hydroxy acids					
Capric	C ₁₀ H ₂₀ O ₂	0	6									
Lauric	C ₁₂ H ₂₂ O ₂	0	44									
Myristic	C ₁₄ H ₂₈ O ₂	0	18					1				
Palmitic	C ₁₆ H ₃₂ O ₂	0	11	2	9	6	7	48	8	11	11	4
Stearic	C ₁₈ H ₃₆ O ₂	0	6	1	4	4	5	4	3	6	4	1
Oleic	C ₁₈ H ₃₄ O ₂	1	7	7	20	22	6	38	13	29	25	8
Ricinoleic	C ₁₈ H ₃₄ O ₂	1		87								
Linoleic	C ₁₈ H ₃₄ O ₂	2	2	3	67	16		9	75	52	51	4
Linolenic	C ₁₈ H ₃₀ O ₂	3				52			1	2	9	3
Eleostearic	C ₁₈ H ₃₀ O ₂	3										80
Licanic	C ₁₈ H ₂₈ O ₂	3					78					
Iodine Value			7.5-10.5	81-91	130-140	155-205	140-160	44-54	140-150	125-136	120-141	160-175
Melting Point (°C)			23-26					27-50				
Uses			Short oil non-drying alkyd resins Epoxy resins	Plasticizer in ink systems Plasticizing alkyds	Alkyd resins	Oleo-resinous varnish Long oil alkyd	Oleoresin varnish Alkyd resins	Short oil non-drying alkyd resins	Alkyd resins	Alkyd resins	Alkyd resins	Oleo-resinous varnish Alkyd resins

Table 2.2 Formulas of fatty acids

Acid	Formula
Caprylic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_6-\text{CH}_3$
Capric	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_8-\text{CH}_3$
Lauric	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_{10}-\text{CH}_3$
Myristic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_{12}-\text{CH}_3$
Palmitic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_{14}-\text{CH}_3$
Stearic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_{16}-\text{CH}_3$
Oleic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$
Ricinoleic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\overset{\text{OH}}{\text{CH}}-(\text{CH}_2)_5-\text{CH}_3$
Linoleic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{CH}_3$
Linolenic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$
Eleostearic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-(\text{CH}_2)_3-\text{CH}_3$
Licanic	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-(\text{CH}_2)_3-\text{CH}_3$

2.2.1 Classification of Oils

Glyceride oils are usually classified as drying, semi-drying, or non-drying. These divisions reflect the ability of the oil to 'air-dry', i.e. to form a coherent film on exposure to the atmosphere. This ability is directly related to the fatty acid composition.

When fatty acids containing at least two double bonds are present, the oil is said to 'air-dry'. Drying oils will form a 'tack free' film, whereas the semi-drying oils form films that are never completely 'tack free'. Non-drying oils are unable to form a cross linked structure by air oxidation.

2.2.2 Drying Process of Oils

Air drying ability of oil is quantified by the drying index.

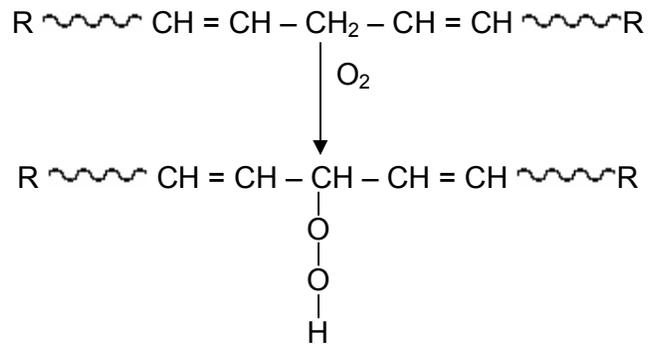
Drying Index = (% linoleic acid + 2 x % linolenic acid)

A drying index greater than 70 indicates a drying oil.

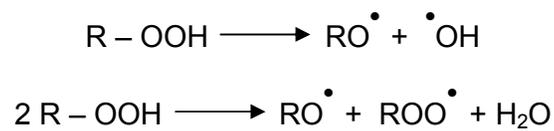
Iodine value is the grams of iodine required per 100 grams of oil and iodine value determinations can be used to measure the degree of unsaturation of oil and this is useful in predicting the drying nature of the oil. An iodine value of about 160 would normally indicate a drying oil.

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

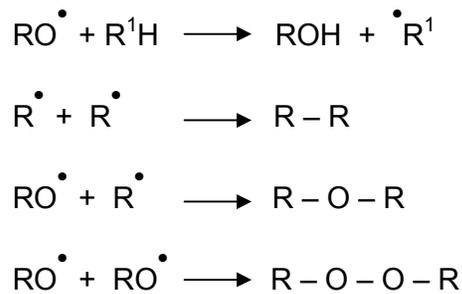
Non-conjugated systems



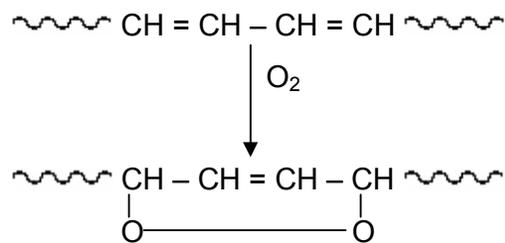
The hydroperoxide then decompose, by the dissociation of the O – O bond, leading to a variety of products including intermolecular linkage, i.e. cross-linking:



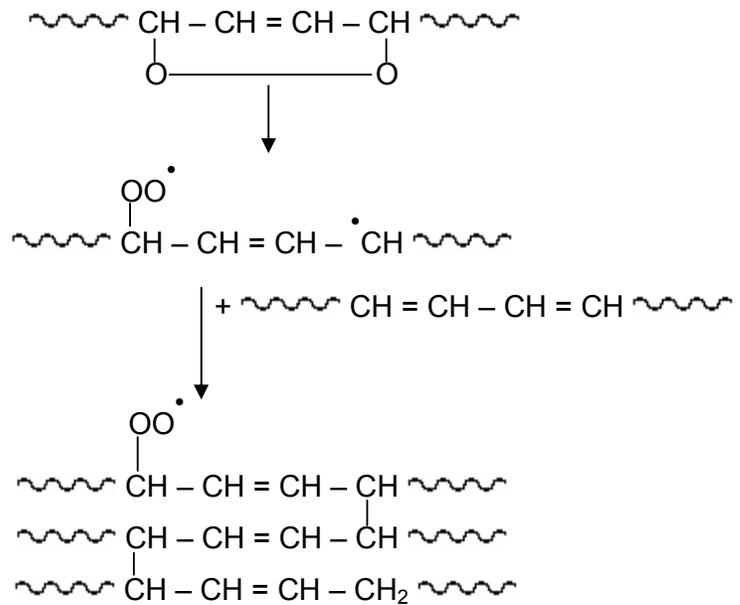
Then,



Conjugated systems



In conjugated systems, the hydroperoxide formed is predominantly 1, 4. The film formed differs from that formed by a non-conjugated structure in that the linkages are predominantly C-C suggesting a vinyl polymerization mechanism.



In practice the length of the polymerization chain is short because the probability of chain termination by oxygen is high. Schematic representation of a cross-linked oil film may be represented as in Figure 2.3.

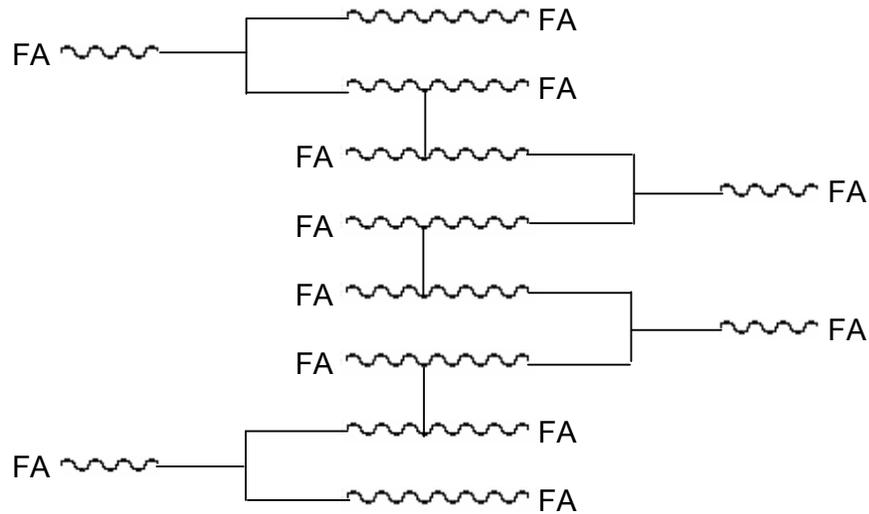


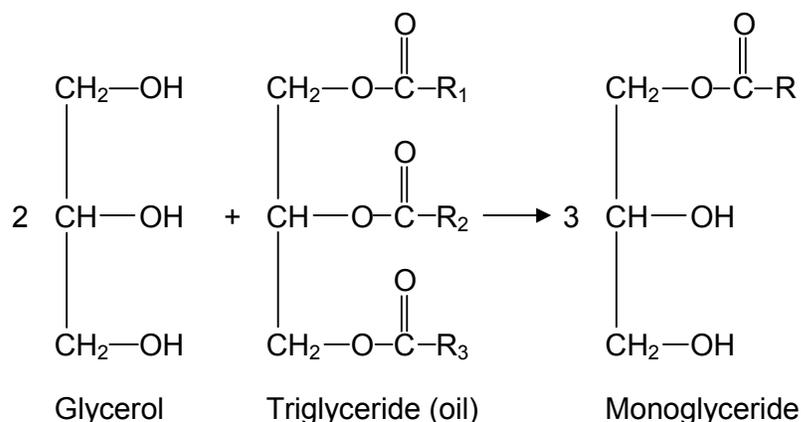
Figure 2.3 The schematic representation of the cross-linked oil film.

Where FA  represents the fatty acid and  represents the glycerol portion of the oil molecule [24].

2.2.3 Alcoholysis of the Oil

In this process, which is also called the monoglyceride process, the oil (i.e. tri-glyceride) is converted into reactive monoglyceride by reacting it with the necessary amount of polyol. During alcoholysis ester interchange is brought about between the polyol and oil.

The idealized equation below shows the reaction between an oil and glycerol. A similar reaction occurs with other polyols.



In practice complete monoglyceride formation is not possible and is unnecessary, diglycerides and small amounts of triglyceride and glycerine can be present.

Alcoholysis requires temperatures of 240 °C – 260 °C and ester interchange is greatly speeded up by the use of basic catalysts. The level of catalyst normally used is 0.03–0.04% w/w on the oil charge for lead acetate and 0.01–0.03% for lithium hydroxide. Sodium hydroxide can also be used as catalyst. The reaction is normally carried out under a slightly positive inert gas pressure to prevent ingress of air, which would otherwise result in discoloration of the product. The progress of the ester interchange reaction is monitored by measuring the tolerance of the reaction mixture towards alcohol. Initially the mixture of oil and polyol has a low tolerance, but as the level of triglyceride decreases the alcohol tolerance of the reaction mixture increases [24].

2.3 Alkyd Resins

Alkyds are still of major importance though they are no longer the largest volume binders in coatings [17]. The term alkyd is derived from *alcohol* and *acid*. They are the products of the esterification of polybasic acids, monobasic acids and polyhydric alcohols [20]. Because of this wide choice of

starting materials, probably there is no other class of resins which is capable of such wide variations in physical properties and uses. Alkyds tend to be lower in cost than most other binders because of its relatively inexpensive raw material, manufacturing cost, and high solubility in less expensive solvents. Also they tend to give coatings that exhibit fewer film defects during application. Since they are compatible with most of the other resins, easy to pigment, and less expensive with respect to other resins they have a wide usage area in coating industry [16, 17, 21].

Alkyd resins are mainly used in decorative paints, air drying and stoving paints, industrial paints, inks, machine toll finishes, and marine topside and weatherwork paints.

2.3.1 Raw Materials

2.3.1.1 Polyhydric Alcohols

Glycerol is most widely used polyol because it is present in naturally occurring oils from which alkyds are commonly synthesized. The next most widely used polyol is pentaerythritol. In order to prevent gelation, the tetrafunctionality of pentaerythritol must be taken into account. At the same mole ratio of dibasic acid to polyol, more moles of fatty acid can be esterified with pentaerythritol. The average functionality for cross-linking is higher and the time to reach a given degree of solvent resistance is shorter for a pentaerythritol alkyd as compared to a glycerol alkyd. Ethylene glycol, propylene glycol, and diethylene glycol are the polyhydric alcohols that can be used in alkyd resin production.

2.3.1.2 Polybasic Acids

Polybasic acids used to prepare alkyds are usually aromatic. Cycloaliphatic anhydrides such as hexahydrophthalic anhydride are also used. By far the most important is phthalic anhydride. Another important acid is maleic,

usually sold as the anhydride. The next most widely used dibasic acid is isophthalic acid.

The fundamental properties of an alkyd resin are very markedly affected by the choice of polybasic acid used. The glycerol esters of phthalic acid and maleic acid are hard, brittle resins. On the other hand, the corresponding esters of sebacic and adipic acids are soft. The two carboxyl groups in phthalic acid are quite rigidly attached to the benzene ring. They cannot change their spatial relationships to the other. In the case of sebacic and adipic acids, however, the two carboxyl groups are separated by a long flexible chain of carbon atoms; thus the two carboxyl groups can assume almost an infinite number of positions with respect to each other.

2.3.1.3 Monobasic Acids

By far the greatest number of alkyd resins manufactured are not simple esters of polyhydric alcohols and polybasic acids, but are modified with varying amounts of monobasic acids. With the exception of rosin, almost all of these monobasic acids are derived from the vegetable drying and semi-drying oils which are glycerol esters of these acids. Benzoic acid is used in high functionality system to act as chain stopper [17, 21, 24].

2.4 Dendritic Polymers

Most synthetic and naturally occurring macromolecules have a simple linear structure. They are formed by repeating monomeric units, with an end group at each end of the chain. These two end groups have very small effects on the chemical and physical properties of the polymer. It is well known that the shape of organic molecules and the end groups of the molecule play an important role in determining the properties of the polymers. Scientists have introduced a new philosophy of 'dendritic macromolecules' and prepared

spherical molecules which was introduced a large number of branches, in addition to the more conventional linear ones.

Dendritic polymers are a class of polymers characterized by a densely branched backbone and a large number of reactive groups. It is possible to tailor the dendrimer's properties by appropriate chemical modification of the end groups. The properties of dendritic polymers have been shown to exhibit significant differences compared to their linear analogs [27, 28].

One of the first properties of dendritic polymers that are different from those of linear analogs is the high solubility induced by the branched backbone that offers better processability characteristics and rapid dissolution and the solubility depends to a large extent on the structure of the end groups.

Linear polymers have higher viscosities and a more rapid decrease in viscosity with solvent content was noted for the dendritic polymers when they were diluted, thus, dendritic polymers are more soluble than linear polymers.

An important area where linear and dendritic polymers exhibit diverse characteristics is their viscosity behavior. The solution viscosities of dendritic macromolecules are lower than those of conventional linear polymers. The low viscosity implies that dendritic macromolecules are less entangled due to their spherical shape. Also they exhibit a very low ' α ' value in the Mark-Houwink-Sakurada relationship and so, they have lower intrinsic viscosities than their linear analogues (Figure 2.4). This is consistent with highly branched, compact, globular non-entangled structures.

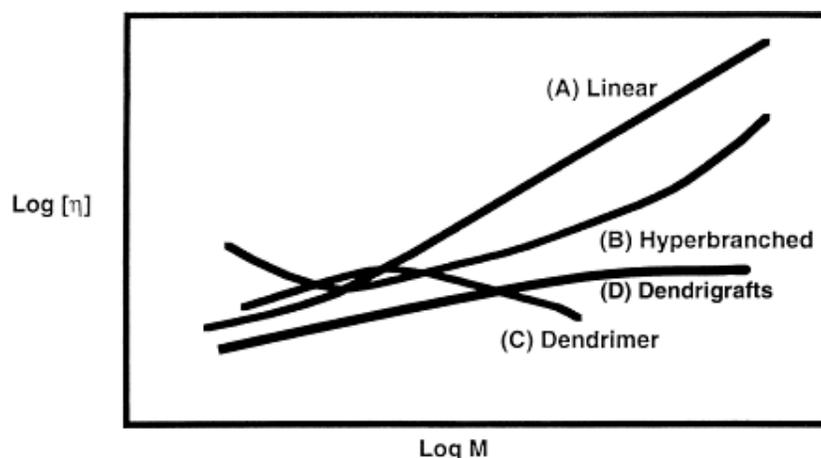


Figure 2.4 Comparison of intrinsic viscosities ($\log(\eta)$) vs molecular weight ($\log M$) for linear, hyperbranched, dendrimer and dendrigraft topologies [29].

Another special feature of dendritic polymers is the possibility to combine an interior structure with one polarity, with a shell (end groups) having another polarity, for instance a hydrophobic inner structure and hydrophilic end groups [4, 5, 28].

Due to their highly branched structure, dendritic polymers are almost exclusively amorphous materials. Therefore, the glass transition temperature is one of the most important thermal properties. The classical visualization of T_g is related to relatively large segmental motions in the polymer chain segments and the fact that the role of the end groups diminishes above a certain molecular weight. This is more difficult to conceive for hyperbranched polymers since segmental motions are affected by the branching points and the presence of numerous end groups. It has instead been proposed that the glass transition temperature of dendritic polymers is due to translational motion of molecules rather than segmental motion. Several other factors such as chemical nature, degree of branching, steric interactions due to crowding, backbone rigidity, and polarity also play an important role for the glass transition temperature. The thermal stability of hyperbranched

polymers is related to the chemical structure in the same manner as for linear polymers; for example, aromatic esters are more stable than aliphatic ones.

The rheological properties of dendrimers are usually characterized by Newtonian behavior in the molten state i.e. no shear thinning or thickening is observed indicating a lack of entanglements. The non entangled state imposes rather poor mechanical properties resulting in brittle polymers. The large amount of branching also makes most of these polymers amorphous although exceptions exist. The melt behavior has been shown to be greatly affected by the structure of the end-groups where an increase in the polarity of the end-groups can raise the viscosity by several orders of magnitude. This is very important where low viscosity is essential for the processing of the material [4, 6].

2.4.1 Synthesis of Dendritic Polymers

The synthesis of branched condensation polymers from multifunctional monomers was first presumed by Flory in 1952. But since he expected non-entangled, highly branched condensation polymers having a broad molecular weight distribution and therefore poor mechanical properties, he did not pursue this theoretical approach further. By the end of 1970s, Vögtle and co-workers described the first cascade synthesis of dendrimers. Tomalia et al. developed a methodology for the synthesis of starburst dendrimers, and Newkome et al. for the synthesis of cascade molecules. The latter methodology for the synthesis of dendrimers came to be known as the divergent growth approach. In 1989 Fréchet et al. introduced an alternative synthetic strategy for the construction of dendritic macromolecules, the so-called convergent growth approach. In the divergent route (Figure 2.5) the dendrimer is built up from a central polyfunctional core and in a repeated reaction cycle the building blocks are added layer by layer. The number of building blocks that can be added is dependent upon the available reactive

sites on the particular core. Each next cycle leads to a higher generation of dendrimer. In the convergent synthesis (Figure 2.6) first complete wedges are prepared and subsequently coupled to a central core. But at some point of wedge development, chemical connectivity to a core will become impossible, or very difficult, due to the juxtaposed steric interference. On the other hand purification becomes less problematic than in the divergent case due to larger byproducts and the smaller number of reactions required [3, 6, 8, 27, 30–32].

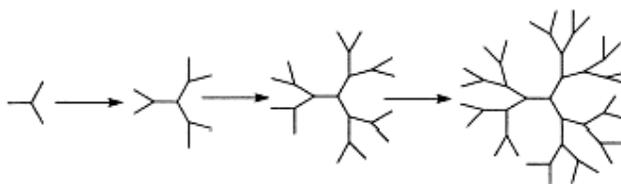


Figure 2.5 Divergent synthesis of dendritic polymers [27].

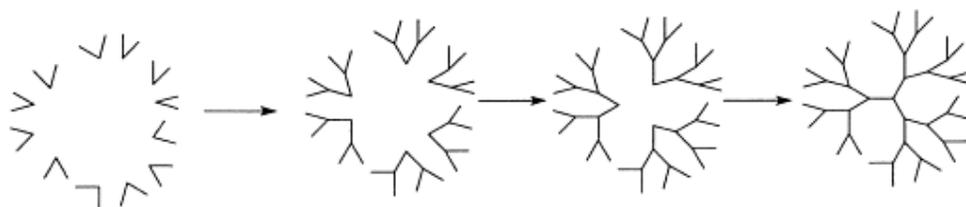


Figure 2.6 Convergent synthesis of dendritic polymers [27].

2.4.2 Categories of Dendritic Polymers

Dendritic polymers have mainly three sub-classes; (i) dendrimers, (ii) dendrigrafts, and (iii) hyperbranched polymers. Dendrimers are highly uniform, three-dimensional, monodisperse polymers ($M_w/M_n = 1.00\text{--}1.05$) with a tree-like, globular structure. The polydispersity index has a value of one if all molecules are of the same molecular weight. Hyperbranched

polymers - unlike dendrimers - exhibit polydispersity ($M_w/M_n = 2-10$) and irregularity in terms of branching and structure and they are not fully reacted at every repeating unit. Dendrigrraft polymers reside between these two extremes of structural control, frequently manifesting rather narrow polydispersities ($M_w/M_n = 1.1-1.5$) depending on their mode of preparation. Schematic representations of dendrimers and hyperbranched polymers can be seen in Figure 2.7. The progress in designing and synthesizing dendritic polymers having unique and different properties compared to their linear analogues enables an unpredictable interdisciplinary variety of applications [5, 6, 8, 9].

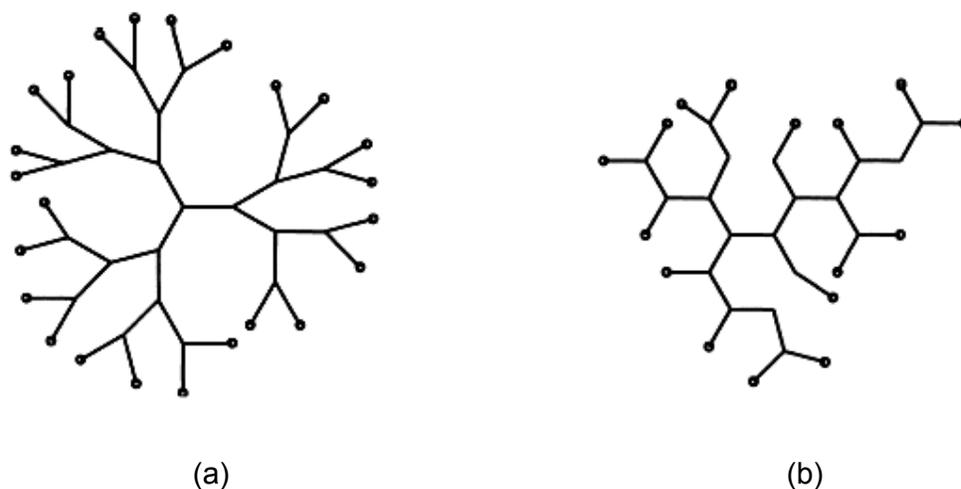


Figure 2.7 Architectures of dendrimer and hyperbranched polymer [27].

2.4.3 Applications of Dendritic Polymers

Since, the freedom of modifying the structure of the end-groups is very high, dendritic polymers can be used for many applications such as toughening additives or rheology modifiers, controlled drug delivery applications, and catalysts [6, 9, 10, 32]. Many scientists have focused their attention on the synthesis of new dendritic polymers and their usage [3-6, 8-10, 28, 30-32]. Hyperbranched polymers have more usage area than dendrimers because of

the dendrimers time consuming and expensive ways of synthesis which prevents large scale production.

2.4.4 Hyperbranched Polymers

The initial aim of dendritic polymers is the preparation of perfect monodisperse dendrimers. They have good material properties, but the synthesis is often time-consuming, complicated, and costly to produce. In the early 1990s, Kim and Webster developed a one-step synthesis that allowed to produce the dendritic resin in large quantities. The result of their uncontrolled growth reaction led to highly branched polydisperse macromolecules with an imperfect architecture since the molecules contained both linear and dendritic sections. Kim and Webster named these products 'Hyperbranched Polymers' [4–6, 11, 12].

The step growth polymerization of AB_x monomers is the most widely used pathway for the synthesis of hyperbranched polymers. The condensation procedure involves a one-step reaction where the monomer and suitable catalyst/initiator are mixed and heated to the required reaction temperature. The reaction involves the typical features of a step growth reaction of multifunctional monomers and the formed oligomers but without the danger of crosslinking. The resulting polymer is generally used without any purification or, in some cases, after precipitation of the dissolved reaction product from a nonsolvent.

The syntheses of dendrimers are time consuming and often produce substances in low yield. This makes dendrimers rather costly to produce and less attractive for large volume applications. On the other hand hyperbranched polymers are often easy to synthesize on a large scale, often at a reasonable cost and their properties are intermediate between those of dendrimers and linear polymers which makes them more attractive for large scale industrial applications [4, 5, 7].

2.4.4.1 Applications of Hyperbranched Polymers

The properties of the hyperbranched polymer can be tailored by modifying all or some part of the end groups. The possibility of tailoring the properties of the polymer causes lots of application areas such as additives, powder coatings, high solid coatings, cross-linkers, catalysis, and delivery devices.

One application that has been suggested for hyperbranched polymers is as an additive, where the hyperbranched polymers improve a property such as polymer toughness. This is possible since the polarity of the hyperbranched polymer can be adjusted to make it either compatible or incompatible with another polymer [4].

Thermosets is another usage area of hyperbranched polymers. Hyperbranched polymers can improve the processing properties, allow high solids formulations and obtain sufficient material strength because they have relatively low melt and solution viscosities, and widespread crosslinking. Hult et. al. [33] modified hyperbranched hydroxy functional polyesters with maleate allyl ether end group to be used for thermoset applications. They synthesized different polyesters by changing the ratios of end groups and they studied the differences of the properties, viscosities and curing rates of the synthesized polyesters.

Johansson et. al. [9] synthesized hyperbranched polyesters having hydroxyl end groups. They reacted the end groups with different compounds such as fatty acids, acrylate, and maleate to obtain different resins ranging from liquid UV-systems to low temperature curing powder coatings and resin additives. They concluded that the use of highly branched resins reduced the need for solvents, and they had low melt viscosities and the numerous end-groups can be modified to produce very different cross-link densities and polarities of the films.

Manczyk et. al. [13] synthesized hyperbranched, star like and conventional alkyd resins and found that hyperbranched and star-like resins showed low viscosity, rapid drying, but lower elasticity, and lower hardness.

Pettersson [14] synthesized an alkyd resin based on a hyperbranched aliphatic polyester and a conventional high solid alkyd. He found that the hyperbranched polyester had improved physical, as well as chemical and mechanical properties and it contributed to low viscosities combined with excellent drying. Since the viscosity of the hyperbranched polyester is lower than the conventional resin, less solvent was needed to obtain a suitable application viscosity.

Van Benthem [15] developed hyperbranched polyesteramides derived from cyclic carboxylic anhydrides and dialkanolamines to be used as powder coating binder components. The presence of the reactive hydroxyl groups makes the hyperbranched polymer suitable material for further modifications to be used in coating applications. He observed a combination of favourable properties, including high hardness and early drying, high solids content, and weatherability.

Bruchmann et. al. [34] synthesized hyperbranched polyurethanes which had either hydroxyl or isocyanate end groups to be used as crosslinkers in two component coating formulations which displayed better hardness than any other isocyanate raw materials.

Lange et. al. [35] evaluated hydroxy functional hyperbranched polyesters for use as barrier coatings and they partially end-capped with acrylate or methacrylate units. They applied the coatings on PP and PET substrates and crosslinked by UV light and determined the barrier of coatings against oxygen and water vapor. They concluded that the hyperbranched coatings gave a pronounced improvement in oxygen barrier on both substrates but didn't improved water vapor barrier. Some other studies about UV curable

polyester, polyurethane, and polyamine esters were presented in the literature [36–41].

2.5 Melamine-Formaldehyde Resin

Amino resin is formed from the reaction between formaldehyde and compounds containing amino groups. The most commonly used amino resins are those produced from urea, melamine and benzoguanamine. Amino resins are widely used in surface coating systems normally in combination with other resins for stoving and baking finishes, e.g. car enamels, radiators, heaters, and finishes for refrigerators.

The first step in synthesis of melamine formaldehyde resin is methylation, the reaction of melamine (2,4,6-triamino-1,3,5-triazine) with formaldehyde under alkaline conditions. Melamine can combine with six molecules of formaldehyde per molecule. In the preparation of coating resins, usually 5-6 moles of formaldehyde are reacted by one mole of melamine. By this reaction methylol groups are formed and in general various methylol melamines form.

Methylol groups can react to give a polymerized structure. To achieve a product suitable for use as a surface coating it is necessary to restrict the amount of condensation occurring due to the methylol-methylol reaction by removing methylol groups. This is carried out by etherification of some of the methylol groups with alcohol to form alkyl ethers.

In order to increase the hydrocarbon solubility of resin, to decrease the amount of cross-linking, and to increase the compability with other resins alkylation (etherification) must be done. The reaction must be carried out under slightly acidic conditions, and excess butanol is needed. In order to shift the reaction to the right, water must be removed during the reaction by

azeotropic distillation. By the end of the reaction the solvent tolerance of the resin must be 1:20 for xylol or 1:5 for white spirit.

The degree of alkylation or etherification can be controlled by temperature, reaction time, and quantity of alcohol used. In general, excess alcohol favors alkylation over the competing polymerization reaction. At high temperatures resin polymerizes very quickly. Usually n-butanol is used for etherification. The alcohol used to etherify the methylol groups must form an azeotrope with water that will separate on cooling, must form alkyl ether that will readily interact with other polymeric species during curing, must react readily with methylol groups, and must be a solvent for the methylolated amino groups. In coating industry n-butanol is the most widely used alcohol.

The films produced from the alkylated amino resins on stoving, are not sufficiently flexible for most surface coating applications and their adhesion, particularly on metal substrates, is poor. Amino resins are therefore used in combination with other resins such as epoxy resins, alkyds and hydroxyl functional acrylic resins.

Amino resins are frequently used in conjunction with alkyd resins. Such melamine-formaldehyde resins are used together with alkyd resins in stoving finishes which are rapid curing and give hard films. The resins hardened in the film form by the addition of small amounts of acids, e.g. hydrochloric and phosphoric acid, and cured at about 100-200°C. The alkylated amino-formaldehyde resins form a film by reaction between adjacent molecules and between hydroxyl groups of the alkyd resin [29, 42, 43]. The curing reactions are given in Figure 2.8 and Figure 2.9.

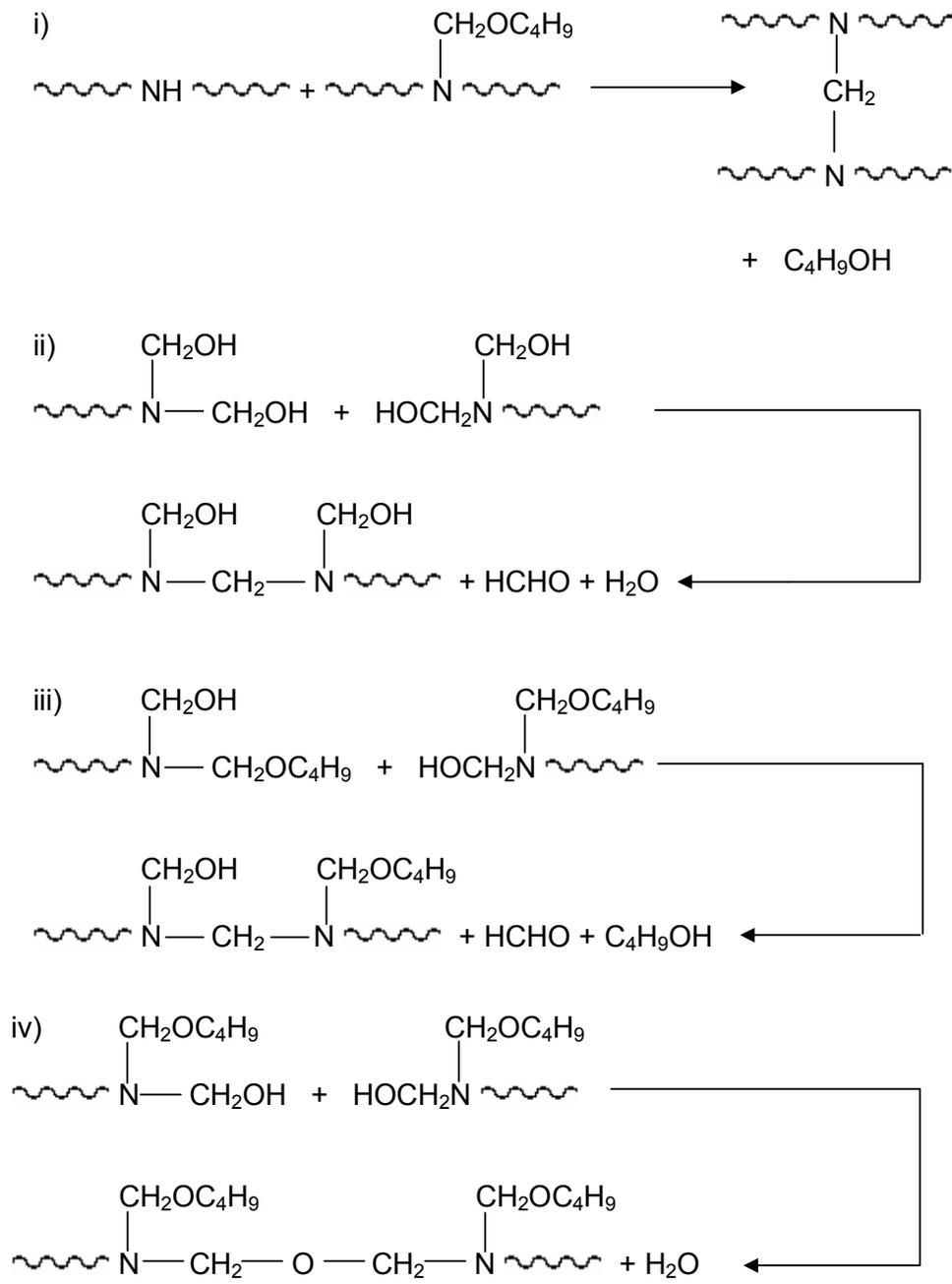


Figure 2.8 Curing reactions of amino resins [29].

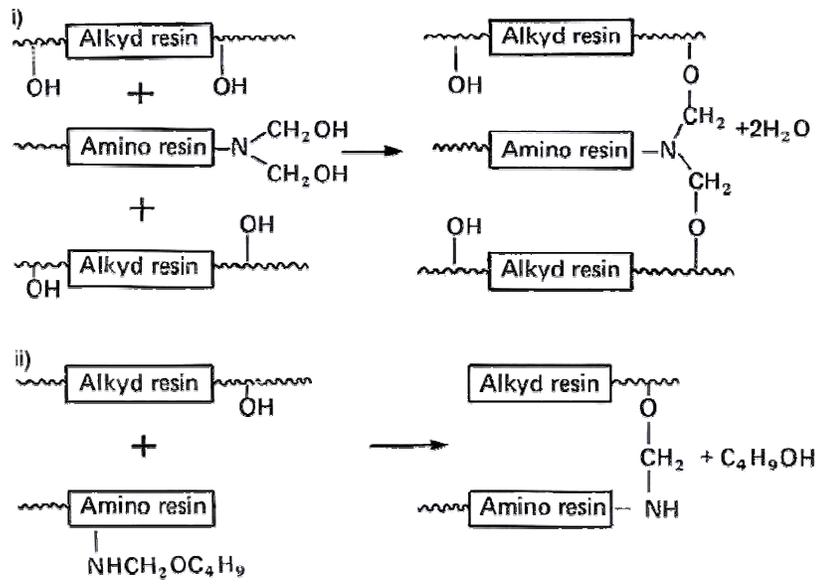


Figure 2.9 Curing reactions of amino resins with alkyd resins [29].

CHAPTER 3

EXPERIMENTAL

3.1 Raw Materials

1. Refined linseed oil (Betek Boya)
2. Castor oil (Akzo Nobel Kemipol)
3. Sodium hydroxide (NaOH), (Merck A. G.)
4. Magnesium sulfate hepta hydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) (Technical Grade)
5. Dimethylol propionic acid (DMPA), (Perstorp AB, Sweden)
6. Dipentaerythritol, (Perstorp AB, Sweden)
7. Para-toluene sulfonic acid (p - TSA), (Merck A. G.)
8. Toluene (Best Kimya)
9. Isopropyl alcohol (Technical grade)
10. Phenolphthalein (Technical grade)
11. Cobalt naphthenate (Volkan Boya)
12. Lead naphthenate (Volkan Boya)
13. Melamine (Sigma Aldrich)
14. Formaldehyde solution (37%; Merck A. G.)
15. Butanol (Technical grade)
16. Phosphoric acid (Merck A. G.)
17. Hydrochloric acid (Merck A. G.)
18. Nitrogen gas (Oksan)

3.1.1 Dehydration of Raw Materials

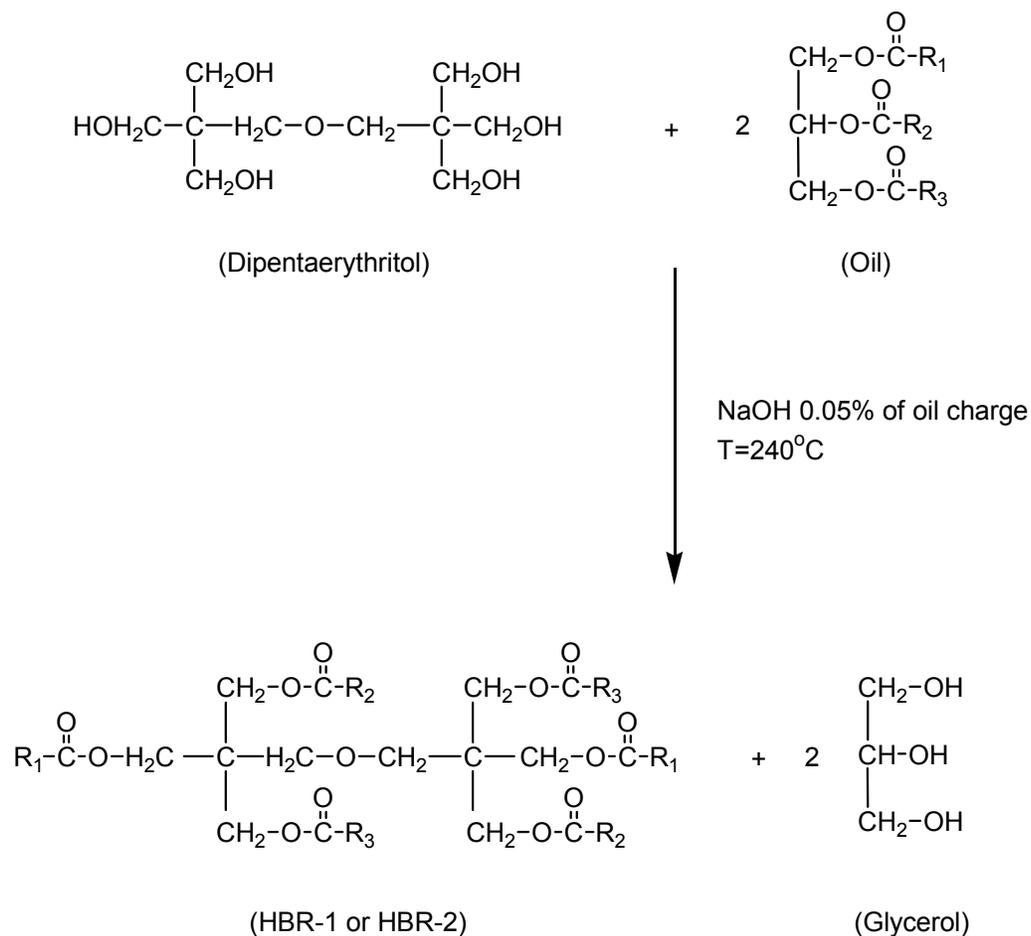
Magnesium sulfate hepta hydrate was ground and then dried in an oven at 120°C for 2 – 4 hours. Para-toluene sulfonic acid was dried for 1 – 2 hours at 85°C.

3.2 Synthesis of the Hyperbranched Resins

Dipentaerythritol which has six hydroxyl groups was used as the core molecule. In order to transesterified the dipentaerythritol by castor oil, which is mainly composed of ricinoleic, linoleic, and oleic acids, 0.5 mole of dipentaerythritol per mole of oil were introduced into a four-necked reactor equipped with a mechanical stirrer, condenser, thermometer, and an inlet for nitrogen gas. In a former work Hult et. al. [44] had synthesized a hyperbranched resin by using dimethylol propionic acid (DMPA) and trimethylol propane and the synthesis procedure that they used was applied in this research. NaOH (0.05% w/w on the oil charge) was used as catalyst. The mixture was continuously stirred and heated to 240°C in an oil bath under nitrogen atmosphere. The reaction proceeded three hours. The end of the reaction was monitored by measuring the viscosity of the reaction mixture. The obtained product was dissolved in white spirit and washed with water in order to remove glycerol formed by the end of the reaction. Two phases formed because resin was not soluble in water but soluble in white spirit and glycerol was soluble in water but not soluble in white spirit. Water phase was removed, and MgSO₄ was added to the resin to further remove water, and then centrifuged to separate the water phase. The solvent was evaporated from the resin and it was named as hyperbranched resin-1 'HBR-1'.

The mixture of castor oil and linseed oil at equal weight percentages was transesterified by dipentaerythritol by the same procedure described above. Linseed oil was used because the high unsaturation of linseed fatty acids

provides easy air drying. This resin was named as HBR-2. The reaction scheme of the synthesis of the HBR-1 and HBR-2 is below.



Where R₁ – R₃ are the fatty acids. The schematic representations of HBR-1 and HBR-2 are given in Figures 3.1 and 3.2 respectively.

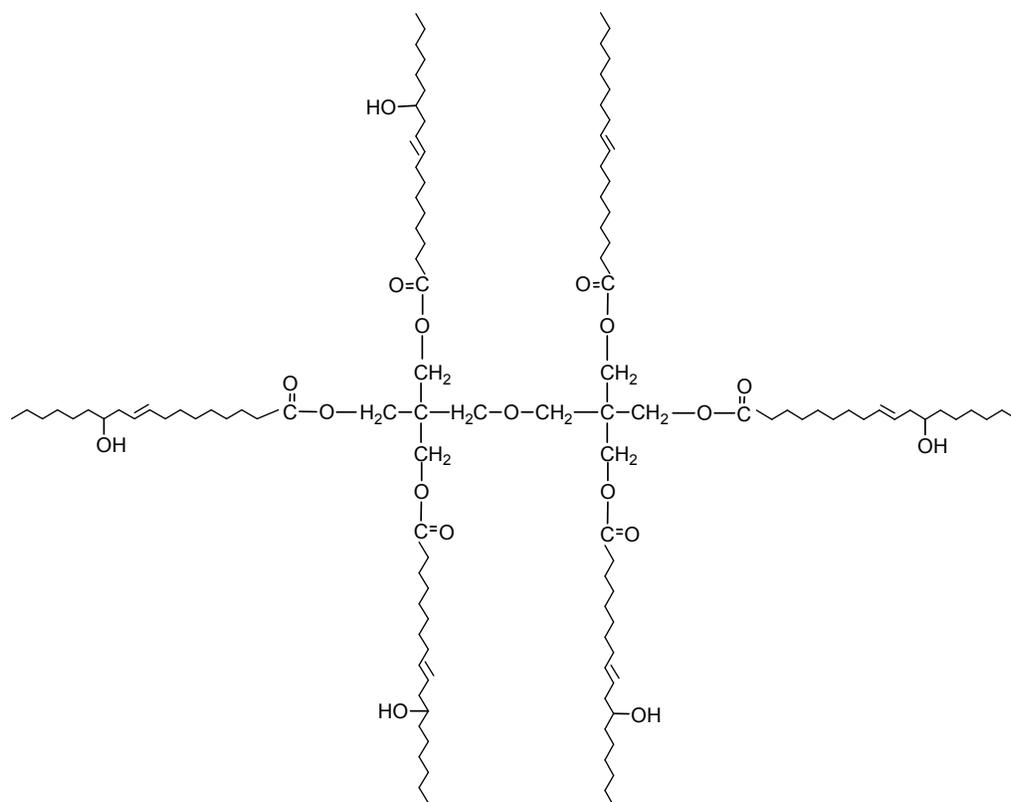


Figure 3.1 The schematic representation of HBR-1.

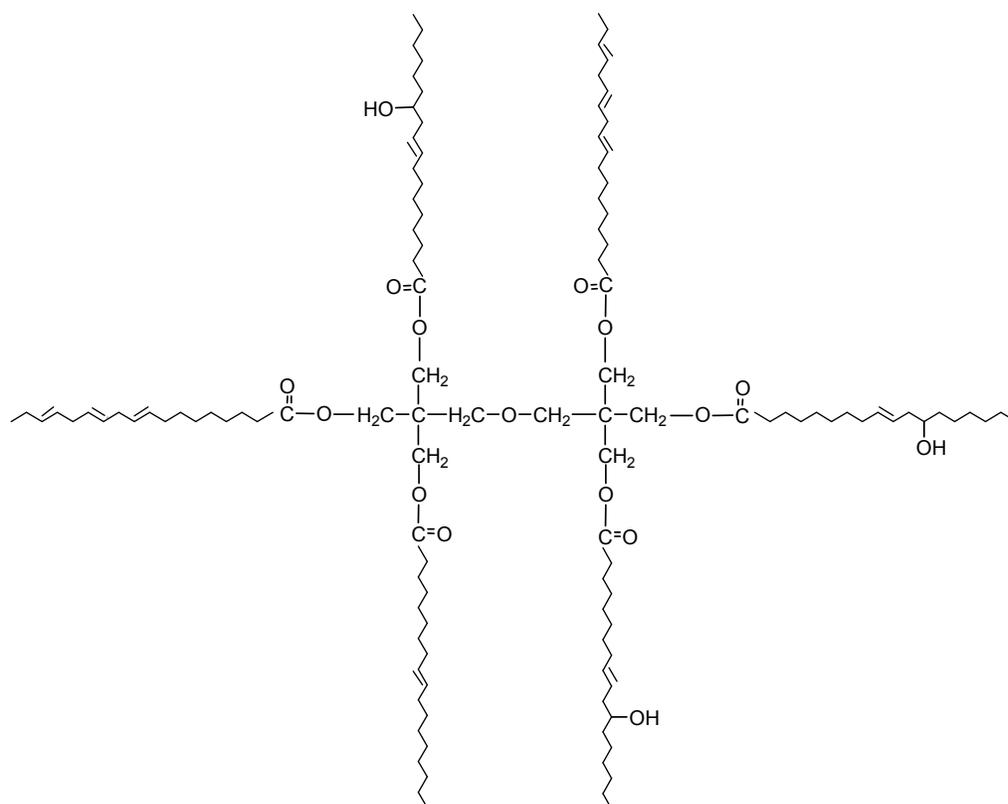
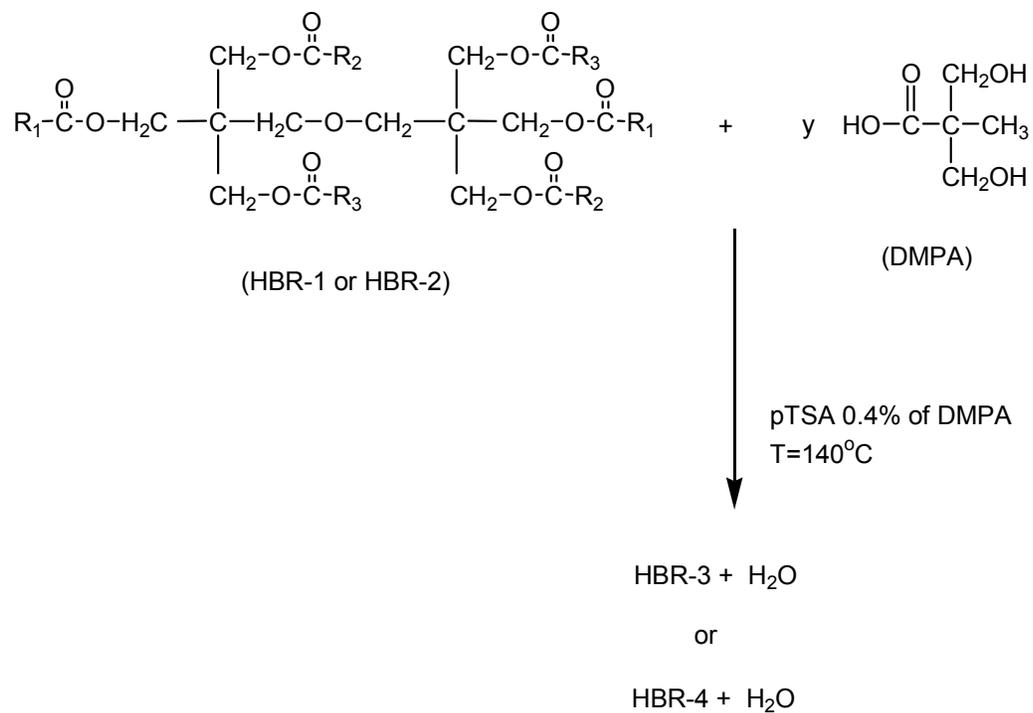


Figure 3.2 The schematic representation of HBR-2.

The resulting oligomeric molecules in either case (i.e. HBR-1 and HBR-2) were then reacted with dimethylolpropionic acid (DMPA). Paratoluene sulfonic acid (pTSA) (0.4% w/w of DMPA) was used as catalyst. The required amount of DMPA was calculated by the hydroxyl group present in the oligomeric molecules. For one mole of hydroxyl group one mole of DMPA was used.

All reactants were introduced into a five-necked flask equipped with a mechanical stirrer, thermometer, inlet for nitrogen gas, and inlet for the condenser for the azeotropic distillation of water. Toluene was used as azeotropic agent. The reactor was immersed in an oil bath and the reaction was carried out at 140°C under nitrogen atmosphere. The condensation product, water, was removed by nitrogen and azeotropic distillation with toluene. The end of the reaction was monitored by calculating the acid number of the product. Acid number determination was given in the Appendix A. The reaction was stopped when the acid number of the product became less than 15. The resin produced by using HBR-1 and DMPA was named as HBR-3 and the resin produced by using HBR-2 and DMPA was named as HBR-4. The reaction scheme is given below and schematic representations of HBR-3 and HBR-4 are given in Figures 3.3 and 3.4 respectively, and the experimental setup was shown in Figure 3.5.



y : mole of DMPA which depends on the number of hydroxyl groups present in the HBR-1 or HBR-2.

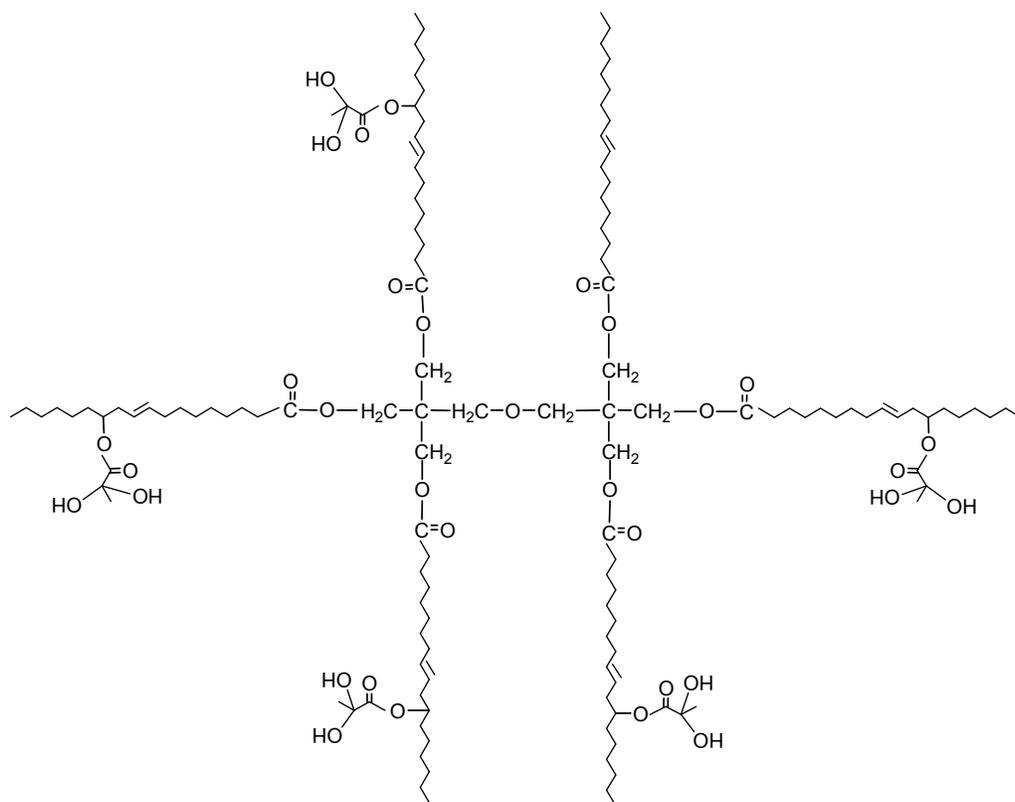


Figure 3.3 The schematic representation of HBR-3.

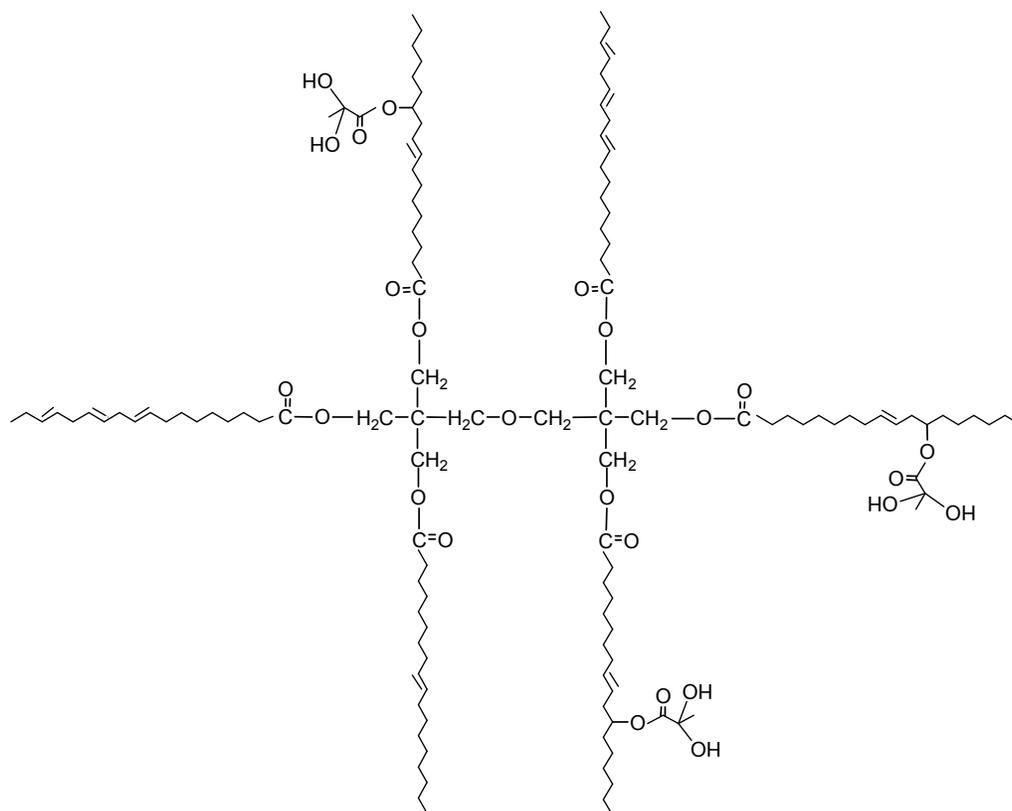


Figure 3.4 The schematic representation of HBR-4.

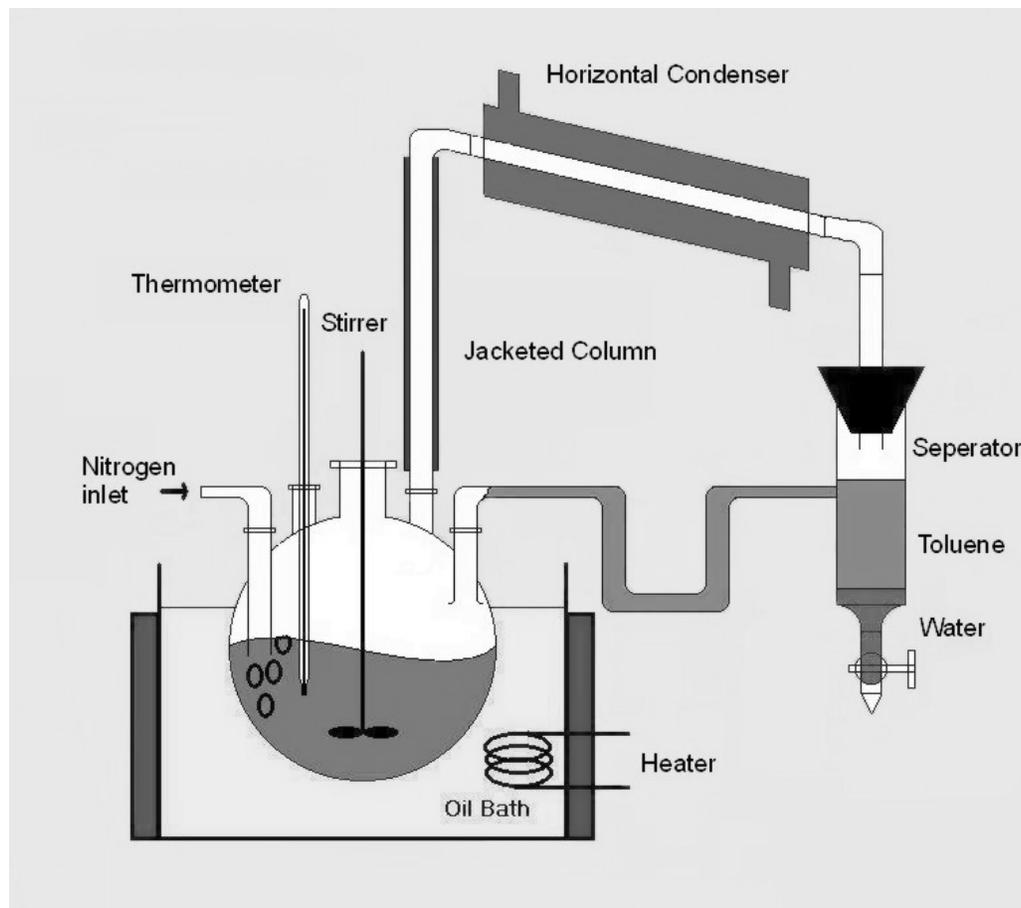
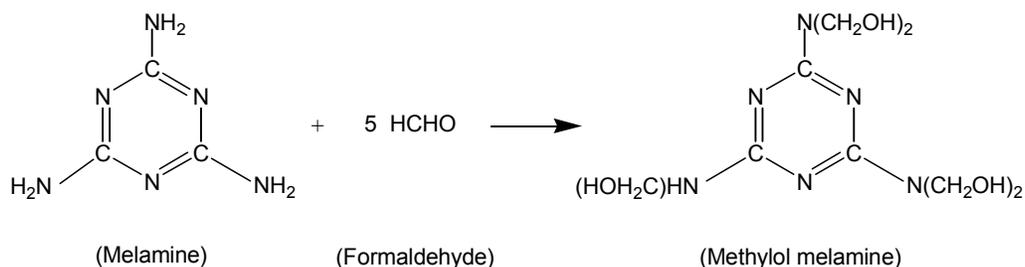


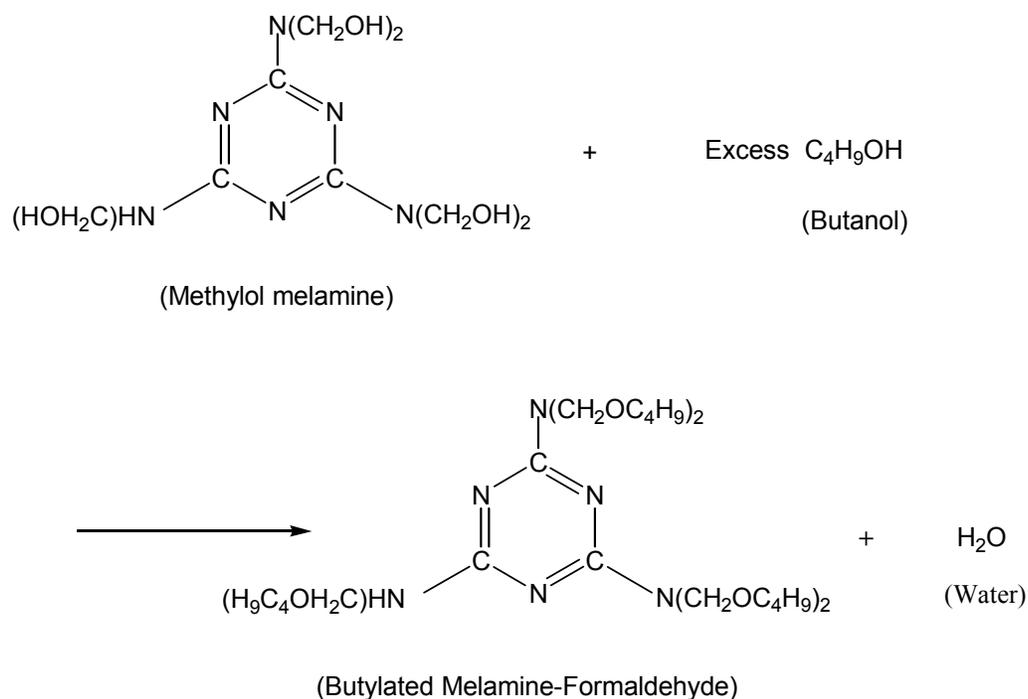
Figure 3.5 The experimental setup.

3.3 Synthesis of the Butylated Melamine – Formaldehyde Resin

The melamine and the formaldehyde solution were mixed at the ratio of 5 moles formaldehyde per mole of melamine. It is then mixed with 100% excess butanol needed for complete alkylation. They were charged into a five-necked reactor equipped with a mechanical stirrer, thermometer, inlet for nitrogen gas, and inlet for condenser as seen in Figure 3.5. The pH of the mixture was adjusted to a pH of 8-8.5 by the addition of a weakly basic catalyst, ammonia. The mixture was heated to 60°C to permit the necessary extent of condensation for 1 hour and distilled azeotropically. Toluene was used as the azeotropic agent. Water and butanol distilled into a receiver and separated into two layers on condensing; butanol and toluene formed the upper layer and was returned to the reaction vessel. The lower layer was essentially water and it was discarded.



Then the pH was adjusted to ~7 by the addition of phosphoric acid and the mixture was heated to 85-90°C. Then etherification of methylol melamine took place and the reaction scheme was given below. The azeotropic distillation removed the water already present and also the water formed from the etherification reaction. The reaction lasted about 2-2.5 hours. The end of the reaction was monitored by white spirit or xylol tolerance of the product.



3.4 Characterization of Hyperbranched Resins

3.4.1 Fourier Transform Infrared (FTIR) Spectroscopy

Nicolet 510 FT-IR Spectrometer was used to characterize the resins. The samples were applied as thin films on KBr pellet.

3.4.2 Differential Scanning Calorimeter (DSC)

Dupont (Model TA 610 S) Differential Scanning Calorimeter was used to determine the thermal properties of the samples. The heating rate was 10 K/min.

3.4.3 Viscosity Measurement

Haake Rotovisco (Model CV20) parallel disk rheometer was used to measure the viscosities of the hyperbranched resins. The diameter of the

disk used was 19.25 mm. Two sets of experiments were done at constant room temperature of 23°C. In the first one, the viscosities of the samples were measured at every five minutes while the shear rate was increasing and ten data were collected. The maximum shear rate that the viscosity measured was 200 s⁻¹. In the second one, the viscosities of samples were measured at constant shear rate (200 s⁻¹) and ten data were collected. The measurements were repeated five times and the average of them was taken as the viscosity values of the resins.

3.5 Physical and Mechanical Tests

3.5.1 Preparation of Test Panels

Metal plates were used for impact, abrasion, and mandrel bending tests, while glass panels were used for pendulum hardness test. Gloss measurements were carried out by using both glass sheets and metal plates. Cobalt naphthanate and lead naphthanate were added to the hyperbranched resins prior to their application on the substrates. About 0.6 % drier was added based on grams of resin. One third of the drier was cobalt naphthanate and the two thirds was lead naphthanate. The hyperbranched resin and the melamine-formaldehyde resin were mixed at a ratio of 1:3. In order to catalyze the curing reaction a little amount of HCl was added to the mixture. The resins were applied to the surface of glass and metal test panels with a wet thickness of 50 µm by using a film-casting knife (Braive Instruments). All hyperbranched resin samples were left for 12 hours in an oven at 90°C to accelerate curing and then left for air-drying for 5 days. The hyperbranched and melamine formaldehyde resin mixture was cured at 150°C for 1 hour in an oven and then left for air-drying for 5 days [45].

3.5.2 Pendulum Hardness Test

A Braive Instruments Persoz Pendulum (Model 3034) was used to measure the hardness of films. The principle of the pendulum hardness test is based on the fact that the amplitude of oscillation of a pendulum swinging on a test specimen decreases more rapidly for the softer films [46]. The hardness pendulum testing instrument is given in Figure 3.6.

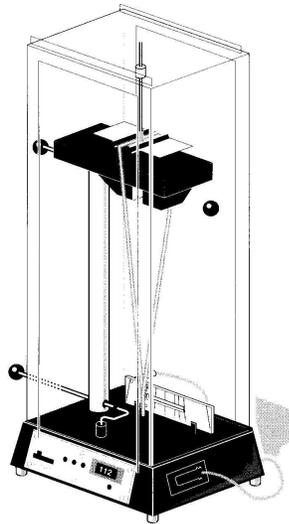


Figure 3.6 Hardness pendulum testing instrument.

3.5.3 Impact Resistance Test

A Gardner Impact Tester (Model 5510) was used and it was given in Figure 3.7. A standard weight (1+0.9 kg) was dropped onto a film coated metal plate from different heights. The value of potential energy at which failure occurs by cracking gives the impact value [47].

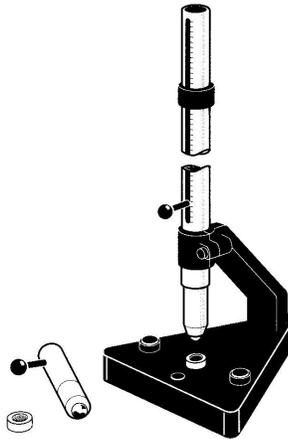


Figure 3.7 Impact resistance testing instrument.

3.5.4 Mandrel Bending Test

A conical Mandrel Bending tester (Braive Instruments, Model 1510) was used (Figure 3.8). Metal test plates were fastened and bent over to observe the resistance of coating to cracking when elongated. The lengths of the cracks were observed along the increasing radius of the conical mandrel [48].

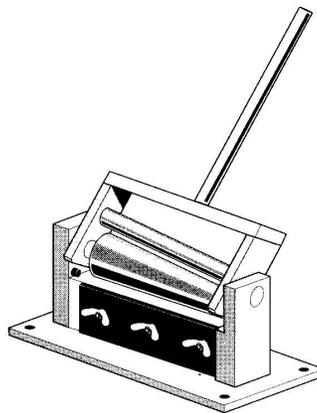


Figure 3.8 Conical Mandrel bending instrument.

3.5.5 Abrasion Resistance Test

The test was used to determine the resistance of organic coatings to abrasion produced by an abrasive falling onto coated test plates. Silica sand was used as abrasive and it was allowed to fall from a specified height through a guide tube onto the coated panel. The apparatus can be seen in Figure 3.9. The amount of abrasive required to remove a certain thickness from the coating is reported as the abrasion resistance of the coating film [49]. A thickness gauge (Elcometer 345) was used to measure the film thickness of the coatings.

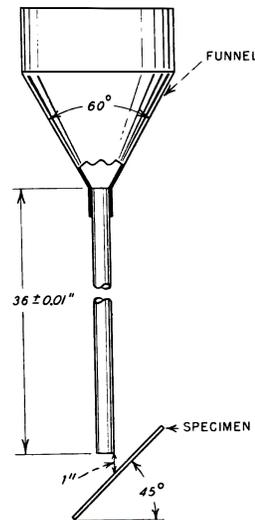


Figure 3.9 Abrasion resistance measurement instrument.

3.5.6 Adhesion Test

This test was used to establish whether the adhesion of a coating is at an adequate level. A cross – hatch cutter was used to cut the film to produce a lattice pattern. After making a cross cut, the film was brushed with a soft tissue to remove any detached flakes or ribbons of coating. Then an adhesive tape was placed on the cross cut. The tape was removed rapidly

back upon itself at an angle of 180° as close as possible. The cross-cut area was inspected for the removal of coating from the substrate and rated for the extent of adhesion according to the scale (Figure 3.10) given in ASTM D 3359 [50].

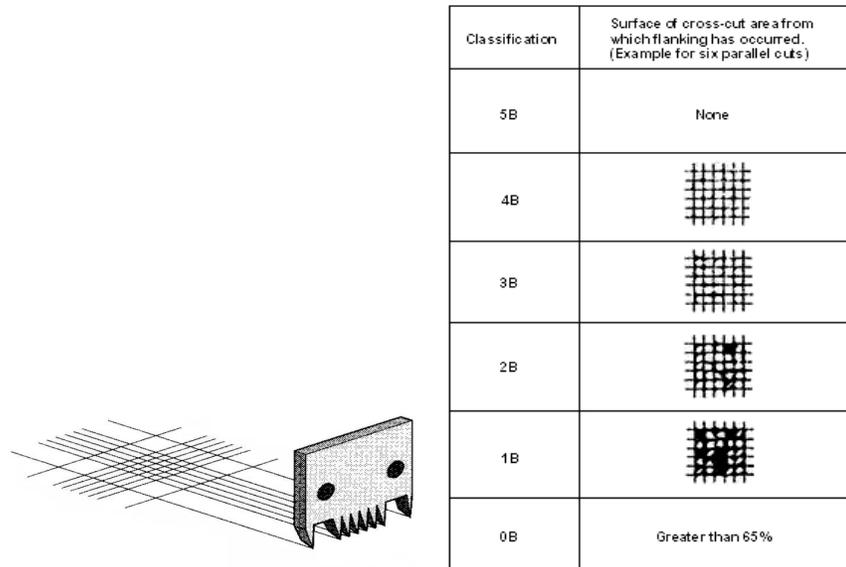


Figure 3.10 A cross – hatch cutter and the scaling of adhesion.

3.5.7 Gloss Measurement Test

A Rhopoint glossmeter (Serial No 26135) was used to measure the gloss values of films on glass and metal plates. This test depends on the measurement of the intensity of light reflected from coated plates in three different directions [51].

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preliminary Experiments

4.1.1 End Point Determination

The end point of HBR-1 synthesis was measured from viscosity measurements. A small amount of sample was taken from the reactor at every 30 minutes for 5 hours and washed to remove glycerol. Its water was removed by the same procedure described in the Section 3.2. At the beginning of the reaction the viscosity was very high and it began to decrease as the reaction proceeded. After 2.5-3 hours the viscosity became constant. This measurement showed that the reaction took 2.5-3 hours.

The end points in the synthesis of HBR-3 and HBR-4 were monitored by acid value. Gelation occurred at acid values below 15, therefore the reaction was stopped the reaction at 15.

4.1.2 Drying of Resins

The HBR-1 applied to glass and metal test panels did not air dry on curing even at 150°C. Therefore HBR-1 was mixed with MFR to make melamine-formaldehyde modified resin. In the second step, in order to synthesize an air drying hyperbranched resin, it was decided to use a mixture of castor oil and linseed oil. The high unsaturation of linseed fatty acids provided easy air drying and the resin thus synthesized was named as 'HBR-2'.

4.1.3 Synthesis of Melamine-Formaldehyde Resin

Several attempts were made to synthesize butylated melamine-formaldehyde resin. In the first trial melamine and formaldehyde were mixed under basic conditions and heated and then butanol was added under acidic conditions but the resin solidified very quickly. Then it was decided to mix all ingredients together in sufficient amounts at the beginning, but the resin solidified again. In the third trial at the beginning, the reaction proceeded under basic conditions and for the etherification the pH was adjusted to ~7. This time the resin solidified later than the other trials. By the next trial, it was seen that the addition of excess butanol increased the solidification time. In the last trial 100% excess butanol was fed to the reactor and at the beginning the reaction proceeded under basic conditions and then at ~7 and at these conditions, resin could be synthesized.

4.1.4 Mixing Ratio of Melamine-Formaldehyde Resin and Hyperbranched Resin

Several attempts were made to determine the best mixing ratio of MFR and hyperbranched resins. Increasing the amino resin content lead to an increase in film hardness and increasing alkyd resin content lead to an increase in film flexibility and adhesion properties. The mixture of resins gave the best results at the MFR:HBR ratio of 3:1.

4.1.5 Curing of Resins

Different temperatures and curing times were tested for the resins. It was found out that the best curing condition for the hyperbranched resins was 90°C for 12 hours, and the best curing condition for mixture of melamine-formaldehyde resin and hyperbranched resins was 150°C for 1 hour.

4.2 Characterization of Hyperbranched Resins

4.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of HBR-1, HBR-2, HBR-3, and HBR-4 were given in Figures 4.1, 4.2, 4.3, and 4.4 respectively. All spectra have common peaks because the structures of all resins are very similar. The broad peak around 3400 cm^{-1} in HBR-1 and HBR-2 spectra corresponds to the hydroxyl group (OH) of the ricinoleic acid, and in the spectra of HBR-3 and HBR-4 it corresponds to the hydroxyl groups of the ricinoleic acid and DMPA. Olefinic =C-H stretching due to fatty acids is seen at about 3010 cm^{-1} in all resins. The peaks at 2930 cm^{-1} and 2855 cm^{-1} correspond to aliphatic -C-H stretching. The characteristic ester peak (C=O) is seen in all the spectra at about 1740 cm^{-1} . The peak at 1464 cm^{-1} is due to methylene bending (-CH₂-) and methyl bending (-CH₃). The peak at 1378 cm^{-1} indicates methyl bending (-CH₃). The peak at 1178 cm^{-1} denotes -C-O-O-C- stretching of ester. The peak at 1050 cm^{-1} corresponds to -C-O-C- stretching of ether. Finally, the peak at about 724 cm^{-1} is also common in all of the spectra and it corresponds to the rocking of multiple (> 4) methylene groups.

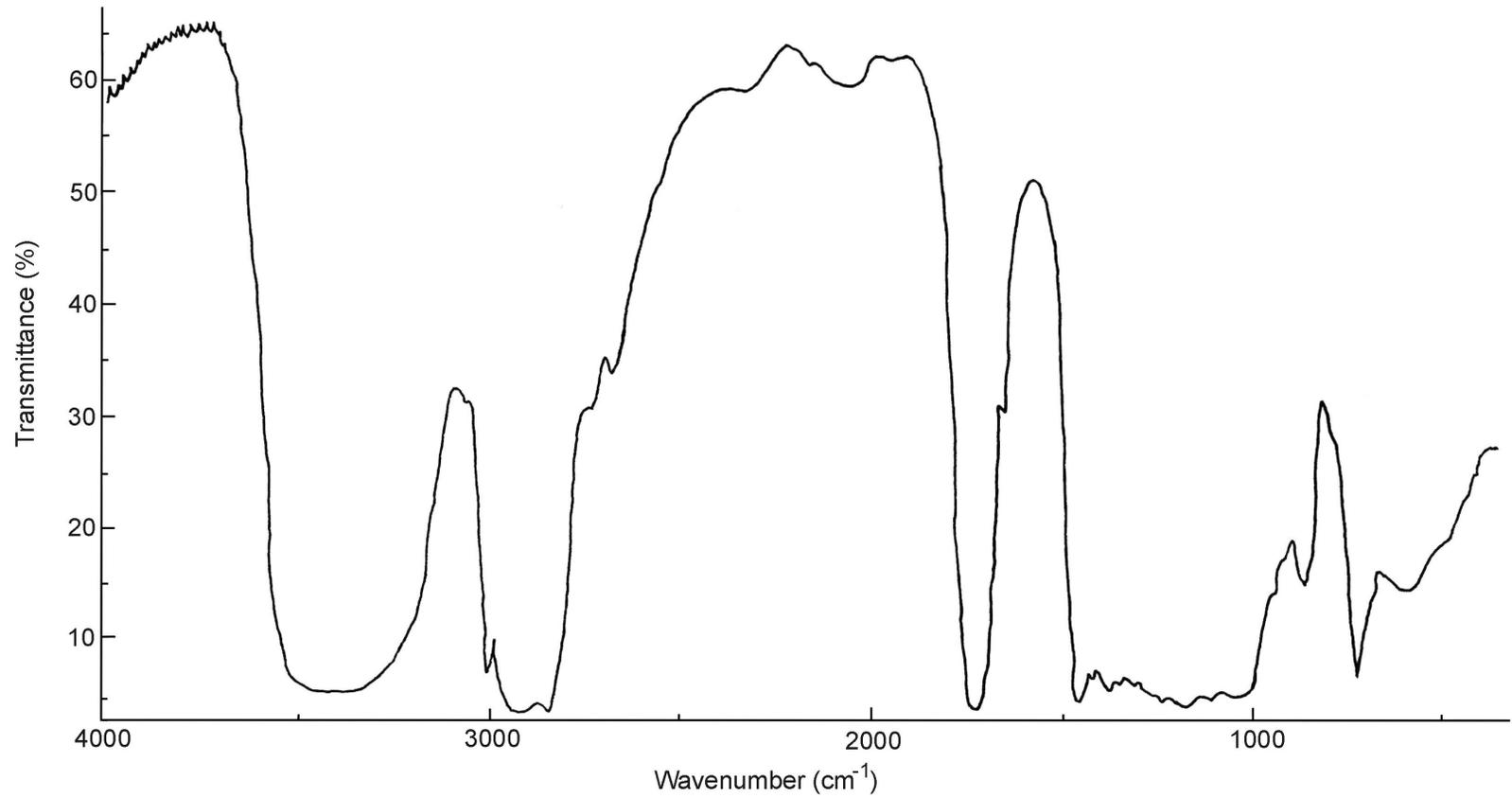


Figure 4.1 FTIR spectrum of HBR-1.

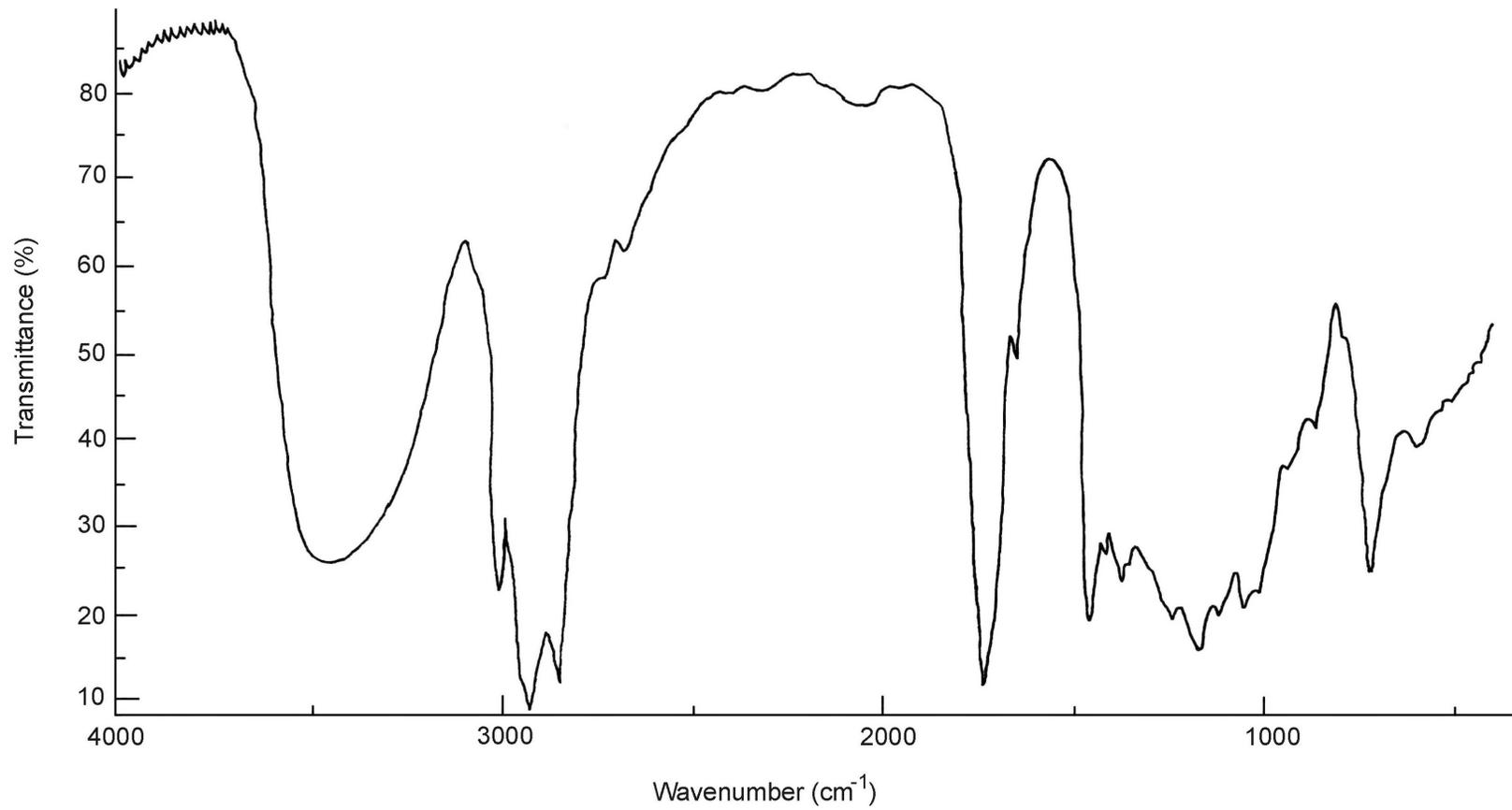


Figure 4.2 FTIR spectrum of HBR-2.

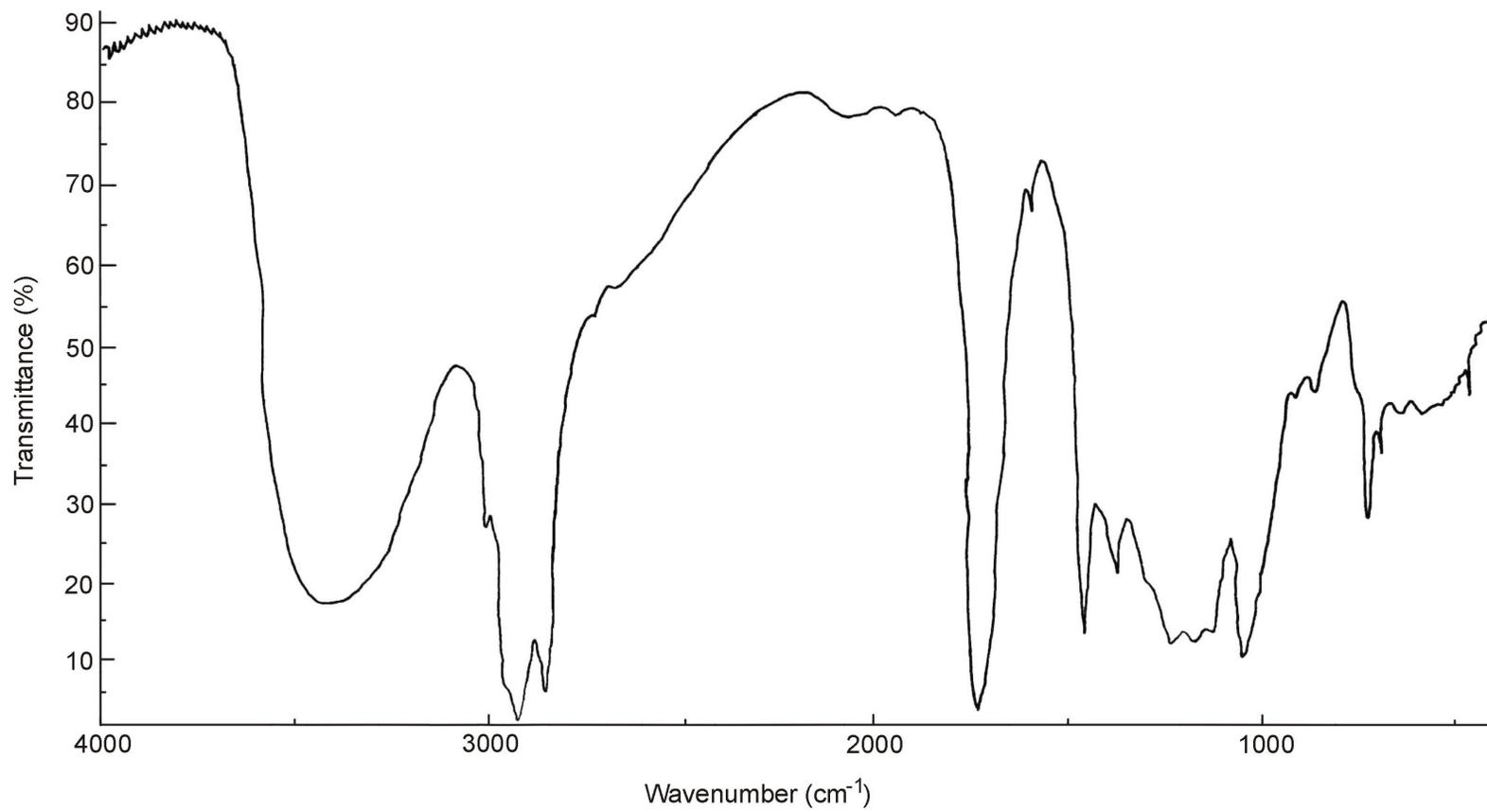


Figure 4.3 FTIR spectrum of HBR-3.

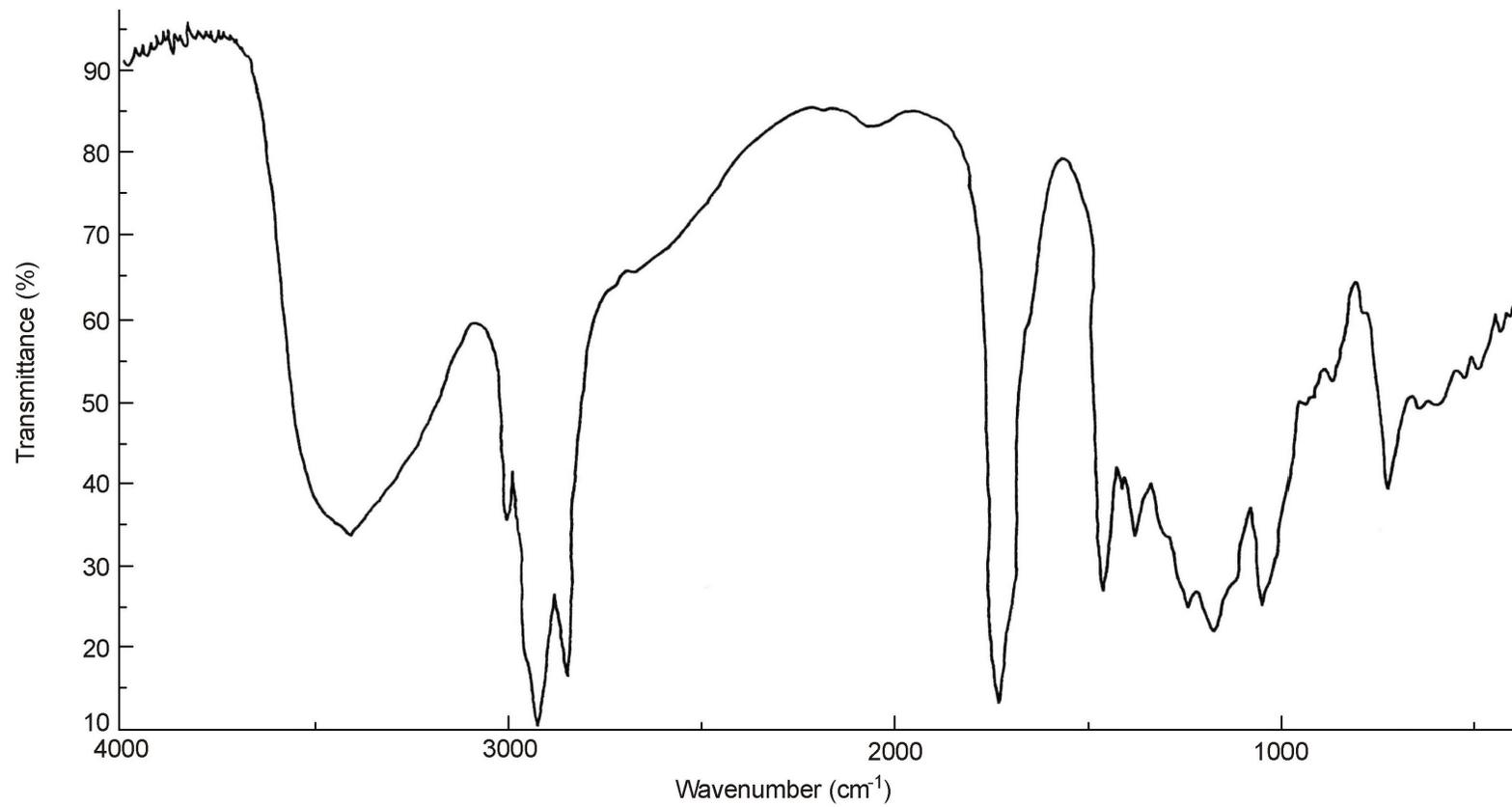


Figure 4.4 FTIR spectrum of HBR-4.

4.2.2 Differential Scanning Calorimetry (DSC)

The DSC spectra of HBR-2, HBR-3 and HBR-4 are given in Figure 4.5, Figure 4.6, and Figure 4.7 respectively. From DSC diagrams only the thermal degradation temperatures of the resins can be detected because the cured resins have crosslinked structures. In the spectra, the glass transition temperatures are not significant. The degradation temperature of HBR-2, HBR-3, and HBR-4 are 322.09°C, 316.33°C, and 346.63°C respectively.

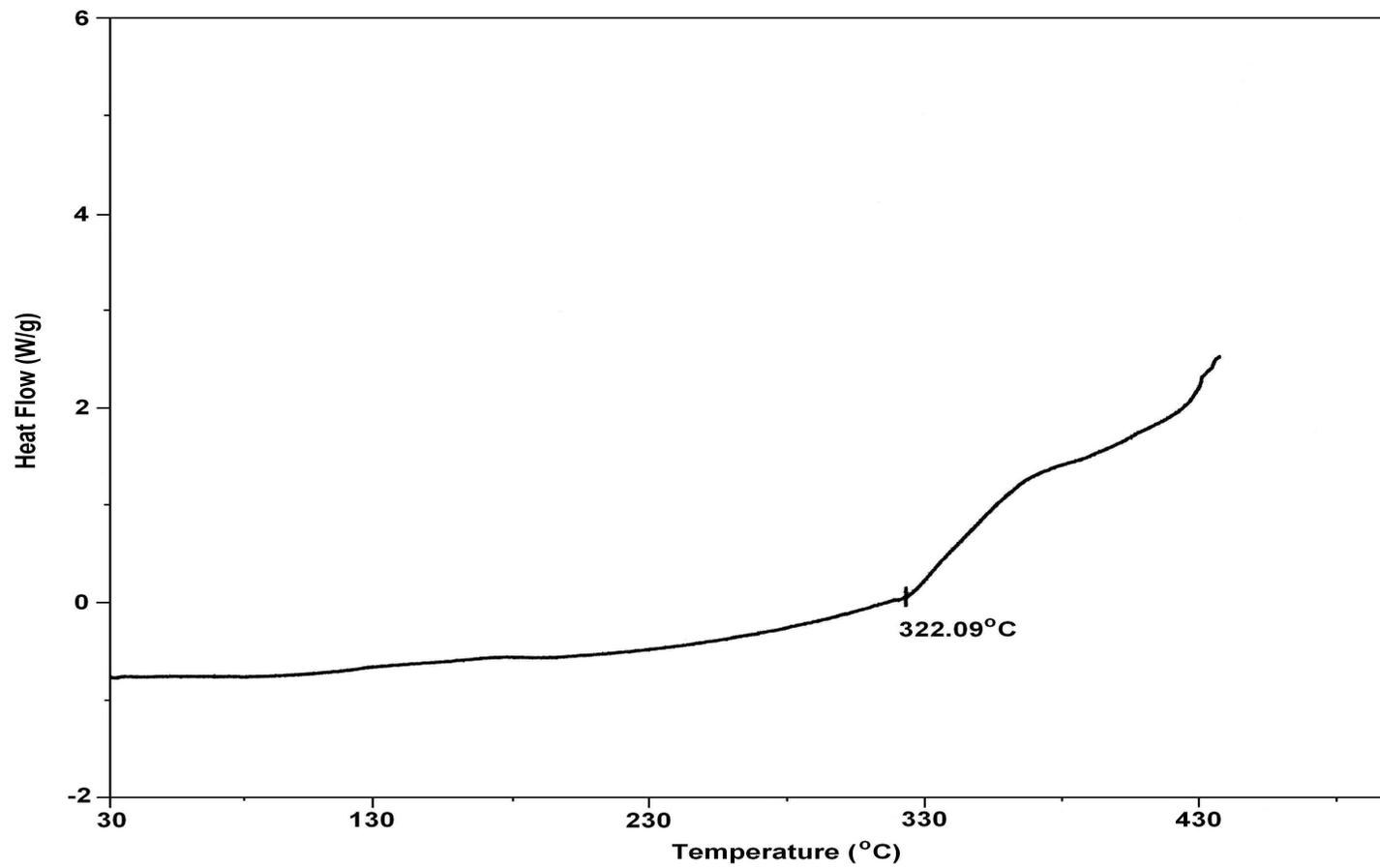


Figure 4.5 The DSC spectrum of HBR-2.

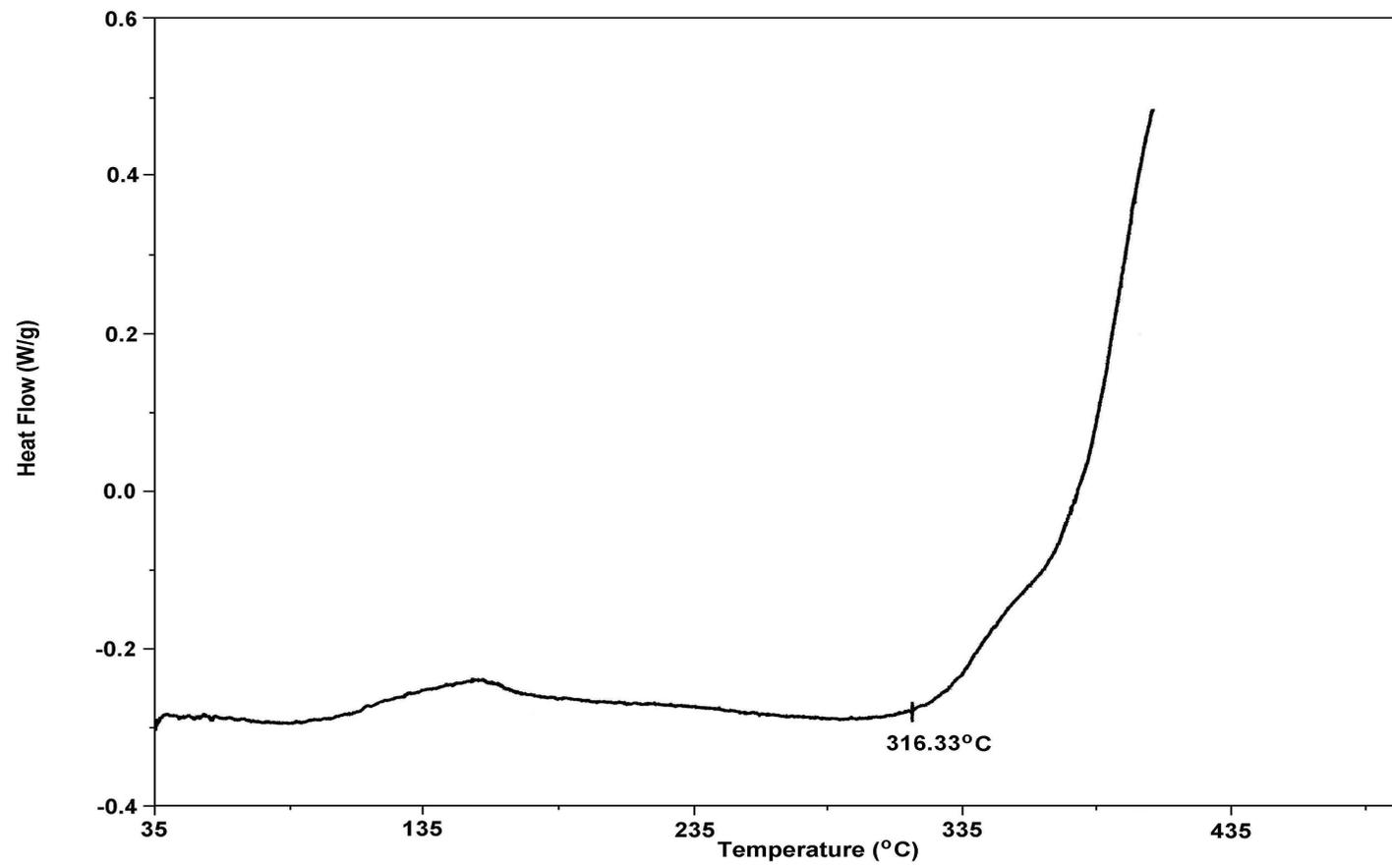


Figure 4.6 The DSC spectrum of HBR-3.

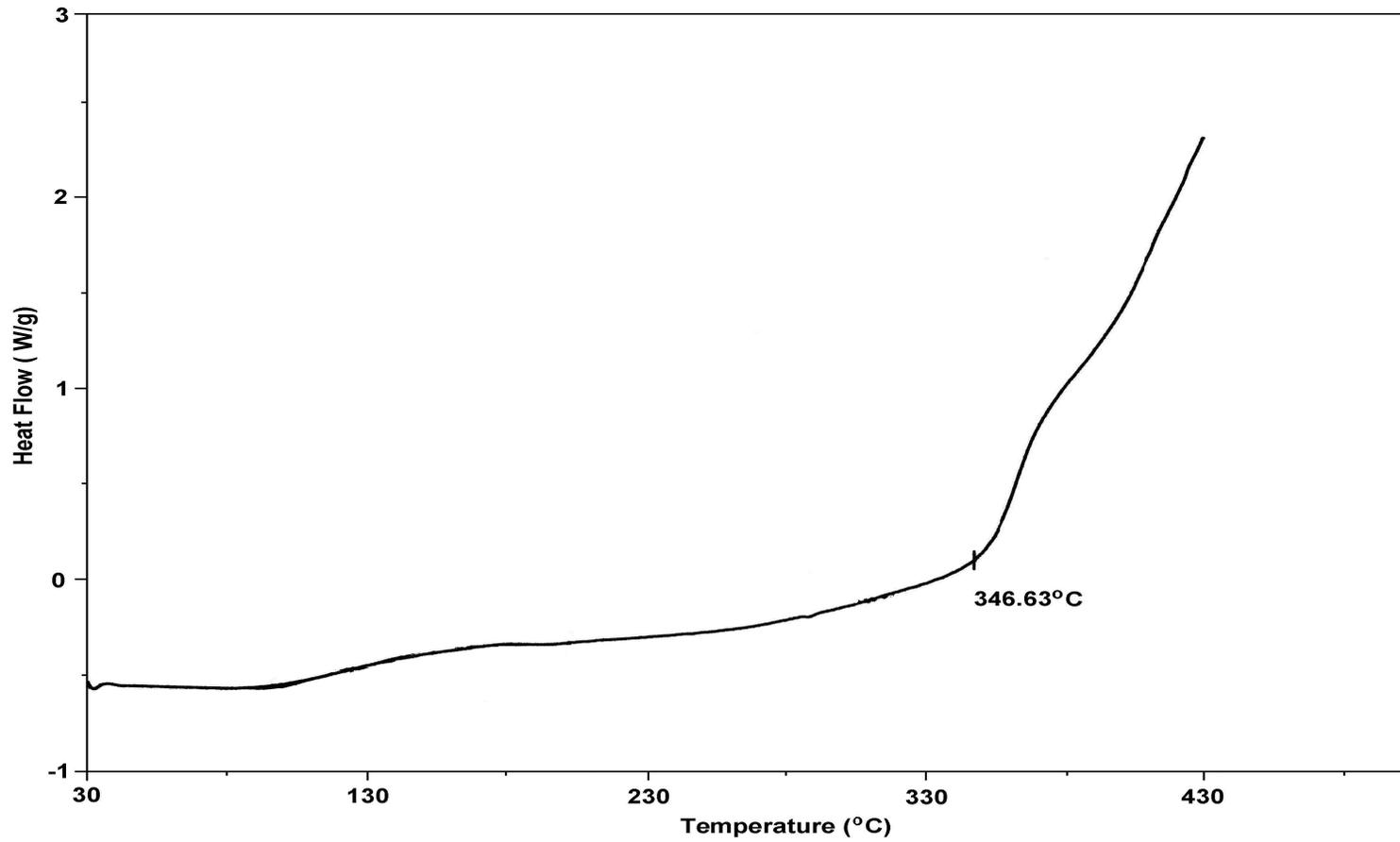


Figure 4.7 The DSC spectrum of HBR-4.

4.2.3 Viscosity Measurement Test

Two sets of experiments were performed at 23°C. In the first set, ten data were taken until the shear rate reached up to 200 s⁻¹. In the second set, another ten data were taken at a constant shear rate of 200 s⁻¹. The measurements were repeated five times for each resin and the average of the measurements was given in Appendix B.

The viscosity versus shear rate graph was given in Figure 4.8. The viscosity of HBR-3 significantly decreased as the shear rate increased. HBR-3 has the highest number of hydroxyl groups on the molecule. The physical network established due to intense hydrogen bonds was probably collapsed under high shear rate. The viscosities of other resins do not seem to be dependent on shear rate. The viscosity of a conventional high solids alkyd resin is given in the literature as 26 Pa·s [13], while HBR-1, HBR-2, HBR-3, and HBR-4 had very low viscosities of about 3.0 Pa·s, 1.0 Pa·s, 7.0 Pa·s, and 3.7 Pa·s respectively at a shear rate of 200 s⁻¹. All of the samples have lower viscosities than a conventional high solids alkyd resin. HBR-3 had a higher viscosity when compared to others. HBR-3 is DMPA added HBR-1 so it has much higher hydroxyl groups. Therefore HBR-3 can form enhanced hydrogen bonding, and so its viscosity naturally came out to be higher than HBR-1. The viscosity of HBR-4 was higher than HBR-2 because of the same reason. The structure of HBR-1 and HBR-2 are also similar, the former contains only castor oil and the second contains '50% castor oil + 50% linseed oil'. Since castor oil contains ricinoleic acid and ricinoleic acid contains hydroxyl groups, the viscosity of HBR-1 came out to be larger than that of HBR-2.

The viscosity versus time graph at shear rate of 200 s⁻¹ was given in Figure 4.9. The viscosities of synthesized resins did not seem to change with the

increase of time at constant shear rate. It seems that the resins do not have thixotropy.

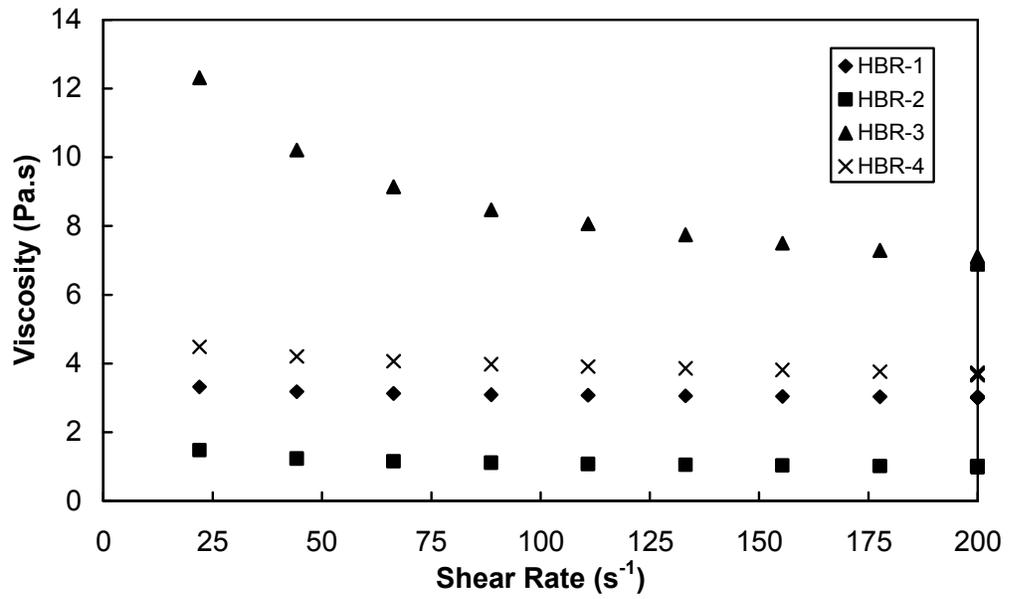


Figure 4.8 Viscosity versus shear rate graph.

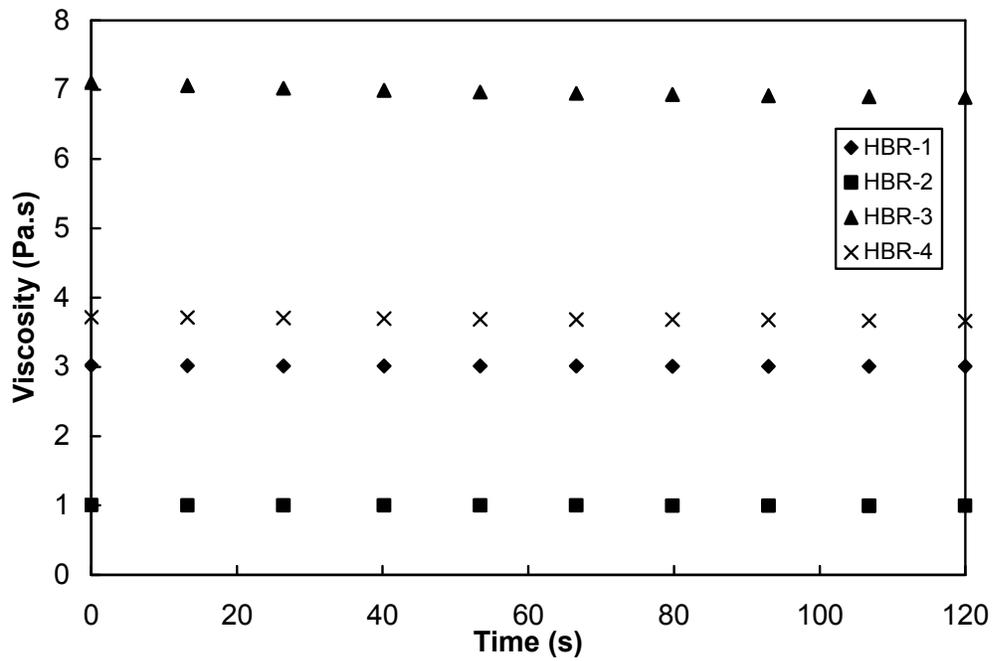


Figure 4.9 Viscosity versus time graph.

4.3 Physical and Mechanical Tests

4.3.1 Pendulum Hardness Test

The hardness values of the hyperbranched resin samples were listed in Table 4.1. The hyperbranched resins are aliphatic in structure, so they are very flexible and they yield low hardness values. However the melamine-formaldehyde modified resins had higher hardness values as seen from Table 4.2. In the literature the viscosity of hyperbranched alkyd resin was found as 25 Persoz [13]. The hardness values of the resins are very close to the given value.

Table 4.1 Hardness values of the hyperbranched resin samples

Sample	Hardness (Persoz)
HBR-2	22
HBR-3	23
HBR-4	26

Table 4.2 Hardness values of the mixture of hyperbranched resin and melamine-formaldehyde resin samples

Sample	Hardness (Persoz)
HBR-1 + MFR	80
HBR-2 + MFR	85
HBR-3 + MFR	97
HBR-4 + MFR	123

4.3.2 Impact Resistance Test

No cracks were observed at the surfaces of specimens. They all showed an impact resistance above 19 J, which is the maximum limit of the impact device. The resins exhibited very good toughness.

4.3.3 Mandrel Bending Test

All hyperbranched resin samples passed the mandrel bending test without any cracks on the surface. They showed excellent flexibility. Some cracks formed on the surface of the mixture of hyperbranched resin and melamine-formaldehyde resin samples because the melamine-formaldehyde resin was not flexible. The lengths of the cracks from the tip of the mandrel were given in Table 4.3.

Table 4.3 Length of cracks formed on the surface of the mixture of hyperbranched resin and melamine-formaldehyde resin samples

Sample	Length of Cracks (cm)
HBR-1 + MFR	3
HBR-2 + MFR	1
HBR-3 + MFR	13
HBR-4 + MFR	2

4.3.4 Abrasion Resistance Test

All samples showed no significant loss of film thickness. They had very high resistance to abrasion.

4.3.5 Adhesion Test

All hyperbranched resin samples had the maximum adhesion number as seen from Table 4.4 but the addition of melamine-formaldehyde resin decreased the adhesion of samples. DMPA modified resins displayed better adhesion than other two resins when mixed with MFR. The adhesion values of the mixture of hyperbranched resin and melamine-formaldehyde resin samples were given in Table 4.5.

Table 4.4 Adhesion values of the hyperbranched resin samples

Sample	Adhesion	
	Glass	Metal
HBR-2	5B	5B
HBR-3	5B	5B
HBR-4	5B	5B

Table 4.5 Adhesion values of the mixture of hyperbranched resin and melamine-formaldehyde resin samples

Sample	Adhesion	
	Glass	Metal
HBR-1 + MFR	3B	3B
HBR-2 + MFR	3B	3B
HBR-3 + MFR	4B	4B
HBR-4 + MFR	3B	5B

4.3.6 Gloss Measurement Test

The gloss values of hyperbranched resin samples were listed in Table 4.6 and the gloss values of the mixture of hyperbranched resin and melamine-formaldehyde resin samples were listed in Table 4.7. The gloss values of the resins on metal plates were lower than the gloss values on glass plates because glass substrates reflect the diffracted light and so yielding higher gloss. If the gloss value of a coating measured at 60° is higher than 70, it is said to be in high gloss range. The hyperbranched resins were said to highly gloss because their gloss values of at 60° were higher than 70. It was also seen that the mixture of hyperbranched resin and melamine-formaldehyde resin samples had lower gloss values than the hyperbranched resins.

Table 4.6 Gloss values of the hyperbranched resin samples

Sample	Angle					
	20°		60°		85°	
	Glass	Metal	Glass	Metal	Glass	Metal
HBR-2	70.8	59.7	113.0	92.4	88.0	84.0
HBR-3	91.0	47.5	120.2	88.4	101.7	82.7
HBR-4	95.9	33.5	128.5	74.9	118.3	70.6

Table 4.7 Gloss values of the mixture of hyperbranched resin and melamine-formaldehyde resin samples

Sample	Angle					
	20°		60°		85°	
	Glass	Metal	Glass	Metal	Glass	Metal
HBR-1 + MFR	7.6	3.2	22.3	16.0	11.5	7.3
HBR-2 + MFR	2.1	0.9	5.1	2.2	3.6	1.1
HBR-3 + MFR	3.9	1.7	8.3	6.6	4.8	2.6
HBR-4 + MFR	5.5	2.2	15.9	8.8	10.0	5.0

CHAPTER 5

CONCLUSIONS

1. Three of the resins, HBR-2, HBR-3, and HBR-4 synthesized in the research were air drying while the castor modified resin, HBR-1, was not air drying.
2. The resins decomposed between 315-345°C.
3. The resin which was synthesized by using only castor oil e.g. HBR-1 had higher viscosity than the resin which was synthesized by using both castor oil and linseed oil e.g. HBR-2. Because castor fatty acids contain 87% ricinoleic acid which contains hydroxyl group, and, it in turn, increases the hydrogen bonding.
4. DMPA modification increased the viscosity of the resins because of the increase in the hydroxyl group and so the hydrogen bonding in their structure.
5. All resins had lower viscosities compared to conventional high solids alkyd resin.
6. The viscosity of HBR-3 decreased significantly with shear rate.
7. The decrease of viscosity with the increase of time at constant shear rate was insignificant. It indicates that the resins were not thixotropic.

8. Impact and bending resistance tests showed that the hyperbranched resins were very flexible.
9. The hyperbranched resins showed good resistance to abrasion and adhered well on metal and glass substrates.
10. The hyperbranched resins had high gloss values.
11. All hyperbranched resins were successfully modified by melamine-formaldehyde resin at a ratio of 1:3.
12. The mixed resin (hyperbranched resin + melamine-formaldehyde resin) samples had higher hardness values than the hyperbranched resin.
13. The mixed resin samples had high impact resistance because no cracks formed on the surface samples.
14. Mandrel bending test has shown that the mixed resin samples were less flexible than the hyperbranched resins, because some cracks were observed on bending.
15. The mixed resin samples showed good resistance to abrasion.
16. DMPA modified resins displayed better adhesion when mixed with melamine-formaldehyde resin.
17. The mixed resin samples had low gloss values.

CHAPTER 6

RECOMMENDATIONS

1. Different core molecules can be used instead of dipentaerythritol and different compounds can be used at the outer periphery to give the required properties to the resin.
2. Acrylic and methacrylic groups can be incorporated into the structure of the hyperbranched resins to obtain UV-curable resins.

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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 such as isopropyl alcohol and toluene. Phenolphthalein is used as indicator and a pink coloration indicates the end point. The acid number is calculated from the following equation:

$$\text{Acid Number} = \frac{V_{KOH} \times N_{KOH} \times MW_{KOH}}{m_{\text{sample}}}$$

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

APPENDIX B

VISCOSITY MEASUREMENTS

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

Shear Rate (s^{-1})	Viscosity (Pa·s)	Std. Dev. (Pa·s)
21.7	3.316	0.04
44.2	3.184	0.02
66.4	3.127	0.02
88.8	3.097	0.02
110.9	3.074	0.02
133.2	3.057	0.02
155.4	3.043	0.02
177.6	3.032	0.02
199.9	3.021	0.01
200.0	3.020	0.01

Table B.2 Viscosity and time data for HBR-1 at 200 s⁻¹

Time (s)	Viscosity (Pa·s)	Std. Dev. (Pa·s)
0.0	3.020	0.01
13.2	3.018	0.01
26.4	3.015	0.01
40.2	3.015	0.01
53.4	3.013	0.01
66.6	3.012	0.01
79.8	3.009	0.01
93.0	3.010	0.01
106.8	3.008	0.02
120.0	3.008	0.02

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

Shear Rate (s^{-1})	Viscosity (Pa·s)	Std. Dev. (Pa·s)
22.0	1.482	0.06
44.2	1.238	0.03
66.5	1.157	0.02
88.7	1.112	0.02
110.6	1.078	0.01
133.2	1.056	0.01
155.3	1.036	0.01
177.6	1.020	0.01
199.8	1.006	0.01
200.0	1.007	0.01

Table B.4 Viscosity and time data for HBR-2 at 200 s⁻¹

Time (s)	Viscosity (Pa·s)	Std. Dev. (Pa·s)
0.0	1.007	0.01
13.2	1.004	0.01
26.4	1.002	0.01
40.2	1.000	0.02
53.4	1.001	0.02
66.6	1.001	0.02
79.8	0.999	0.01
93.0	0.996	0.02
106.8	0.995	0.02
120.0	0.998	0.01

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

Shear Rate (s^{-1})	Viscosity (Pa·s)	Std. Dev. (Pa·s)
22.0	12.310	0.55
44.3	10.211	0.42
66.4	9.139	0.35
88.7	8.472	0.32
110.9	8.064	0.32
133.2	7.743	0.30
155.3	7.497	0.29
177.7	7.291	0.26
199.8	7.101	0.24
200.0	7.101	0.24

Table B.6 Viscosity and time data for HBR-3 at 200 s⁻¹

Time (s)	Viscosity (Pa·s)	Std. Dev. (Pa·s)
0.0	7.060	0.24
13.2	7.022	0.24
26.4	6.988	0.22
40.2	6.963	0.22
53.4	6.947	0.21
66.6	6.927	0.21
79.8	6.913	0.20
93.0	6.898	0.19
106.8	6.888	0.19
120.0	7.060	0.18

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

Shear Rate (s^{-1})	Viscosity (Pa·s)	Std. Dev. (Pa·s)
22.2	4.487	0.10
44.2	4.206	0.11
66.5	4.064	0.12
88.7	3.979	0.12
110.1	3.914	0.12
133.1	3.862	0.12
155.4	3.816	0.12
177.6	3.761	0.11
199.8	3.719	0.11
200.0	3.719	0.11

Table B.8 Viscosity and time data for HBR-4 at 200 s⁻¹

Time (s)	Viscosity (Pa·s)	Std. Dev. (Pa·s)
0.0	3.711	0.11
13.2	3.703	0.12
26.4	3.695	0.11
40.2	3.686	0.11
53.4	3.682	0.11
66.6	3.681	0.11
79.8	3.677	0.11
93.0	3.667	0.11
106.8	3.663	0.11
120.0	3.711	0.11