ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

THE SYNTHESIS AND CHARACTERIZATION OF MODIFIED RESIN

M.Sc. THESIS

Pelin DİNÇER

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Nilgün KIZILCAN

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

MODİFİYE REÇİNELERİN SENTEZİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

Pelin DİNÇER
(515091044)

Polimer Bilimi ve Teknolojisi Anabilim Dalı

Polimer Bilimi ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Nilgün KIZILCAN

ŞUBAT 2012

Pelin DINCER, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **515091044**, successfully defended the **thesis** entitled "**The Synthesis and Characterization of Modified Resin**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Nilgun KIZILCAN**

Istanbul Technical University

Jury Members : **Prof. Dr. Ahmet AKAR**

Istanbul Technical University

Prof.Dr. F. Seniha GUNER

Istanbul Technical University

Date of Submission : 19 December 2011
Date of Defense : 3 February 2012

FOREWORD

This master study has been carried out at Istanbul Technical University, Chemistry Department of Science & Letter Faculty.

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Nilgün KIZILCAN for offering invaluable help in all possible ways, continuous encouragement and helpful critics throughout this research.

I wish to express my special thanks to Assos. Prof. Dr. Nesrin KöKEN for her helpful and understanding attitudes during my laboratory and thesis study in ITU. It has been a pleasure to work her.

I wish to express my special thanks to Res.Assist.Ömer Faruk VURUR for his helpful and understanding attitudes during my laboratory and thesis study in ITU. It has been a pleasure to work with him.

I would like to also extend my sincere gratitude Esin ATEŞ for her friendly and helpful attitudes and unbelievable sensibility during my laboratory works. In addition, I would like to thank my friends Mustafa Edhem KAHRAMAN, Tuba DEDEOGLU, Selda SEN for their support and sincerity during my laboratory study.

I also acknowledge to my FAMILY for their encouragement and support throughout my education.

February 2012

Pelin DİNÇER

(Chemist)

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ABBREVIATIONS

^{1}H NMR **:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
ATRP **:** Atom Transfer Radical Polymerization
CH_2Cl_2 **:** Dichloromethane
CD_2Cl_2 **:** Deutera chloroform
THF **:** Tetrahydrofuran
BCFR **:** Modified Boric Acid Cyclohexanone Formaldehyde Resin
FT-IR **:** Fourier Transform Infrared
NMR **:** Nuclear Magnetic Resonance
TGA **:** Thermogravimetric Analysis
UV **:** Ultra Violet
SEM **:** Scanning Electron Calorimetry
EMK **:** Ethyl Methyl Ketone
CFR-TEOS **:** 3-(triethoxysilyl) propyl isocyanate modified cyclohexanone formaldehyde resin

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THE SYNTHESIS AND CHARACTERIZATION OF MODIFIED RESIN

SUMMARY

Ketonic resins containing α-hydrogen atoms, such as reactive aldehydes and ketones and formaldehyde is reacted. Cyclohexanone-formaldehyde resins are the most commonly used ketonic, asetofenon - formaldehyde, methyl ethyl ketone formaldehyde resins such as thermoplastic. Resins are commercially popular, mostly low-molecular-weight, crumbles easily solid thermoplastics. Can not be used alone. In most cases, nitro-cellulose, such as alkyd resin mixed with other polymeric materials used in surface coatings industry. Use other than as an area of surface coating, varnish, ink, textile, paper industries can be said as the most important areas. In addition, to increase adhesion with the use of resins in various fields ketonic, lustrous, and provides light for the development of strength-building properties.

The cyclohexanone formaldehyde resin (CFR) has low molecular weight and shows unique compatibility with a great number of polymers. It is soluble in most organic solvents such as aromatic hydrocarbons, ketones, esters, alcohols, etc. Because of its good compatibility, it is usually used as a coating additive. The commen *in situ* modified cyclohexanone formaldehyde resins formed from cyclohexanone, formaldehyde and modifier compound in the presence of sodium hydroxide. The roles of the types of the modifier compound and concentration, the solubility, molecular weight and thermal properties of the modified cyclohexanone formaldehyde resin have been investigated. The modifier compounds are phenols, bisphenols, melamine, p-toluenesulfonamide , salicylic acid, o-cresol, p-cresol, citric acid, polydimethylsiloxane, aniline, 4- aminodiphenylamine and N-N-diphenyl-1,4-phenylenediamine, carbazole-9-carbonyl chloride, ketonic resin has a methylene and methylol groups, so it has relatively higher freedom rotation. Some reports have appeared on the synthesis and application of boron- containing phenol and bisphenol formaldehyde resin, while the synthesis structure and thermal properties of boron-containing cyclohexanone formaldehyde resin have not been investigated until now.

In this study, a new BCFR were synthesized. In the boron-containing cyclohexanone-formaldehyde resins formed from *in situ* modified method, the methylene borate linkage was mainly formed during the synthesis process. The borate linkage had better heat resistance than ether linkage, so the boron-containing ketonic resin had good thermal stability. These resins have higher T*g* and T*m* value than CFR alone and they also have thermal properties. Resulting boran containing cyclohexanone formaldehyde resins may provide an opportunity for a new breakthrough in the area of polymeric materials for advanced technologies. It can be used as reinforced laminate, heat-resistant adhesives and coating materials. Also, A new 3-(triethoxysilyl) propyl isocyanate modified cyclohexanone formaldehyde resins were synthesized by reaction of hydroxyl group with TEOS. These resins have higher T*g* and T*m* value than CFR alone and they also have thermal properties.

MODİFİYE REÇİNELERİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Ketonik reçineler α-hidrojeni içeren ketonlar ve formaldehit gibi reaktif aldehitlerin reaksiyonundan elde edilir. En çok kullanılan ketonik reçineler siklohekzanon-formaldehit, asetofenon – formaldehit, metil etil keton-formaldehit gibi termoplastik reçinelerdir. Ticari bakımdan ilgi gören reçineler, çoğunlukla düşük molekül ağırlıklı, kolayca ufalanabilen katı termoplastiklerdir. Tek başlarına kullanılamazlar. Çoğu kez nitro selüloz, alkid reçinesi gibi diğer polimerik maddelerle karıştırılarak yüzey kaplama sanayinde kullanılır. Kullanım alanı olarak yüzey kaplamadan başka, vernik, mürekkep, tekstil, kağıt sektörleri en önemli alanlar olarak söylenebilir. Ayrıca çeşitli alanlarda ketonik reçine kullanımı ile yapışmayı artırıcı, parlaklık verici ve ışığa dayanımı artırıcı özelliklerinin gelişmesini sağlar. Son yıllarda ketonik reçinelerin polipirol ve polikarbazol ile kopolimerleri sentezlenerek çözünür ve iletken malzemeler elde edilmiştir. Ketonik reçinelerin uygulamaları çok sayıda istihdam edilmektedir. Kaplama sektöründe, çoğu diğer uygulamalarda olduğu gibi, ürünlerin diğer bağlayıcılar, yumuşatıcılar, pigmentler ve yardımcıları ile kombine olarak kullanılır. Son formülasyonları, deniz boyaları, metal primerler ve yıkama primerler, toz boya ve yol çizgi boyaları içerir. Baskı mürekkepleri ve diğer amaçlar arasında, sadece selüloz nitrat dayalı köklü flekso ve gravür baskı mürekkepleri söz değil, aynı zamanda transfer baskı mürekkepleri, radyasyon tedavi edilebilen sistemler ve mürekkep püskürtmeli mürekkepler yapılabilir. Pasters günümüzde üretilen ballpoints öncelikle acetophenone-formaldehit reçineleri hidrojene dayalı. Diğer önemli uygulamalar, kayıt ve kopyalama teknolojisi (toner), baskılı devreler, yapıştırıcılar, oluklu mukavva için bağlayıcı, döküm döküm kumları ve laminatlardır.

Keton reçineler gibi reçineler tarif aldehid kaplama malzemeleri için başka bir bağlayıcı ile orantılı olarak eklenebilir. Böylece, alkid reçineleri, selüloz nitrat veya klorlu, polimer esaslı kaplamalar, iyileştirmeler sertlik, parlaklık, dolgunluk, tesviye, sararma ve katı içeriği direnç ile ilgili olarak elde edilir. Genellikle possibleby içinde aynı zamanda bu önlemler regüle iyileştirmek, toz kaplamalar, örneğin genel formül maliyetini düşürmek için reçine ilave edilir. Bir başka yol çizgi uygulamaları için hot-melt kompozisyonlar ve plastik spreyler bulunmaktadır.

Termoplastik polimerler özellikle çok mükemmel özellikleri, dış dayanıklılıkları vardır, ama onlar çözücü büyük miktarlarda uygulama için yeterince düşük viskoziteyi azaltmak için gerektiğinden kullanımı azalmıştır. Termoplastik akrilik polimer esaslı Laklar otomotiv üst kat için kullanılmıştır. Onlar yüzeye filmi paralel olarak alüminyum pul pigment yönelimi permite yana yüksek çözücü seviyeleri mümkün olur. Akrilik kopolimerler yumuşatıcılar ile birlikte kullanılır. Metil metakrilat, stiren, ve n-bütil akrilat sıklıkla kullanılmaktadır. Kritik sentezinde molekül ağırlığı kontrolü yaklaşık 90 000 arasında yukarıda Mw, artan moleküler ağırlığa sahip değişim özellikleri küçük olmakla birlikte film tabakası, moleküler ağırlığı ile artar. Spreylenebilir düşüşler olabilir molekül ağırlığı artar, çözümler artar ve katıların viskozitesi. Viskozite çok yüksek molekül ağırlık fraksiyonlarının

etkilenir, ve bunun için dar bir aralığa moleküler ağırlık dağılımı (Mw / Mn) kontrol ederek bu fraksiyon en aza indirmek için kritiktir.

TP polimerler daha düşük termoplastik reçinenin molekül ağırlığı. Molekül ağırlığı 1 000-5 000 civarındadır. Bu ham materils olarak kullanılabilir.

Bu basınç kadar ısıtıldı ve maruz kaldığında termoset po lymer akmaz. Termoset polimerler kalıcı kimyasal komşularına bağlı zincirleri, ya doğrudan veya kısa köprü zincirleri aracılığıyla, birbirine bağlı bir ağ oluşur. Termoset polimerler çözücüler boşanmak istemiyorum, ama onlar yumuşatmak ve şişer olabilir.

Lineer alifatik ketonlar, metil etil keton ve aseton gibi ketonlar reçine oluşturmak için formaldehit ile reaksiyona girerler. Aynı yöntemle, metil izobütil ketondan yapıştırıcı olarak kullanılmak üzere reçine elde edilir. Yüksek alifatik ketonlar uzun süreli reçineler oluşturmazlar. Siklopentanon, sikloheptanone ve halkalı ketonların yanı sıra, sikloalifatik ketonlar, siklohekzanon ve metil siklohekzanon çok önemlidir. Çünkü, zincirlerin uzun kısımları reçinler için hammadde olarak tanımlanır.

Metil etil keton reçineleri kaplamalarda ve yapıştırıcılarda kullanılır. Metil etil keton reçineleri, sikloalifatik veya alifatik-aromatik ketonların çözünürlüğü ve uygunluğundan farklıdırlar. Onların özellikleri ketonların polaritesi ve alkali kataliz reaksiyonu boyunca özel davranışlarda bulanmasından kaynaklanır. Metil etil keton-formaldehit reçineleri hafif bir içsel renklenmeye sahiptirler ve alkoller, esterler, ketonlar ve glikol eterler gibi polar çözücülerde çözünürler. Hidroksil sayısı 80 KOH / g 190mg aralığındadır. Polar kütlesi 3 000 ve 5 000 g / mol arasındadır ve 80 ve 125 ^{0}C arasında yumuşama gösterir. Aseton-formaldehit kondenzasyon ürünleri, kağıt ve ahşata yapıştırmada kullanan geniş bir yelpazeye sahiptir. Uygulamalarda genellikle, hava direnci ile su geçirmez bir yapıştırma sağlamak için sunta ve ahşap malzemeler elde etmek için fenol resoller yoğunlaşmış olarak bulunmaktadır.

Siklohekzanon reçineler, solmaz, birçok solvent içinde çözünür ve kaplamalarda kullanılan ham maddelerin çoğunluğu ile uyumludur. Sikloheksanon-formaldehit reçinelerine göre daha pahalı reçinelerdir.

Siklohekzanon, metilol bileşikleri veya reçine üretmek için aldehitler ve özellikle formaldehitlerle reaksiyona girerler. Mol oranları ve reaksiyon durumları üretim sonucunda elde edilir. Yüksek formaldehit fazlalığı, temel kataliz reçine oluşumuna yol açar ise metilen bileşiklerinin oluşumunu destekler. Birçok durumda, reçineler, kurutma, sertlik, dolgunluk, parlaklık ve katı içeriği geliştirmek amacıyla kullanılır. Kaplamalarda alkid / akrilik kaplama malzemeleri, örneğin, çimento, boyalar , epoksi reçine sistemleri ve deniz boyaları her durumda sadece diğer bağlayıcı eşliğinde kullanılır. Geleneksel baskı mürekkepleri, UV-kürleme baskı mürekkepleri ek olarak aynı zamanda giderek artan bir rol oynar. Bir diğer uygulama temel alan yapıştırıcılar ve hermetik tarafından temsil edilmektedir. Tri metil siklohekzanon üzerinde bazlı reçineler, evrensel bir uygulama yeteneğine sahip pigment pastalar kullanmak için uygun hale getirir.

Reçineler, hidroksil ve karbonil ile modifiye edilmiştir. Keton reçineler, formaldehit gibi reaktif aldehitler ile α-hidrojen içeren ketonlar tepkimeye hazırlanır. En çok kullanılan termoplastik ketonik reçineler sikloheksanon-formaldehit ve asetofenon formaldehit reçineleridir. Onlar düşük molekül ağırlıklı bileşikler ve kaplama endüstrisi yüksek molekül ağırlıklı filmi kalıplarının, örneğin özelliklerini değiştirmek için katkı maddeleri kullanılır, asetofenon formaldehit reçine, parlaklık ve kağıt ışık haslığı geliştirir.

Bu çalışmada, beş adet modifiye edilmiş borik asit siklohekzanon formaldehit reçinesini, borik asit ile siklohekzanon formaldehitin metilolu ile eterleşme reaksiyonuyla elde ettik. Modifiye borik asit siklohekzanon formaldehit reçinesinin mol oranları, siklohekzanon/ formaldehit/ boric asit; 1/2/0.5 (BCFR1), 1/2/0.75(BCFR2), 1/2/1 (BCFR3), 1/2/1.5 (BCFR4), 1/2/3 (BCFR5). Bor reaktifler içeren bu reçineler, aseton, kloroform, alkol, dimetil formamid, gibi organik çözücülerde çok çözünür.

Modifiye borik asit siklohekzanon formaldehit reçinesi ATR-FTIR spektroskopisi ile teyit edilmiştir. İnfrared spectroskopsi 3430-3320 cm^{-1} güçlü metilole ve –B-OH grubuna it –OH piki gözlemlenmiştir. 1715-1640 cm^{-1} piki karbonil bağına ve borata ait olan -C=O gözlemlenmiştir. 1350 cm^{-1} pikinde ise borata ait olan B-O gözlemlenmiştir. Bor ve karbona ait olan metilen alifatik hidrojen köprüsü, 2930 cm^{-1} and 1450 cm^{-1} pikinde gözlemlenmiştir. Metilol grupları 1040-1060 cm^{-1} arasında gözlemlenmiştir. Ether bağı C-O, 1130-1140cm^{-1}piki modifiye borik asit siklohekzanon formaldehit methilen köprüsüyle benzerlik gösteriyor.

BCFR1, BCFR2 ve BCFR5'e ait olan ^{1}H-NMR spectroskopisi 3-4.5 ppm aralığında metilole ait olan metilen protonları ve eter bağ protonları gözlemlenmiştir. Siklohekzana ait olan alifatik hidrojenlerse 1-3 ppm aralığında gözlemlenmiştir.

Modifiye borik asit siklohekzanon formaldehit reçinesinin yanı sıra, modifiye 3-(triethoksil)propil izosiyonat siklohekzanon formaldehit reçinesi elde edildi. CFR-TEOS reçinelerinin mol oranları, (reçine/ modifiye 3-(triethoksil)propil izosiyonat); 1/0.25 (CFR-TEOS1), 1/0.5 (CFR-TEOS2), 1/1.25 (CFR-TEOS3).

FTIR spektroskopisin de CFR-TEOS, 3360 and 3390 cm^{-1} pikinde reçineye ait -OH grupları ve N-H grubu gözlmlenmiştir. 1700-1710cm^{-1} pikinde ketonik reçinelere ve karbomat grubuna ait karbonil grupları gözlemlenmiştir. 980-987cm^{-1} ve 1040-1067cm^{-1} pikinde Si-O-CH_2'a ait Si-O ve 700-770cm^{-1} pikinde ise Si-CH_2 gözlemlenmiştir.

Sonuç olarak bu çalışmada, yeni bir modifiye borik asid siklohekzanon formaldehit reçinesi (BCFR) sentezlenmiştir. Bor içeren in situ modifiye yöntemi ile oluşan sikloheksanon-formaldehit reçineleri, metilen borat bağ esas sentez işlemi sırasında kurulmuştur. Borat bağının eter bağından daha iyi ısı direnci vardır, bor içeren ketonik reçine de iyi termal stabilite vardır. Bu reçineler siklohekzanon formaldehit reçinelerinden (CFR) tek başına daha yüksek Tg ve Tm değeri vardır ve onlarda termal özellikleri var. Boran içeren sikloheksanon formaldehit reçineleri sonuçlarına göre gelişmiş teknolojiler için polimerik malzemeler alanında yeni bir atılım için bir fırsat sunabilir. Güçlendirilmiş laminant, ısıya dayanıklı yapıştırıcı ve kaplama malzemesi olarak kullanılabilir. Ayrıca, yeni formaldehit reçineleri sikloheksanona değiştirilmiş 3-(triethoksil)propil izosiyanat TEOS hidroksil grubu ile reaksiyona girerek sentezlenmiştir. Bu reçineler, siklohekzanon formaldehit reçinlerinden (CFR) tek başına daha yüksek Tg ve Tm değerine sahiptirve onların da termal özellikleri vardır.

1. INTRODUCTION

Boric acid and borate salts have been used as flame retardant additives since early 1800s but they have been less studied than phosphorous, halogen and other compounds. The use of borates in enchancing in the flame retardancy of polymeric materials was reported earlier in the 20th century [1]. The flame retaedant action of the boron-containing compounds on polymeric materials is chemical as well as physical. The influence of boron containing reactive groups such as polystyrene and poly(vinyl alcohols) has been reported [2].

The boron-containing phenol-formaldehyde resin (BPFR) is a modified phenolic resin. It is obtained by introducing boron into the main chain of a phenolic resin. The boron-containing phenol-formaldehyde resin (BPFR) has high performance properties, such as thermostability, mechanical strength and electric properties. Some reports have been appeared on the synthesis and application of boron-containing phenol-formaldehyde resin (BPFR) [3- 6].

The cyclohexanone formaldehyde resin (CFR) has low molecular weight and shows unique compatibility with a great number of polymers. It is soluble in most organic solvents such as aromatic hydrocarbons, ketones, esters, alcohols, etc. Because of its good compatibility, it is usually used as a coating additive. The commen *in situ* modified cyclohexanone formaldehyde resins formed from cyclohexanone, formaldehyde and modifier compound in the presence of sodium hydroxide. The roles of the types of the modifier compound and concentration, the solubility, molecular weight and thermal properties of the modified cyclohexanone formaldehyde resin have been investigated. The modifier compounds are phenols, bisphenols, melamine, p-toluenesulfonamide [7- 8], salicylic acid, o-cresol, p-cresol, citric acid [9], polydimethylsiloxane [10], aniline, 4- aminodiphenylamine and N-N-diphenyl-1,4-phenylenediamine [11], carbazole-9-carbonyl chloride [12], ketonic resin has a methylene and methylol groups, so it has relatively higher freedom rotation. Some reports have appeared on the synthesis and application of boron-containing phenol and bisphenol formaldehyde resin [13- 16], while the synthesis

structure and thermal properties of boron-containing cyclohexanone formaldehyde resin have not been investigated until now.

In this study, Boron-Containing Cyclohexanone Formaldehyde Resin are synthesized by the in situ method, and characterized by the physical, thermal and spectroscopic properties of resin samples have been investigated and determinated.

2. THEORETICAL PART

2.1 Resin

2.1.1 Introductıon

The term ‘resins’ is now generally accepted although misleading since the compounds referred to are low moleculer mass or oligomeric compounds. Resins are in general raw materials, for example for binders, curable moulding compositions adhesives and coatings. They normally have a melting or softening range, are brittle in the solid state. Resin can be devided as natural resins and synthetic resins.

The most important synthetic resins are phenol-formaldehyde resins, urea-formaldehyde, melamine-formaldehyde resins, polyesters resins, silicone resins, ketone-aldehyde resins, epoxy resins, acrylic resins and alkyd resins.

Synthetic resins can be divided two groups such as thermoset and thermoplastic resins.

2.1.1.1 Thermoplastic and Thermoset Resins

Thermoplastic polymers have many excellent properties, especially exterior durability, but their use has declined because they require large amounts of solvent to reduce viscosity low enough for application. Lacquers based on Thermoplastic acrylic polymers were used for automotive top coats. Their high solvent levels make possible brillant meyallic colors since they permite orientation of aluminum flake pigment in the film paralel to the surface. The acrylic copolymers are used with plasticizers. Methyl methacrylate, styrene, and n- butyl acrylate are often used. Control of molecular weight in the synthesis critical. Film strength increases with molecular weight, although above Mw of about 90 000, the change properties with increasing molecular weight is small. The upper end of molecular weight is limited because solutions of acrylic polymers with Mw greater than about 100 000 exhibit cobwebbing on spraying; rather than atomizing to small droplets from the orifice of a spray gun, the lacquer comes out as threads. As molecular weight increases, viscosity of solutions increases and solids, which can be spray applied decreases. Viscosity is

particlary affected by the very high molecular weight fractions; therefore, it is critical to minimize this fraction by controlling molecular weight distribution(Mw/Mn) to a narrow range.

The molecular weight of thermoplastic resins lower than TP polymers. The molecular weight is about 1 000-5 000. They can be used as raw materils.

Thermoset po lymer does not flow when it is heated and subjected to pressure. Thermoset polymers consist of an interconnected network of chains that are permanently chemically connected to their neighbors, either directly or via short bridging chains. Thermoset polymers do not dissolve in solvents, but they can soften and swell.

Commercially, we create thermoset polymers directly by step growth reaction or by crosslinking a thermoplastic polymer to form a thermoset material in a separate reaction. To create a thermoset by step growth, we need to incorporate a significant proportion tri-functional monomers, which creates the type of networks illustrated. We can crosslink linear polymer to form thermosets via various reactions, depending on the chemical structure of the base polymer. We heat the polymer sufficiently fort he peroxide to decompose into peroxy radicals, which abstract hydrogen atoms from the chains to leave radicals which combine with each other to form covalent carbon-carbon bonds between adjacent chains.

2.2 Ketone and Aldehyde Resins

Ketone and aldehyde resins are obtained by self-condensation or, more frequently, by cocondensation with formaldehyde, of aliphatic, cycloaliphatic or aliphatic-aromatic ketones or, respectively aldehydes [17, 18]. In addition, further monomers, such as phenols been described. The aromatic hydrocarbon-formaldeyde resins are prepared from alkylated aromatic hydrocarbons, formaldehyde and – sometimes – other monomer [19, 21]. Although the resin groups involved have been knows for a long time, their chemistry and applications remain areas of change even today.

The following monomers are frequently employed:

A.Ketones

B. Aldehydes

C. Alkylated aromatics

The condensation of monomers can be accelerated using basic, acidic or neutral catalysts [22]. In the cocondensation of the ketones with formaldehyde, basic catalyst play the major role. The reaction follows the mechanism of the aldol condensation, and leads to aldol-type products and, after elimination of water, to unsaturated compounds [23, 24]. In the first step of the reaction, formaldehyde is added to form the ketone alcohol [25].

Figure 2.1: Formation of enalot anion and methylol of ketone

Subsequently, depending on the molar ratio of ketone to formaldehyde and on the other reaction conditions (temperature, Ph, concentration), ketone alcohol can either undergo dehydration to form polymerizable vinyl ketones, or with further formaldehyde can form highly reactive methylol compounds.

Figure 2.2: Formation of three methylol of ketone.

The resin are formed by polymerization of the vinyl ketones, giving polymers having an alternating structure, or by complex condensation reactions of the methylol compounds with one another or with further ketone molecules, leading to partially branched oligomers. In industrial processes, the two mechanisms usually take place

alongside one another. Excess formaldehyde may lead to the reduction of the carbonyl groups to hydroxyl groups [26]. Provided no substitution is carried out at the vinyl group, the nature of the ketone employed [27, 28]. Further reaction mechanisms are dealt with in the subsequent chapters.

The industrial preparation of the resins is performed in reactors for condensation reactions, usually in a batchwise procedure. Exemplary batch sizes and processes have been described [18, 23, 29].

Ketone and aldehyde resins are employed in a large number of applications. In the coatings sector, as with most other applications, the products are used in the combination with other binders, plasticizers, pigments and auxiliaries. The final formulations include marine paints, metal primers and wash primers, powder coatings and roadmarking paints. Among inks for printing and other purposes [30], mention may be made not only of the well-established flexographic and gravure printing inks based on cellulose nitrate but also of transfer printing inks, radiation-curable systems and ink-jet inks. The ballpoints pasters produced nowadays are primarily based on hydrogenated acetophenone-formaldehyde resins. Further important applications are in recording and copying technology (toners), printed circuits, adhesives, binders for corrugated card, foundry moulding sands and laminates [29].

2.2.1 Resins from Aliphatic Ketones

Linear aliphatic ketones such as methyl ethyl ketone and acetone are reacted to form resins with formaldeyde in particular. In the same way, methyl isobutyl ketone is used to produce resins for adhesive [31, 32]. Higher aliphatic ketones no longer form resins. As regards the cycloaliphatic ketones, cyclohexanone and methylcyclohexanone are the most important, although cyclopentanone, cycloheptanone and cyclic ketones with longer side chains have been described as raw materials for resins [33]. Here too, it is cocodensation with formaldehyde which predominates. Only in the case of the cyclohexanone has self-condensation acquired any industrial significance.

2.2.1.1 Methyl Ethyl Ketone-Formaldehyde Resins

These resins are used in particularas binders for coatings and adhesives. They differ from the resins based on cycloaliphatic or on aliphatic-aromatic ketones in their so

lubility and compatibility with other raw materials used in coatings. Their properties derive from the polarity of the ketone and from its specific behaviour during the alkaline-catalysed condensation [34].

The methyl ethyl ketone-formaldehyde resins possess a slight inherent coloration and are soluble in polar solvents such as alcohols, esters, ketones and glycol ethers. The hydroxyl numbers are in the range from 80 to 190mg of KOH/g. The resins are strongly polar, hygroscopic and have an oxygen content of from 21 to 29 per cent by mass. The polar masses are between 3000 and 5000 g/mol, the softening range between 80 and 125 ^{0}C. Other physical properties have been described [18].

The resins cannot be hydrolysed, and possess not only keto and hydroxyl groups but also C-C double bonds. Their chemical reactivity is exploited in industry: the OH groups react with carboxylic acids and anhydrides [34] or with isocyanates [35], while the double bonds can be hydrogenated [36].

The resins are prepared by alkaline-catalysed condensation of methyl ethyl ketone and formalde in a molar ratio of from 1: 2 to 1:2.5 in a batch process [27, 37, 38]. Without purification beforehand, the ketone is reacted with formaldehyde in the presence of water. NaOH and KOH have proven to be the best catalyst for this reaction. The increase in the melting point from 80 to 120 ^{0}C can be achieved by raising the excess of formaldehyde. High softening points are also obtained by phase transfer catalysis [33]. Special cleaning processes likewise lead to high-melting products which are light colour [39]. Continuous preparation has also been described [40]. The reactions which take place correspond to reaction mechanisms. The course of the reaction, however, is not fully understood. The structure shown below is greatly simplified, since hydroxyl groups and double bonds are also found in the resins.

Figure 2.3: Methyl Ethyl Ketone(EMK)-Formaldehyde Resins.

More recently it has also proved possible to obtain high molecular weight methyl ethyl ketone-formaldehyde and acetone-formaldehyde resins by specipic vinyl polymerization (molar masses 40 000 to1 000 000 g/mol) [90]. In this process, the ketone alcohol is first prepared under alkaline conditions and seperated off by fractional distillation. Then, pound which is then subjected to free-radical polymerization.

Figure 2.4: Formation of Ethyl Methyl Ketone (EMK) Resin.

The resins are often used together with formers such as cellulose nitrate, acethycellulose, cellulose ethers or natural resins. Among the properties endowed are, in particular, hardness, drying, sandability and good light stability. The resins possess the capacity to bring about gelatinization of cellulose nitrate. The free hydroxyl groups are exploited for crosslinking in isocyanate two-pack coatings, in adhesives [41] and in moulding sands [35].

2.2.1.2 Acetone-Formaldehyde Resins

The alkaline-catalysed condensation of acetone and formaldehyde does not give rise to any solid synthetic resins which can be used. The substantially greater resinification tendency of the unstable methylolation stage of acetone [40, 43] leads to a crosslinked, insoluble final structure. However, self-curing precondensates can also be prepared, which can be employed alone or in combination with other curable precondensates, such as phenol resols. Water-soluble products having 4 OH groups per molecule are obtained when acetone and formaldehyde are reacted in a ratio of 1 to 3 [45]. These products can be crosslinked under alkaline conditions [90].

Rigid foams [28] are obtained when the methylol compounds are foamed in the presence of alkali metal hydroxide, alone or in the presence of elastomer latex [35]. In the production of mouldings, sands can be solidified using acetone-formaldehyde precondensates [46]. Description have also been given of quick-setting mouldings

from cement [47, 48]. Acetone-formaldehyde condensation products find a wide variety of uses in the adhesive bonding of paper [49] and of wood [50, 90]. In the applications, phenol resols are often co-condensed in order to obtain chipboard and wooden materials with particular weather resistance [51] or to provide corrugated cards with waterproof bonding [52]. Further applications of acetone precondensates are as photoreceptors in electrophotography [53] and for the production of additives [38].

2.2.1.3 Cyclohexanone Resins

Cyclohexanone and methylcyclohexanone not only can be cocondensed with formaldehyde but are also capable of self-condensation [29, 56, 90]. In this case an aldol condensation takes place between the carbonyl group and the activated methylene group of a second molecule. The carbonyl group of the intermediates reacts with a further molecule of cyclohexanone: similar reactions follow until the final products is formed. The reaction, which takes place at elevated tempature, can be catalysed by basic, acidic or neutral agents, with potassium methylate being used most often.

Figure 2.5: Condensation of cyclohexanone inpresence of base catalyse.

Examples of preparation produces are decried [18, 57, 90].
The softening points of the light-coloured, neutral resins are between 80 and 120 ^{0}C. Under normal conditions the resins are resistant to acids and bases. However, under the action of acid they eliminate water at elevated temperatures (>80 ^{0}C), and their properties are altered substantially. The cyclohexanone resins are lightfast, soluble in many solvents and compatible with the majority of raw materials used in coatings. They are more expensive than cyclohexanone-formaldehyde resins.

In coatings materials, the primary functions of cyclohexanone resins are to improve fullness, gloss and hardness. They may also increase the lihgtfastness and weather resistance and the adhesion. The quantities of from 5 to 50 per cent by mass (based

on the film former) to coating materials based on alkyd resins, vinyl chloride copolymers, chlorinated rubber, cellulose nitrate or oils. Their use as a carrier resins for pigments preparations has also been described [59]. Reduction and partial esterificiation are possible ways to improve stability and flexibility [60].

2.2.1.4 Cyclohexanone-Formaldehyde Resins

Cyclohexanone can be reacted with aldehydes, especially formaldehyde, to give defined methylol compounds or resinous products. In this case it is the molar ratio and the reaction conditions which determine the properties of the end products [90]. A high formaldehyde excess promotes the formation of the methylol compounds, whereas basic catalysis leads to resin formation [61-63]. Higher aldehydes can likewise be used to produce resins, but have not found any industrial significance. On the other hand, methylcyclohexanone or mixture with aliphatic ketones [64] and, more recently, trimethylcyclohexanone have been employed. The modification of the resins with phenols [57, 65], epoxides [66], polyesters [67], and sulphonamides [68] is known. Small beads are obtained by addition of dispersants [69]. The continous preparation process has been described [70, 71]. Hydrogenation [72] and treatment with reducing agents [57] are ways in which the light stability can be increased.

Figure 2.6 : Structure of cyclohexanone formaldehyde resin.

Cyclohexanone-formaldehyde resins do not have the broad compatibility and solubility of the pure cyclohexanone resins. However, they are less expensive while being of adequate light stability. Although they can no longer be combined with oils, combination with a range of important paints binders is possible. The use of methylcyclohexanone as a raw material usually leads to enhanced solubility and compatibility. By using trimethylcyclohexanone, resins can be obtained whose compability and solubility are virtually universal.

A reaction which has become important fort he industrial production of the resin is the condensation of cyclohexanone with formaldehyde in the presence of alkalis. The resin formation has been systematically investigated [90]. A description is given an example of a preparation produce, and of the modification with phenol [18]. Copolymerization with styrene has likewise been carried out [74].

In many cases, the resins are used in order to improve drying, hardness, fullness, gloss and solid content. In coatings they are used in every case only as an accompaniment to other binders, for example in alkyd/acrylic coating materials [75], cement paints [76], epoxy resin systems [77] and marine paints [78]. In addition to conventional printing inks [79, 80, 90], UV-curing printings inks also play an increasing role. A further principal area of application is represented by adhesives [84, 85, 86] and sealing compounds [87]. Another application which has been described is in optical recording media [88, 89]. The broad compatibility of resins based on trimethylcyclohexanone makes them ideally suited to use in pigment pastes capable of universal application.

2.2.2 Resins from Aliphatic-Aromatic Ketones

Among the aliphatic-aromatic ketones, it is predominantly acetophenone which is reacted on the industrial scale with formaldeyhde to give resins. It is, however, also possible to use ring-alkylated acetophenones, such as methyl-, ethyl-, tert-butyl- or cyclohexylacetophenone [91]. In addition to the non-modified resins, their hydrogenation products and resins derived therefrom have become established on the market.

2.2.2.1 Acetophenone-Formaldehyde Resins

Acetophenone-formaldehyde resins are unhydrolysable products which are light in colour have sufficent light resistance and possess softening points of from 75 to 85 ^{0}C. They are of good solubility in aromatic hydrocarbons, esters, ketones and glycol ethers, but are insoluble in alcohols, aliphatic hydrocarbons and mineral oils. The resins are compatible with cellulose nitrate, vinyl chloride copolymers, chlorinated rubber, maleic, urea, melamine and ketone resins, plasticizers and some alkyd resins. The majority of alkyd resins, drying oils, polyesters and polyacrylates, however, are incompatible. Factors worthy of emphasis include the relatively low price, the gloss enhancement properties and the solids-increasing action in coating materials.

Figure 2.7: Formation of modified ketonic resin.

Soluble hard resins, light in colour, can be obtained by heating acetophenone, formaldehyde and potassium hydroxide to boiling temperature in aqueus phase. Working in solvents such as alcohols is a further possibility. The condensing agents used are alkalis, strong acids such as sulphuric acid, or dehydrating salts such as zinc chloride. However, strong alkalis such as potassium hydroxide or sodium hydroxide are the most common. Quaternary nitrogen or phosphorus compounds [92] are employed in order to obtain particularly high-melting resins. Under suitable

conditions, the use of sodium sulphite leads to water-soluble condensation products of low molecular weight [93]. The formaldehyde is usually added in the form of 30% strength aqueous solution as strength aqueous solution or as paraformaldehyde. Using relatively large quantities of alkali metal hydroxide relatively high temperatures results in the formation of unmeltable resins of poor solubility, since the methylol intermediats crosslink highly with one another. Meltable condensation products of good solubility are obtained with about 0.2 mol of hydroxide in a reaction whose duration is such as not to let the molar mass rise to more than 400 to 800 g/mol. In general, as the reaction temperature and duration are increased, the softening point of the resin becomes greater while at the same time its solubility and compatibility become worse. The reason for this may lie in the reaction mechanisms, which compete with one another in the course of condensation. If condensations are chosen so as to give predomiantly a vinyl phenyl ketone intermediate, the resins formed have a low melting points and broad solubility. For example, by reacting 1 mol of acetophenone with from 0.05 to 0. 5 mol of formaldehyde, an oilcompatible resin can be obtained. If primarily methylol compounds are produced as intermediates, then the resins melt at higher temperatures anda re limited in their solubility and compatibility. Acetophenone and formaldehyde in a molar ratio of 1:1 then given resins having the spectrum of properties described above.

Acetophenone-formaldeyhde resins are employed as cost-effective binders in coating metarials and printing inks, in combination with other raw materials such as cellulose nitrate. They improve gloss, fullness, hiding power, solids contents, adhesion and drying. In cellulose nitrate lacquers, pigmentability and sandability on wood are improved. Their use in vinyl chloride copolymer coatings coating metarials for metarials for metal coatings and roadmarking paints is deserving of mention. Adhesives and hot-melt compositions are also formulated with these hard resins.

2.2.2.2 Modified Acetophenone Resins

The hydrogenation, in particular, of acetophenone- formaldehyde resins leads to products which show distinct differences in relation to the customary ketone and aldehyde resins, thereby opening up new applications. The reaction of hydroxyl groups, which form from the ketone groups in the course of hydrogenation, with aliphatic diisocyanates leads to high-grade speciality binders.

The hydrogenated resins are very light in colour and have particular resistance properties. The complete freedom from formaldehyde, which can no longer be produced even by a reversal of the condensation process, is worthy of mention. Depending on the spesific hydrogenation conditions, resins are obtained in which only keto groups have been converted to hydroxyl groups, or in which the aromatic ring is hydrogenated. Only the former compounds are currently available. They have softening points in the range from 110 to 120 ^{0}C anda re readily soluble in alcohols. The resins can be cut with aromatics, and do not dissolve in aliphatics and mineral oil. In comparison with the unhydrogenated products, compatibility with alkyd resins improved.

The hydroxyl numbers of the resins more than 300 mg of KOH/g. The OH groups can be reacted with iscyanates. In the way it is possible to obtain extremely high melting resins (with melting points around 160 ^{0}C). The resins are likewise soluble in alcohol. They are characterized by resistance properties which are improved stil further and by very rapid solvents release.

When preparation is carried out using mild hydrogenation conditions, only the keto groups are hydrogenated. By changing the catalyst systems, it is also possible to hydrogenate the aromatic ring, to give resins soluble in petroleum spirit [94]. The reaction is monitored by determining the oxygen content and the melting point [95]. Catalytic hydrogenation can be carried out in solvents or in the melt [96, 97].

Reactions with isocyanates take place at slightly elevated temperatures with the usual catalysts.

The modified acetophenone-formaldehyde resins have higher melting points and greater resistance properties. Accordingly, they are employed as the hard resin component, together with other binders, in coating materials, printing inks and adhesives when the desire is to achieve high-quality coatings. The hydrogenated resins are used for light-resistant paper overprint varnishes based on cellulose nitrate. They also found in ballpoint pastes, inks and toners and as flow control agents for powder coatings. Moreover, they can be used as the hard resin component in isocyanate reactive systems and for the modification of alkyd resins.

The isocyanate-modified resins are employed in high-quality printing inks, paper coatings and wood varnishes. In addition, coating materials with good adhesion can

be formulated for plastic surfaces. The resins are particularly suitable for the wetting stabilization of aluminium pigments in paints and printing inks.

2.2.3Resins from Aldehydes

Aldehydes can also be resinified with catalysis by bases or acids [17]. Following formation of aldol, water is probably eliminated and the unsaturated aldehyde forms rings or adds on further aldehyde molecules. Resins prepared in this way, however, are of virtually no industrial importance today [22].

Figure 2.8: Aldol condensation of acetaldehyde.

In the nineteen-seventies, aldehyde resins consistings of the monomers isobutyraldehyde, formaldehyde and urea were brought to a state of technical maturity. The principle of chemical synthesis underlying this development is α-ureidoalkylation, which has been described in detail [98]. Further aldehyde resins from the reaction of isobutyraldehyde and phenol, which may be employed in hot-melt adhesives, should also be mentioned [99, 100].

2.2.3.1 Isobutyraldehyde-Formaldehyde-Urea Resins

Both reaction of urea with CH-acidic aldehydes [101] and the reaction of urea, formaldehyde and CH-acidic aldehydes [102] in an acid medium lead, given subsequently treatment with alkali metal alcoholates, to resinous products.

The resins are slightly coloured and fairly lightfast. They have melting points in the range from 80 to 110 ^{0}C. Depending on the preparation process, the spectrum of solubility and of compatibility with other binders can be varied. For instance, aliphatic-soluble products are on the market, which also dissolve in all other common solvents. Compatibility is restricted only in the ures of acrylic resins and sme cellulose derivates.

Like the ketone resins, the aldehyde resins described can be added proportionately to other binders for coatings materials. Thus, in coatings based on alkyd resins,

cellulose nitrate or chlorinated polymers, improvements are obtained in relation to hardness, gloss, fullness, levelling, resistance to yellowing and solids content. It is often possibleby adding resins to reduce the cost of the overall formulation, for example in powder coatings, in which these measures at the same time improve the levelling. A further applications is in hot-melt compositions and plastic sprays for roadmarking. Particular references should be made to the solubility of certain aldehyde resins as grinding resins for pigment pastes of broad solubility and compatibility. The high pigment binding capacity and the low solution viscosity are exceeded only by ketone resins based on trimethylcyclohexanone. With regard to aqueous dispersions, reference is made to the literature [103].

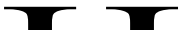

Figure 2.9 : Formation of urea formaldehyde resin.

2.2.4 Resins from Aromatic Hydrocarbons and Formaldehyde

Alkylated aromatic haydrocarbons can be reacted with formaldehyde in the presence of syrong acids [17, 22]. Under controlled reaction, m-xylene and formaldehyde in particular give rise to usefull resins [104]. Following the formation of substituted benzyl alcohols, larger molecules linked by way of methylene or methylene ether bridges are formed from these alcohols. About 6 to 8 aromatic rings are linked to one another. A preparation procedure is decribed [110].

Similarities with the reaction mechanisms of the formation of phenol resins should not be overlooked. More detailed information on the reaction mechanism is given in the literature [22, 110]. The resins can also be modified by cocondensation with phenols [105], novolaks [106], ketones [107], alcohols [108] and sulphonamides [109].

The thermal instability of ether and acetal groups is exploited for further reactions (post-condensation). Esterification or etherification is carried out at about 250 ^{0}C or lower, using acid catalysts, with compounds containing acid or alcohol groups. Reaction can be carried out with carboxylic acids, polyalcohols, polyesters, alkyde resins, oils, phenols and rosin. At the present time, however, the only customary commercial products are pure aromatic hydrocarbon-formaldehyde resins and cocodensation products with substituted phenols.

Figure 2.10: Condensation reaction of aromatic hydrocarbons and formaldehyde.

The resins are used in particular combination with cellulose nitrate or polyurethanes, where they function as plasticizers and to improve adhesion, gloss and resistance to water and chemicals. They are also employed as anti-pinholing agents and in CN gravure printing inks. They are used by manufacturers of rosin as a raw material for boiling down, in order to obtain high-melting oil-compatible products. The cocondensation products with phenols are used for boiling down with tung oil (high viscosity grades) and for accelerating the drying of alkyd resins. They possess solubility in esters, ketones, aromatics and in some alcohols and aliphatic compounds. The resins are compatible, for compatible, for example, with drying oils, alkyd resins and chlorinated rubber. Only the pure xylene-formaldehyde resins can be mixed with cellulose nitrate and cellulose acetobutyrate.

2.3 Modified Resin

Resins have been modified via their hydroxyl and carbonyl. Ketone resins are prepared by reacting ketones containing α-hydrogen with reactive aldehydes such as formaldehyde. The most used ketonic resins are thermoplastic cyclohexanone-

formaldehyde and acetophenone-formaldehyde resins. They are low molecular weight compounds, and are used in the coating industry as additives to modify the properties of high molecular weight film formers, e.g, acetophenone-formaldehyde resin improves brightness and light fastness of the paper lacquers.

Resins have been in situ modified during their prepatarion with a number of substants which reactc with formaldehyde and ketone under basic condition.

2.3.1 Modified Cylohexanone-Formaldehyde Resins

The Cylohexanone-Formaldehyde Resins (CFR) has low molecular weight and shows unique compatibility with a great number of polymers. It is soluble in most organic solvents such as aromatic hydrocarbons, ketones, esters, alcohols, etc. Because of its good compatibility, it is usually used as a coating additive.

The in situ modification of cyclohexanone–formaldehyde (CF) resins has been previously studied [2, 5]. The modifier compounds are carboxylic anhydrides [1, 2], ketones [2], phenol [3], methyl isobutyl ketone [6], methyl ethyl ketone [6], methylcyclohexanone [6] , crotonaldehyde [6], benzaldehyde [6], propanal [6], acetaldehyde [6], cinnamaldehyde [7], dicyandiamide [7], aminotriazine [7] , terephthalaldehyde [8], 1,4-cyclohexanedione, salicylic acid, o-cresol, citric acid, glyoxal, benzaldehyde, acetaldehyde, acrylamide phenol, p-cumylphenol [4], carbazole 9-carbonyl cloride, aniline, 4-aminodiphenylamine, and N-N0-diphenyl-1,4-phenylenedaimine, α,w-daimine polydimethylsiloxanes, α,w-dihydroxy polydimethylsiloxanes and p-cresol [5]. The resulting resins are used for adhesives and binders. Modified cyclohexanone-formaldehyde resins are also prepared using MEK, MIBK, methylcyclohexanone, acetaldehyde, propionaldehyde, and cinnamaldehyde. They are used as binders for self-hardening molds.

Modifier compounds are usually added to the reaction flask either at the beginning of polymer preparation or the later stage of resin formation, depending on their reactivity. Several patents are available where ketonic (cyclohexanone-formaldehyde) resin is used as an additive to improve the coating properties of alkyd resins [1–4]. The proper choice of modifier compoundsusually results in satisfactory physical properties, such as solubility, melting point, and chemical reactivities.

2.4 Modified Boric Acid Resin

Boric acid and borate salts have been used as flame retardant additives since early 1800s but they have been less studied than phosphorous, halogen and other compounds. The use of borates in enchancing in the flame retardancy of polymeric materials was reported earlier in the 20th century [1]. The flame retaedant action of the boron-containing compounds on polymeric materials is chemical as well as physical. The influence of boron containing reactive groups such as polystyrene and poly(vinyl alcohols) has been reported [2].

The boron-containing phenol-formaldehyde resin (BPFR) is a modified phenolic resin. It is obtained by introducing boron into the main chain of a phenolic resin. The boron-containing phenol-formaldehyde resin (BPFR) has high performance properties, such as thermostability, mechanical strength and electric properties. Some reports have been appeared on the synthesis and application of boron-containing phenol-formaldehyde resin (BPFR) [3- 6].

3. EXPERIMENTAL PART

3.1 Materials

Cyclohexanone and cyclohexane were obtained from Fluka Chemica Co. (Switzerland), 37% formaline solution was received from J.T.Baker and boric acide(merck). All chemicals were used without further purification.

3.2 Equipments for Resins Analysis

3.2.1 Infrared analysis(IR)

FT-IR spectra was measured using model recorded Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer.

3.2.2 Nuclear magnetic resonance (NMR)

All ^{1}H-NMR data were obtained from a Varian (500 MHz, Germany) spectrometer, using CD_2Cl_2-d_6 as solvent and TMS as internal reference.

3.2.3 Thermogravimetric analysis (TGA)

Thermal stability of copolymers was measured by thermogravimetric analysis (TA, TGA Q50) in a flowing nitrogen atmosphere at heating rate of 20^{o}C/min.

3.2.4 Scanning Electron Microscopy (SEM)

Morphologies of products were examined by scanning electron microscope, ESEM XL30 ESEM-FEG Philips.

3.2.5 Differential Scanning Calorimetry (DSC)

DSC thermograms were obtained by using Perkin-Elmer DSC-6 instrument (USA); the heating rate was 10^{o}C/min under a nitrogen atmosphere.

3.3 Synthesis

3.3.1 Synthesis of Boric Acid Modified Cyclohexanone Formaldeyde Resin (BCFR)

Into a three-necked flask equipped with a stirrer, and a condenser were added 104g of cyclohexanone, 20 ml of cyclohexane, 30 ml of 37% formalin and 31.5 g of boric acide were added. When the temperature of the mixture was raised to 65-70 ^{o}C, refluxing started. Subsequently, 100 ml of 37% formalin was added. The reaction

was further continued under pH values of 11-12 for 5h. After complete reaction time, two layers were formed. The modified resin was separated and purified by decanting the water layer(water layer is going to use over reaction and BCFR5.1 will be produced). Modified ketonic resin was washed several times with warm water till it was free from formaldehyde and boric acide odour, and dried at 60 ^{o}C in vacuo. In the second step, the water layers of BCFR5 was stirred and heated to 90 ^{o}C, then the reaction was maintained at this temperature under pH values of 11-12 for 2h; thereafter, complete reaction time, two layers were formed. The resin phase(BCFR5.1) was separated and purified by decanting the reactive water layer. BCFR5.1 was washed several times with warm water till it was free from formaldehyde and boric acide odour, and dried at 60 ^{o}C in vacuo finally the solid BCFR5.1 was obtained.

Commercial cyclohexanone formaldehyde resin was modified with boric acid using three molar ratios: (ketone/ Formaldehyde/ boric acide) (1/2/0.5), (1/2/0.75), (1/2/1), (1/2/1.5) and (1/2/3) of the cyclohexanone, formaldehyde and boric acide, respectively, to give BCFR1, BCFR2, BCFR3, BCFR4 and BCFR5.

3.3.2 3-(Triethoxysilyl)Propyl Isocyanate Modified Cyclohexanone Formaldehyde Resin

Into an one-necked flask equipped with a stirrer, and a condenser were added 2,5 g cyclohexanone formaldehyde resin and 1,25 ml 3-(triethoxysilyl) propyl isocyanate were dissolved in dry dicloromethane (30 mL) under a nitrogen atmosphere at 50 ^{o}C. DBTDL (1- 2 drops) was added to the reaction mixture and the resulting solution refluxed for 2 h. Upon completion of the reaction mixture was poured into hexane, and precipitate was filtered and dried at 60 ^{o}C under vacuo. The molar ratios of diisoyanate to ketonic resin was taken to: (resin/3-(triethoxysilyl)propyl isocyanate) (1/0.25), (1/0.5), (1/1.25) of the resin and 3-(triethoxysilyl)propyl isocyanate) respectively, to give CFR-TEOS1, CFR-TEOS2 and CFR-TEOS3.

3.4 Analysis

Following tests; Infrared Analysis (IR), Nuclear Magnetic Resonance Spectroscopy (NMR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC).

3.4.1 Infrared Analysis (IR)

Infrared spectroscopy (IR) is used to analyse compounds in which the absorption of infrared radiation triggers vibrations and rotations in the molecules. The ıınfrared radiation is in the range from 5000 to 200 cm^{-1}.

Vibrations or rotation which bring about a change in the bonds lenghts and bond angles, however, can only be initiated if the atoms in the molecule possess different electronegativities, such that dipole moments are present. The vibration initiated must lead to periodic change in the dipole moment in order to be IR-active.

Molecular vibrations in which bond lenghts change are termed valency vibrations; where bond angles change, the term used in deformation vibrations.

The position of the bands in the spectrum is determined by the masses of the participating atoms and the bonding strenghts. The range which is of interest for polymers and resins is between 4000 and 400cm^{-1}.

The Fourier transform (FT) technique offers the advantages of high speed in recording the spectra, with a substantially improved signal-to-noise ratio [111]. The core of an FT-IR spectrometer is a Michelson interferometer, which consist of a so-called beam splitter, a movable mirror and a fixed mirror. At the beam splitter, the radiation of the IR source is divided. One half is reflected on to the movable mirror, while the other is incident on the fixed mirror. At the mirrors the radiation is reflected, and the two halves meet again at the beam splitter, where interference occurs. Depending on the optical path difference, which is predetermined by the movement of the free mirror, either destructive or constructive interference takes place, so that the entire wavelength range is available quasi-simultaneously. The radiation then passes through the sample and reaches the detector. The detector records a superposition of all wavelengths present in the spectrum in the interferogram. By a mathematical operation, Fourier transformation, a spectrum is obtained from the interferogram.

A review article by Putziget al. [112] gives an overview of currient literature and describes new techniques and special applications. Some of the special techniques will be dealt with briefly below, since they are employed inter alia to analyse resins used in coatings.

In photoacoustic FT-IR spectroscopy, the sample is irradiated with modulated infrared lights. The intensity decreases exponentially in the course of passage through a material. The absorbed energy is converted into heat, which flows to the surface of the sample. The efficiency of heat transfer is determined by the thermal diffusion coefficient of the sample and by the modulation frequency of the irradiated infrared light. In other words, a defined quantity of heat is transported periodically from the inside of the sample to the surface, and manifests itself in the photoacoustic intensity. If there is a change in the thermal properties of the sample during recording, because of crosslinking for example, this can be monitored by way of the photoacoustic signal [113].

Using ATR (attenuated total reflection) spectroscopy it is possible to analyse materials wit low permeability to radiation, such as pigmented coating materials, since this technique involves IR analysis of the surface. The sample is brought into contact with the surface of a reflection element and the infrared light is radiated onto the interface. The reflection element consists of a crystal or mixed crystal which must have a sufficently high refractive index, in comparison with the sample, to ensure total reflection. In addition, it must be permeable to infrared radiation. The angle of incidence of the IR radiation is then chosen to be greater than the critical angle of the total reflection. The radiation reflected at the interfaces of the reflection element passes to a minor extent into the optically less dense medium, i.e the sample, covers a short path length and then goes back into the optically more dense medium of the crystal. If the sample absorbs part of the radiation, this leads to an attenuation

of the total reflection. In this way a reflection spectrum of the sample is obtained which is similar to the transmission spectrum. The position and shape of the bands are virtually identical to the transmission spectrum of the same substance, provided the refractive index of the crystal is greater than that of the sample over the entire spectral region.

3.4.2 Nuclear Magnetic Resonance Analysis (NMR)

Nuclear magnetic resonance (NMR) is a property that magnetic nuclei have in a magnetic field and applied electromagnetic (EM) pulse or pulses, which cause the nuclei to absorb energy from the EM pulse and radiate this energy back out. The energy radiated back out is at a spesific resonance frequency which depends on the strenght of the magnetic field and other factors. This allows the observations of spesific quantum mechanical magnetic properties of an atomic nucleus. Many types of information can be obtain from a NMR spectrum. Much like using IR to identify functional groups, analysis of a NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR. All stable nuclies that contain an odd number of protons other words a nonsero spin, while all nuclides with even numbers of both have spin 0. The most commonly studied nuclei are ^{1}H and ^{13}C, although nuclei from isotopes of many other elements (e.g. ^{2}H, ^{10}B, ^{11}B, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{23}Na, ^{29}Si, ^{31}P, ^{35}CI, ^{113}Cd, ^{129}Xe, ^{195}Pt) are studied by high-field NMR spectroscopy as well. When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field. The magnetic field at the nucleus is therefore generally less than the applied field by a fraction.

The electron density around each nucleus in a molecule varies according to the types of nuclei and bond in the molecule. The opposing field and therefore the effective field at each nucleus will vary. This is called the chemical phenomenon. The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standart, relative to the standart.

In this study, NMR analysis were used to support characterization of the materials beside IR analysis.

3.4.3 Thermogravimetric Analysis (TGA)

Thermogaravimetry has become a general method for comparing the thermal stability of polymers. TGA measures the amount and rate of change in the weight of a material as a function temperature or time in a controlled atmosphere[114]. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000 ^{o}C. the technique can

characterize materials that exhibit weigt loss or gain due to decomposition, oxidation, or dehydration. In comparing thermal stability, it should be remembered that TGA measurements only record the loss of volatile fragments of polymers, caused by decomposition. TGA cannot detect any chemical changes or degradation of properties caused by cross-linking[115].

In this study, samoles heated from 10 ^{o}C to 900 ^{o}C at an applied heating rate of 20 ^{o}C/ min. During the heating period, the weight loss and temperature difference were recorded as a function of temperature.

3.4.4 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light, specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

3.4.5 Differential Scanning Calorimetry (DSC)

With differential scanning calorimetry (DSC), a sample and a reference are heated separately in a measurement cell in metal boats. The heating rate for the reference is kept constant. By means of a control unit, the temperature of the sample is regulated such that there is no temperature difference between sample and reference.

In transformation phenomena, such as, for example, melting, boiling, crystallization or solidification, endothermic or exothermic heat effects ocur. The change in the heating energy required maintain the sample boat at the same temperatures is recorded. A recorder plots in differential thermal energy as heat flux.

In the case of resins for coatings, which are prodominantly amorphous, DSC is used primarily to determine the glass transition temperature (Tg). The glass transition is a second-order transition which appears in the thermogram as a step in the spesific heat $c_{p.}$ The glass transition stage is defined by the centre of the c_p step. If the sample undergoes defined heating from a low to a higher temperature, then in the glass transition the sample changes from a brittle, glass-like state to a rubber-like viscoelastic.

4. RESULTS AND DISCUSSION

4.1 Boric Acid Modified Cyclohexanone Formaldeyde Resin (BCFR)

We prepared five boric acide modified cyclohexanone formaldehyde resin by esterification of boric acide with methylol of cyclohexanone formaldehyde resin by one step. (Figure 4.1)

Formation of boric acide modified cyclohexanone formaldehyde resins(BCFR) from cyclohexanone, formaldehyde and boric acid is shown in scheme 1. BCFRs were synthesised in a basic media with cyclohexanone/formaldehyde/boric acid mol ratios of 1/2/0.5 (BCFR1), 1/2/0.75(BCFR2), 1/2/1 (BCFR3), 1/2/1.5 (BCFR4), 1/2/3 (BCFR5). These resins, which act as boron-reagents, are very soluble in organic solvents such as acetone, chloroform, alchol, dimethyl formamide, which make the reaction with hydroxyl groups easier (Table 4.1).

Figure 4.1 : Boric acid modified cyclohexanone formaldeyde resin (BCFR).

Table 4.1: Physical Properties of Resins

Resins	Mol Ratio	Solubility					
	Cyclohexanone/H3BO3/Formaldehyde	THF	DMSO	$CHCl_3$	CH_3OH	$(CH_3)_2CO$	DMF
CFR	1 / 0 / 2	sl	s	s	sl	sl	sl
BCFR1	1 / 0.5 / 2	s	s	s	sl	sl	s
BCFR2	1 / 0.75 / 2	s	s	s	sl	s	s
BCFR3	1 / 1 / 2	s	s	s	sl	s	s
BCFR4	1 / 1.5 / 2	s	s	s	sl	s	s
BCFR5	1 /3 / 2	s	s	s	sl	s	s
BCFR5.1	Water layer of BCFR5	i	i	i	i	i	i

s: soluble

sl: slightly soluble

i:insoluble

The structure of the BCFR was identified by ATR-FTIR spectroscopy. Spectra of BCFR1, BCFR2, BCFR3, and BCFR5 are outlined in Figure 4.1. Infrared spectra of all resins showed strong bands of absorption at 3430-3320 cm^{-1} includes both stretching vibrations of –OH group of methylols and –B-OH group. Strong bands of absorption characteristic for the carbonyl linkage and the borate appeared at 1715-1640 cm^{-1} assigned to C═O stretching vibration, the borate B–O at 1350 cm^{-1}. Aliphatic hydrogens of methylene bridges between bor and carbon are observed as peaks at 2930 cm^{-1} and 1450 cm^{-1}, methylol group at 1040-1060 cm^{-1}, ether linkage C-O at 1130-1140 cm^{-1} those are similar to methylene bridges of boric acide modified cyclohexanone-formaldehyde resins(Figure 4.2, Line 1-V). The FTIR spectra details are shown in Table 4.2.

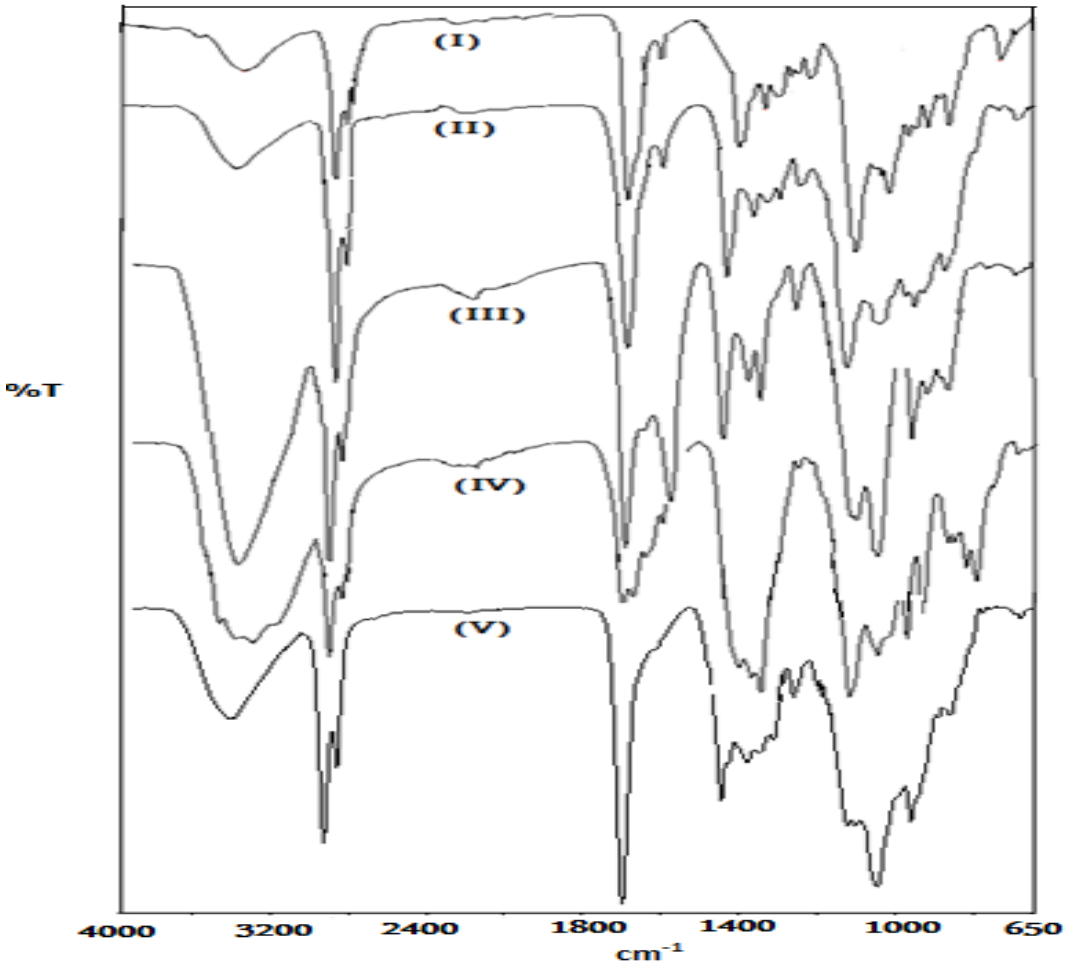

Figure 4.2 : FTIR spectra of I) BCFR1, II) BCFR2, III) BCFR3, IV) BCFR4, V) BCFR5.

Table 4.2 : FT-IR results of BCFRs

	-O-H	-CH_2-	-C=O	-CH_2-	-B-O, -CH_2-O	-C-O	-C-O-C	-C-OH
CFR	3430	2933 2860	1704	1449	1378	1261	1140	1060
BCFR1%0.5	3422	2928	1715	1446	1375	1259	1140	1047
BCFR2%0.75	3419	2927	1708	1447	1377	1255	1138	1052
BCFR3 %1	3387	2927	1698	1448	1351	1260	1135	1053
BCFR4 %1.5	3320	2928	1713	1475	1382	1265	1139	1042
BCFR5 %3	3408	2928	1696	1447	1380	1261	1130	1049
BCFR5.1 %3	3360 3327	2989	1640	1407	1351	1251	1090	944

BCFR5.1 was synthesized by one step condensation reaction, at 90˚C for 2 h. BCFR5.1 was achieved by the reaction of the unreacted cyclohexanone, boric acid and formaldehyde. The structure of the BCFR5.1 was identified by ATR-FTIR spectroscopy. The FTIR spectra of BCFR5 and BCFR5.1 (line I and II) were given in Figures 3. As well as typical peaks of cyclohexanone groups disapperead at 1695 cm^{-1} , the absorption peak of borate B–O linkage 1350 cm^{-1} increased(Figure 4.2, Line II). So, BCFR5.1 did not contain cyclohexanone ring. BCFR5.1 has not solubility properties (Table4.1).

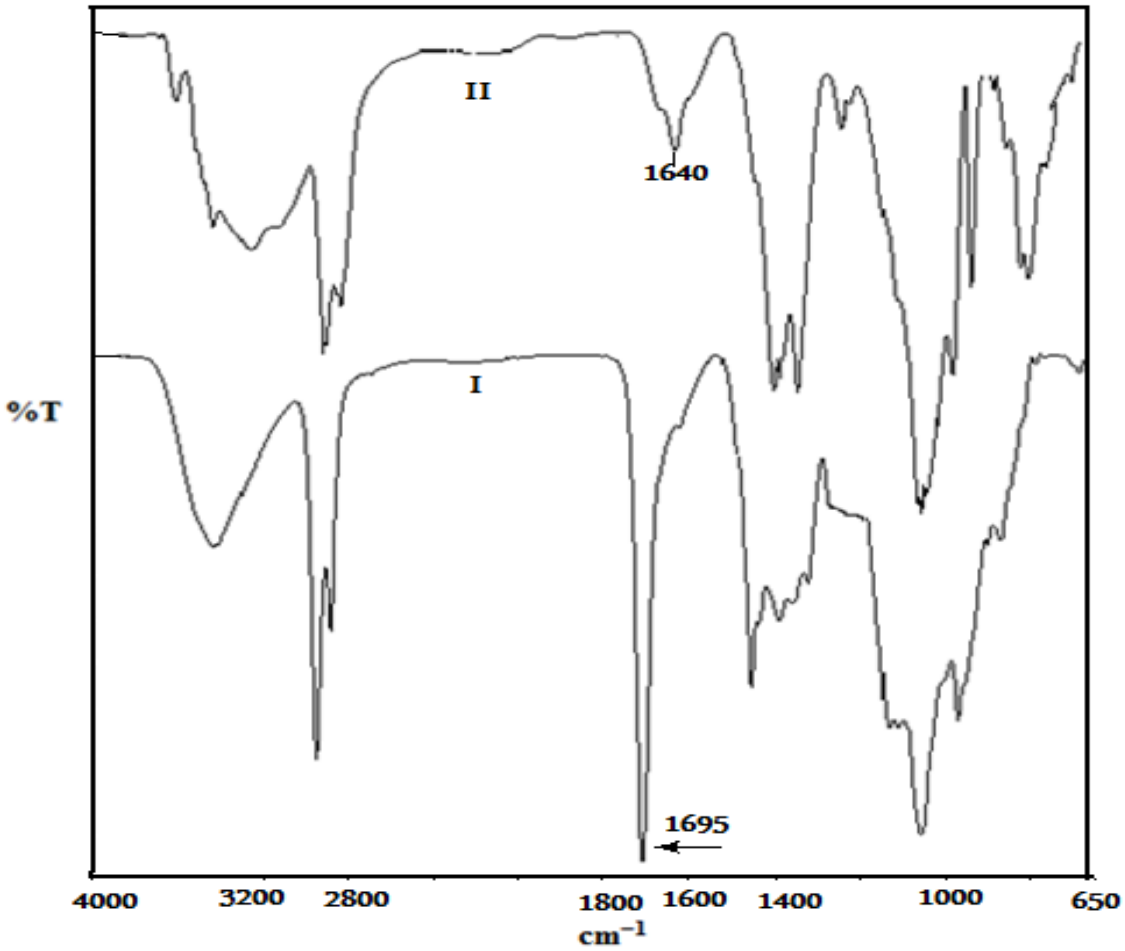

Figure 4.3 : FTIR spectra of I) BCFR5, II) BCFR5.1.

^{1}H-NMR spectra of the BCFRs confirm also the purposed structural formulas in Figure 4.4. The ^{1}H-NMR spectra of BCFR1, BCFR2 and BCFR5 showed signals between 3-4.5 ppm were due to methylene protons of methylols and ether linkage protons, and 1–3 ppm due to aliphatic hydrogens of cyclohexanone (Figure 4.4).

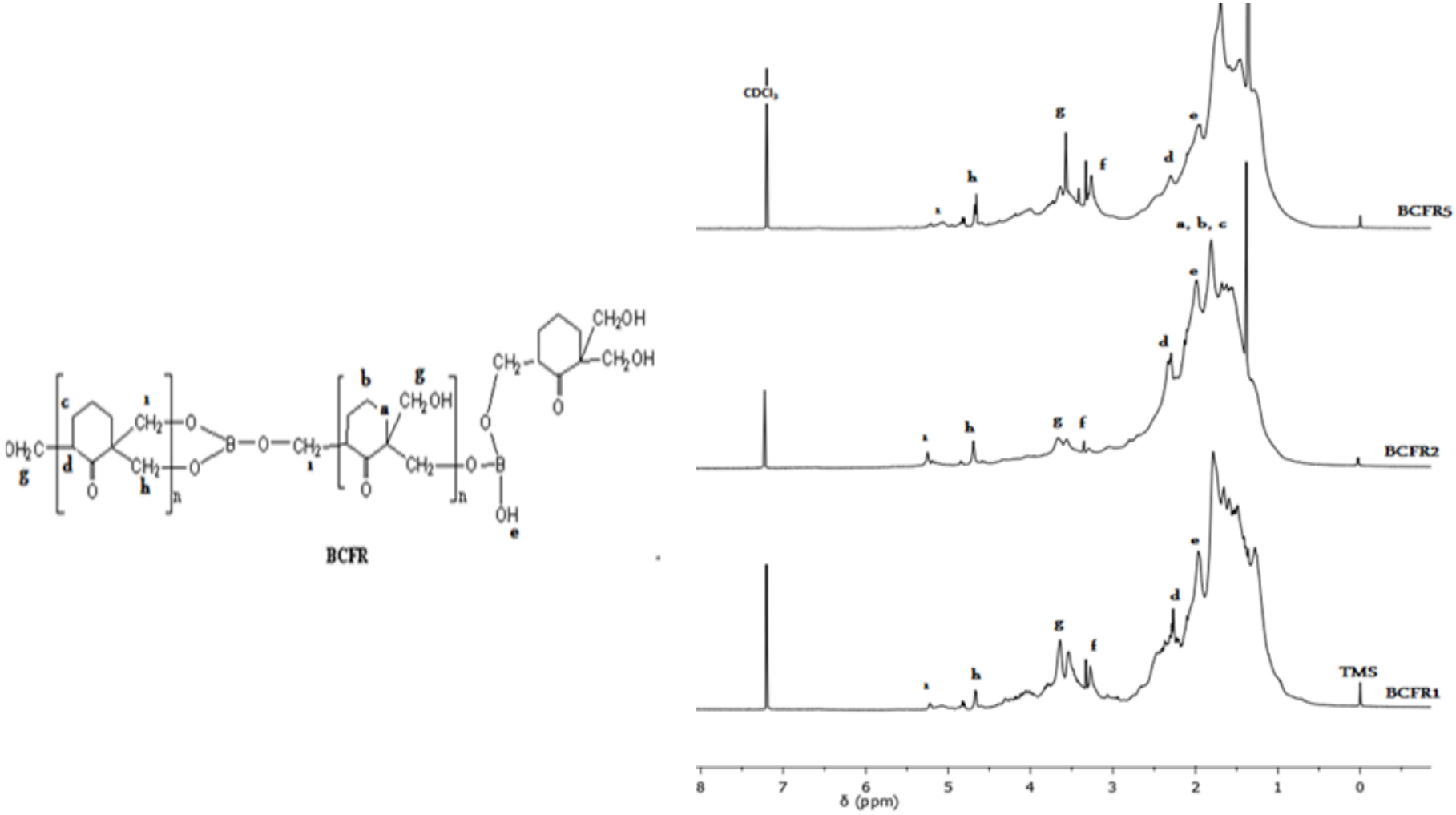

Figure 4.4: ^{1}H-NMR spectra of the BCFRs

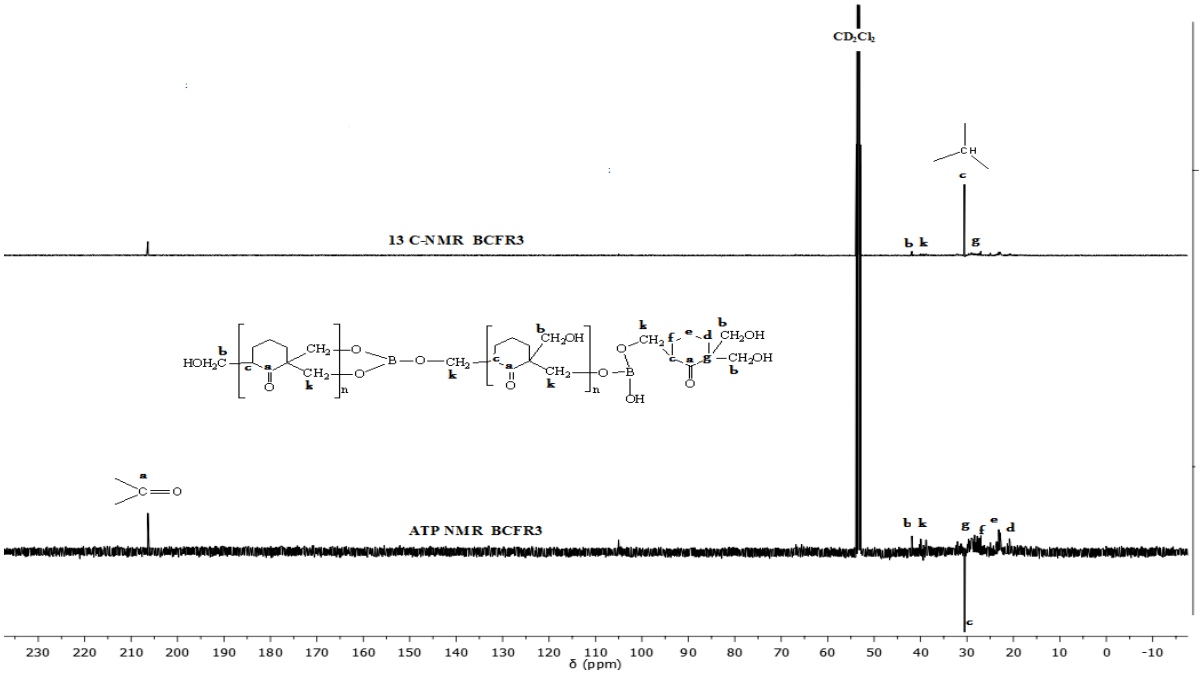

Figure 4.5: ^{13}C NMR spectra of BCFR3.

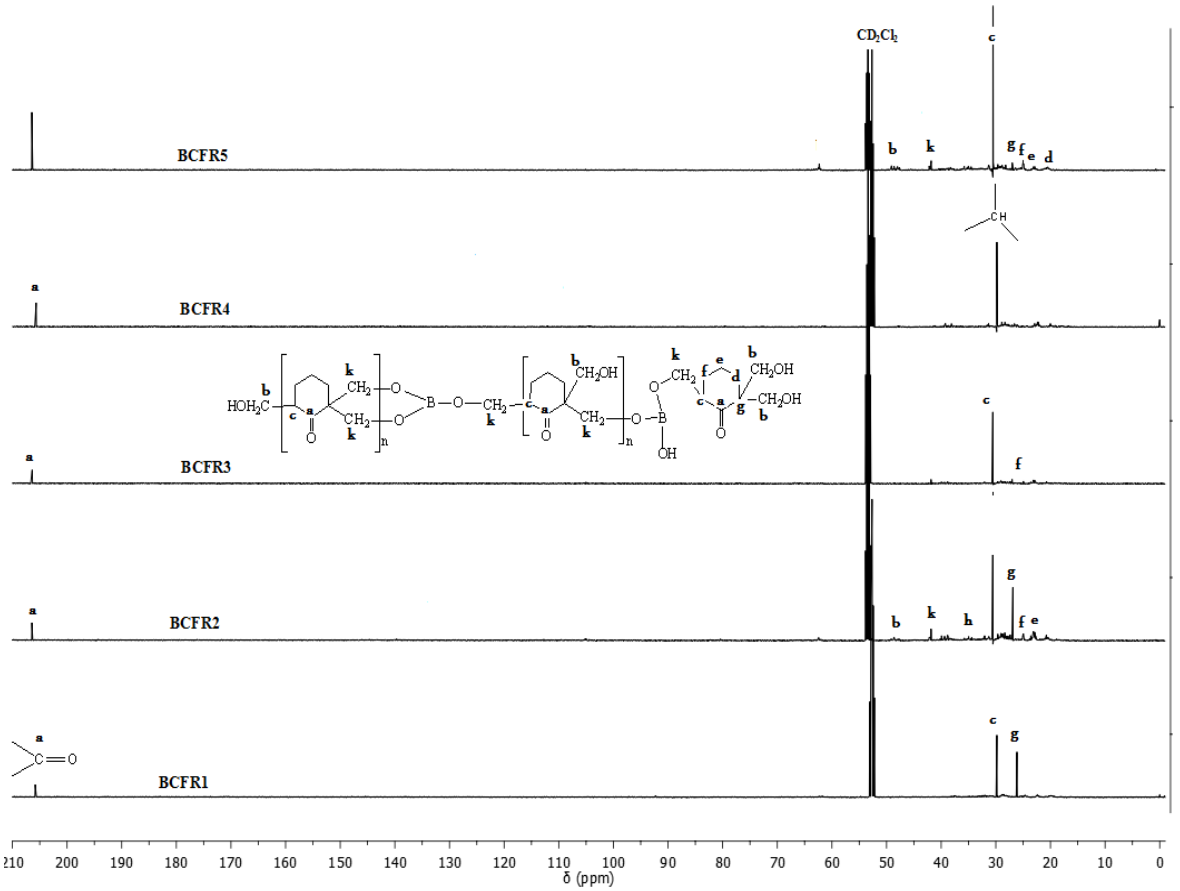

Figure 4.6: ^{13}C NMR spectra of BCFRs.

^{13}C-NMR spectra of the BCFRs and BCFR3 confirm also the purposed structural formulas in Figure 4.5and Figure 4.6. The ^{13}C NMR and APT (Attached Proton Test) spectra ofBCFR3 (Figure 4.6) showed no peaks of quarternary carbon atoms between 20–30 ppm and no peaks of methyl carbon atoms below20 ppm. Small peaks at 42 and 40 ppm were due to methylol bond carbons each having two hydrogen. The peak at 206 ppm was due to carbonyl carbon and the peak at 30 ppm was due to CH of cyclohexanone rings each having one hydrogen.

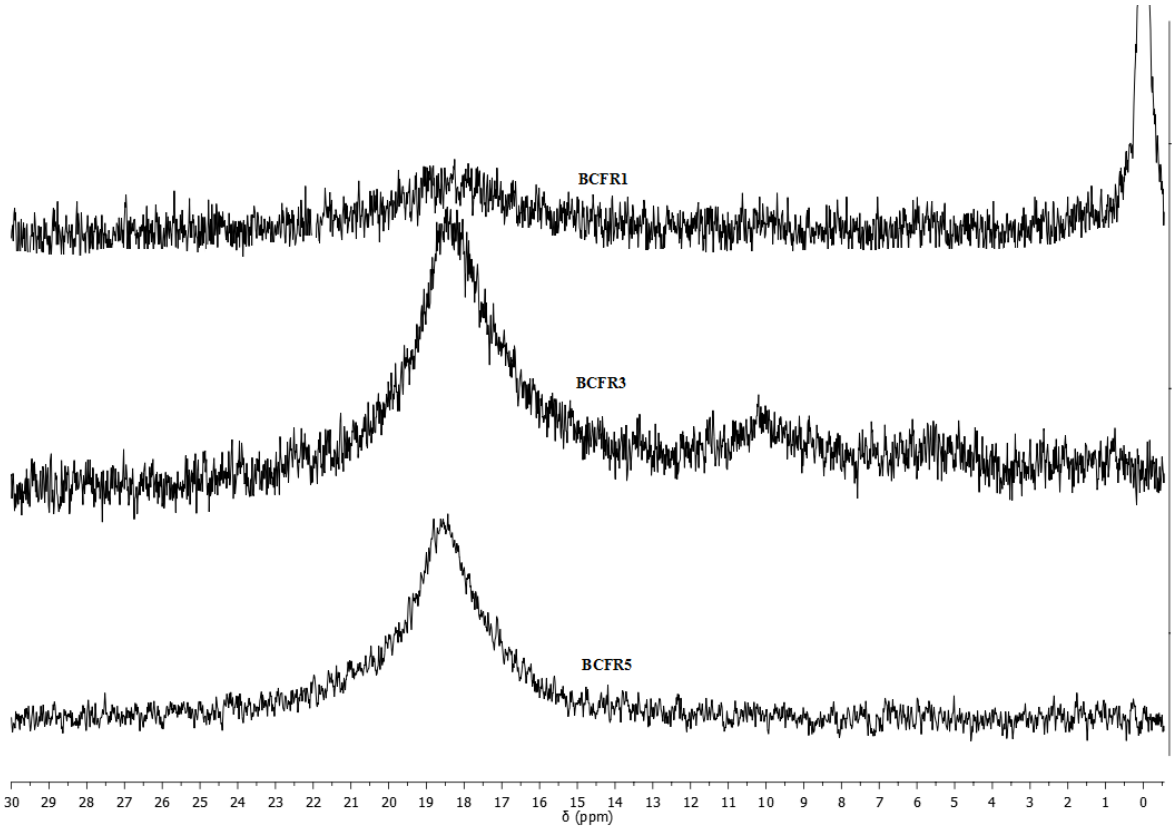

Figure 4.7: Bor NMR spectra of BCFR1, BCFR2, BCFR3

Bor NMR spectra of the BCFR1, BCFR3 and BCFR5 confirm also the purposed structural formulas in Figure 4.7. When we look at at the boron bond, we are seeing three connected to Bor bond. The Bor-NMR spectra of BCFR1, BCFR2 and BCFR5 showed signals between 18-19 ppm were due to bor .

Thermal behaviour of resins were examined by differential scanning calorimeter in the range of 20- 300 °C. The softening points higher than that of the CF-R by about 26-143 °C(Table 4.3). In order to prepare TGA samples, the boron-containing cyclohexanone-formaldehyde resins were dried at 100 °C for 3 h. A 5mg powder sample of the cured resin was subjected to TGA analysis, and heated at linear heating rate of 10 °C (Table 4.3). Degradation was carried out in a static air atmosphere to the maximum temperature of 900 °C. The weight loss of the resin was calculated, the weight loss rates are shown as a function of temperature in Figure 4. 8 and Table 4.3.

Table 4.3 : DSC and TGA results for BCFRs

Samples	Tg (^oC) [a]	Tm (^oC) [a]	T50% (^oC) [b]	Residue at 900^oC (weight %) [b]
CFR*	-	115	367.8	3.7
BCFR1	83	258	370	6.23
BCFR2	110	234	395	6.89
BCFR3	-	228	402	7.66
BCFR4	106	180	408	18.23
BCFR5	100	136	431	29.64
BCFR5.1	60	146	-	54.54

a: Determined by DSC

b: Determined by TGA

As shown in Figure 4.8 and Table 4.3, the weight loss rates of common cyclohexanone formaldehyde resins were higher than that of boron-containing cyclohexanone-formaldehyde resin.

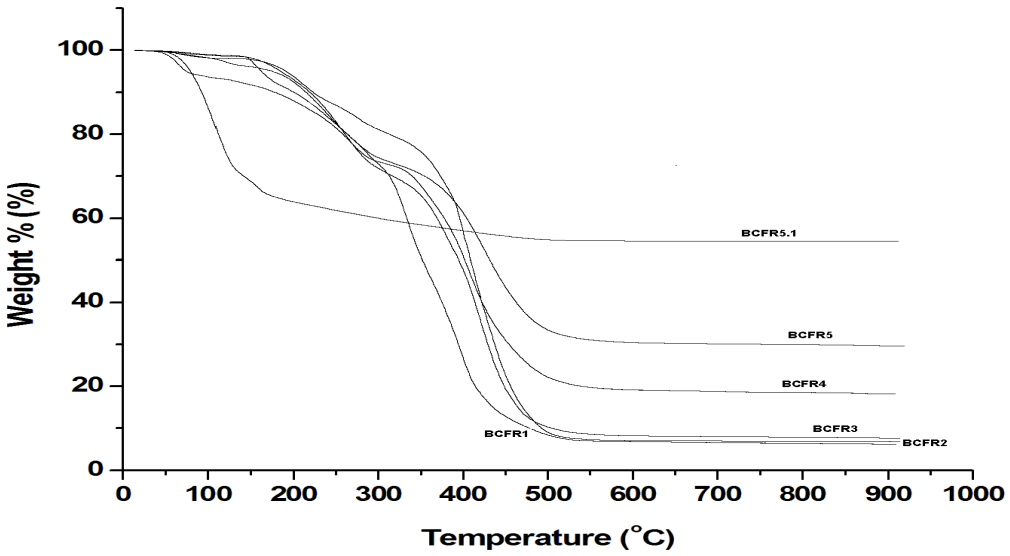

Figure 4.8 : TGA termograms of BCFRs.

The SEM pictures of BCFRs obtained chemical polymerization show (Figure 4.9) the differences on the roughness of the BCFR1, BCFR5 and BCFR5.1 surfaces. This might be due to the different bounded bor. ESEM micrograph for BCFRs shows continuous homogeneous of the resin suitable for usage as a coating material.

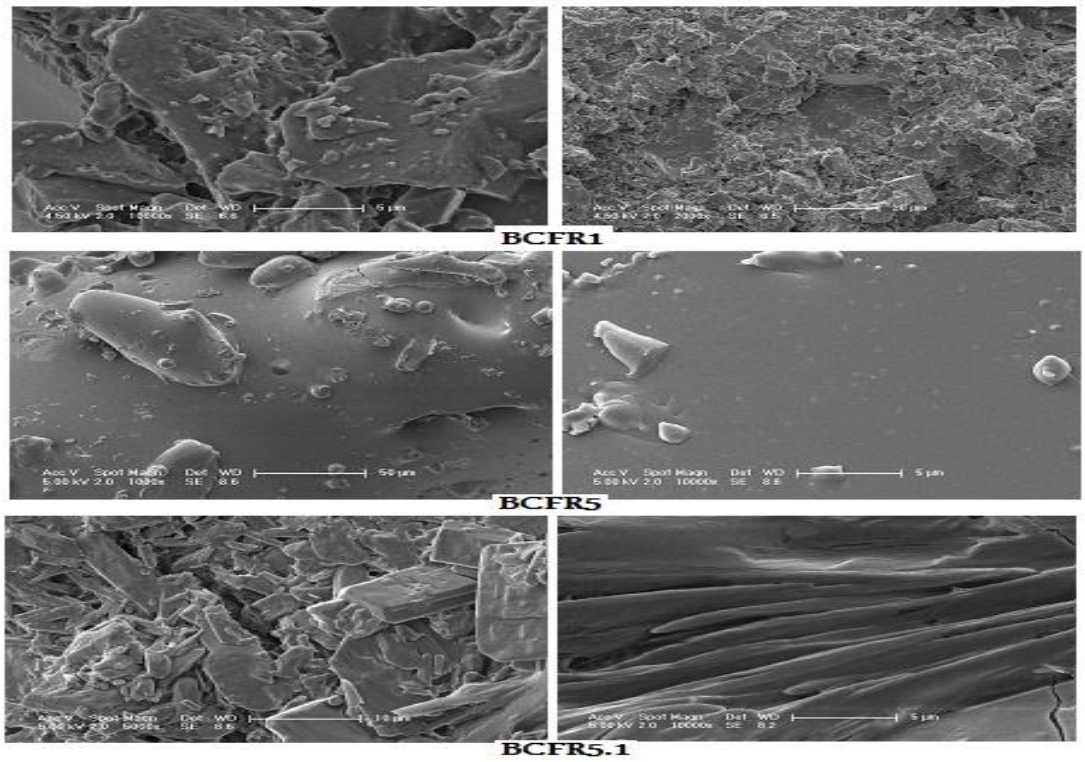

Figure 4.9 : SEM micrograps of BCFR1, BCFR5, BCFR5.1

4.2 3-(Triethoxysilyl)Propyl Isocyanate Modified Cyclohexanone Formaldehyde Resin

We prepared three 3-(triethoxysilyl) propyl isocyanate modified cyclohexanone formaldehyde resin. Formation of 3-(triethoxysilyl) propyl isocyanate modified cyclohexanone formaldehyde resin is shown in Figure 4.10. The molar ratios of diisoyanate to ketonic resin was taken to: (resin/3-(triethoxysilyl)propyl isocyanate) (1/0.25), (1/0.5), (1/1.25) of the resin and 3-(triethoxysilyl)propyl isocyanate) respectively, to give CFR-TEOS1, CFR-TEOS2 and CFR-TEOS3.

Figure 4.10: Formation of cyclohexanone formaldehyde resin- 3-(triethoxysilyl)propyl isocyanate (CFR-TEOS).

Table 4.4: Physical Properties of CFR-TEOS

Resins	Mol Ratio	Solubility					
	resin/3(triethoxysilyl) propyl isocyanate	**THF**	**DMSO**	**$CHCl_3$**	**CH_3OH**	**$(CH_3)_2CO$**	**DMF**
CFR	1 / 0	s	s	s	s	s	s
CFR-TEOS1	1 / 0.25	s	s	s	s	s	s
CFR-TEOS2	1 / 0.5	s	s	s	s	s	s
CFR-TEOS3	1 / 1.25	s	s	s	s	s	s

s: soluble

The structure of the CFR-TEOS was identified by ATR-FTIR spectroscopy. Spectra of CFR-TEOS1, CFR-TEOS2 and CFR-TEOS3 are outlined in Figure 4.8. The CFR-TEOS The FTIR spectra details are shown in Table 4.5.

3-(triethoxysilyl) propyl isocyanate modified cyclohexanone formaldehyde resin were characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) analysis. The FTIR spectra of these CFR-TEOS modified resins showed peaks due to 3-(triethoxysilyl) propyl isocyanate (TEOS) and ketonic resins. In the FTIR spectra of CFR-TEOS, the peaks at 3360 and 3390 cm^{-1} were due to the -OH groups and N-H groups of the resins (Figure 4.11). These OH absorptionpeaks decrease at the NCO reaction with 3-(triethoxysilyl) propyl isocyanate(TEOS), (Figure 4.11). The broadened peak at 1700-1710cm^{-1} was due to carbonyl groups of both the ketonic resins and the carbamate group. The peaks at 980-987cm^{-1} and 1040-1067cm^{-1} due to Si-O bonds of Si-O-CH_2 and at 700-770cm^{-1} due to Si-CH_2 groups were present.

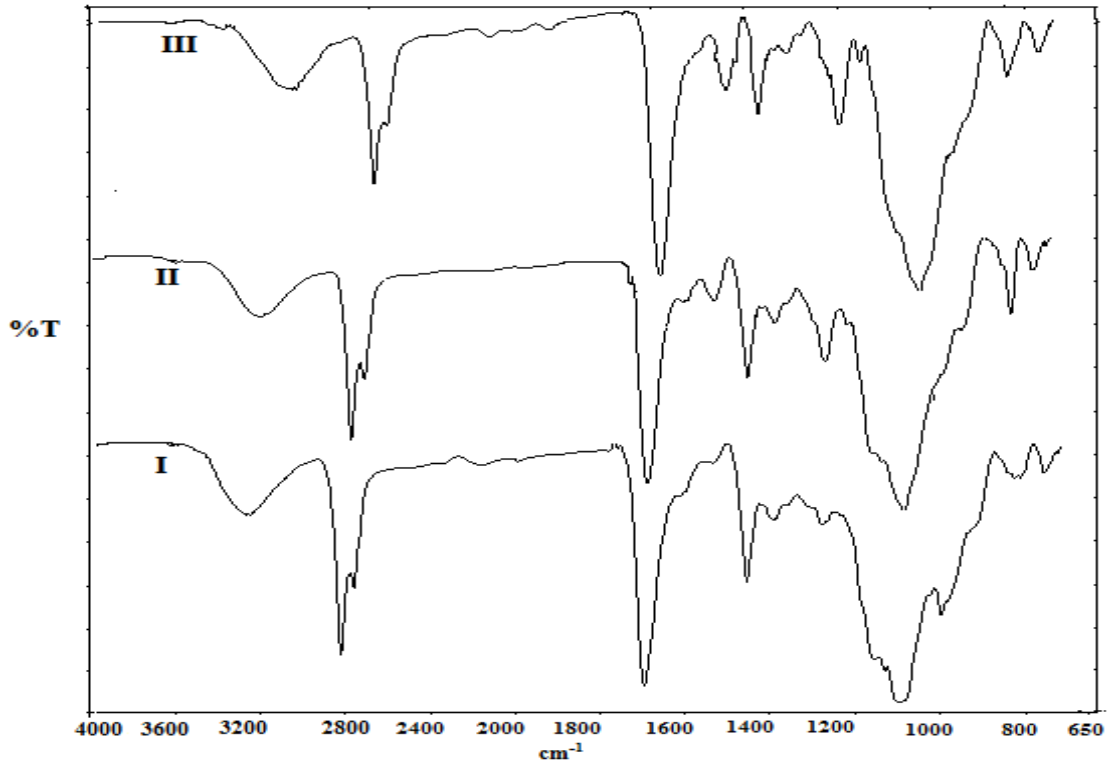

Figure 4.11 : FTIR spectra of I) CFR-TEOS1, II) CFR-TEOS2, III) CFR-TEOS3.

Table 4.5 : FT-IR results of CFR-TEOSs

	-O-H	-CH_2	-C=O	-N-H	-CH_2-	-C-O	Si-O-CH_2	Si-O	Si-CH_2
CFR-TEOS1	3386	2930	1710	1545	1447	1250	1067	982	770, 710
CFR-TEOS2	3389	2929	1701	1550	1447	1251	1051	980	755, 705
CFR-TEOS3	3363	2928	1700	1555	1445	1247	1040	987	760, 700

^{1}H-NMR spectra were reported from the CD_2CI_2 solution with a TMS internal standart. The ^{1}H-NMR spectra of the CFR-TEOSs were shown in Figure 4.12. The 1H-NMR spectra of CFTEOS1, CFR-TEOS2 and CFR-TEOS3 showed signals between 3-4.5 ppm were due to methylene protons (g,h,j,i,k) of methylols and ether linkage protons, 1.8–2.5 ppm due to aliphatic hydrogens of cyclohexanone(d) and 8.03 ppm due to N-H protons of carbamate groups. (Figure4.12).

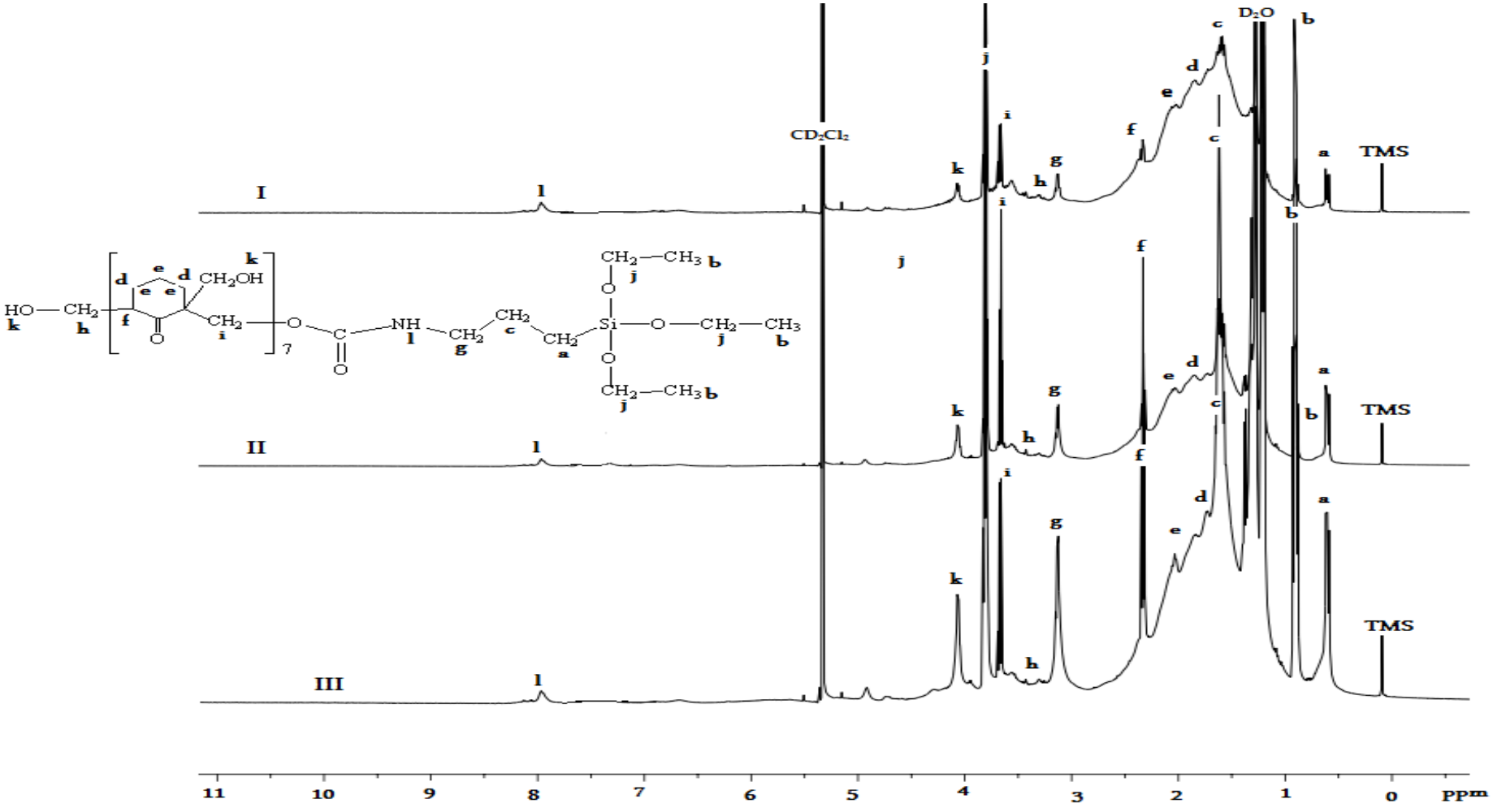

Figure 4.12 : ^{1}H-NMR spectra of the CFR-TEOSs.

Thermal behaviour of resins were examined by differential scanning calorimeter in the range of 20- 300 °C. The softening points higher than that of the CFR by about 26-143 °C(Table 4.6). In order to prepare TGA samples, the 3-(triethoxysilyl) propyl isocyanate modified cyclohexanone formaldehyde resins were dried at 100 °C for 3 h. A 5mg powder sample of the cured resin was subjected to TGA analysis, and heated at linear heating rate of 10 °C (Table 4.6). Degradation was carried out in a static air atmosphere to the maximum temperature of 900 °C. The weight loss of the resin was calculated, the weight loss rates are shown as a function of temperature in Table 4.6.

Table 4.6 : DSC and TGA results for CFR-TEOSs

Samples	Tg (^oC) [a]	Tm (^oC) [a]	T50% (^oC) [b]	Residue at 900^oC (weight %) [b]
CFR*	-	115	367.8	3.7
CFR-TEOS1	46,5-140,5	171,5		
CFR-TEOS2	100.5	110-124,5		
CFR-TEOS3	47	-	405	18.4

a: Determined by DSC

b: Determined by TGA

As shown in Table 4.6, the weight loss rates of common cyclohexanone formaldehyde resins were higher than that of 3-(triethoxysilyl) propyl isocyanate modified cyclohexanone formaldehyde resins.

The SEM pictures of CFR-TEOSs obtained chemical polymerization show (Figure 4.13) the differences on the roughness of the CFR-TEOS1 and CFR-TEOS2 surfaces. This might be due to the different bounded bor. ESEM micrograph for CFR-TEOSs shows continuous homogeneous of the resin suitable for usage as a coating material.

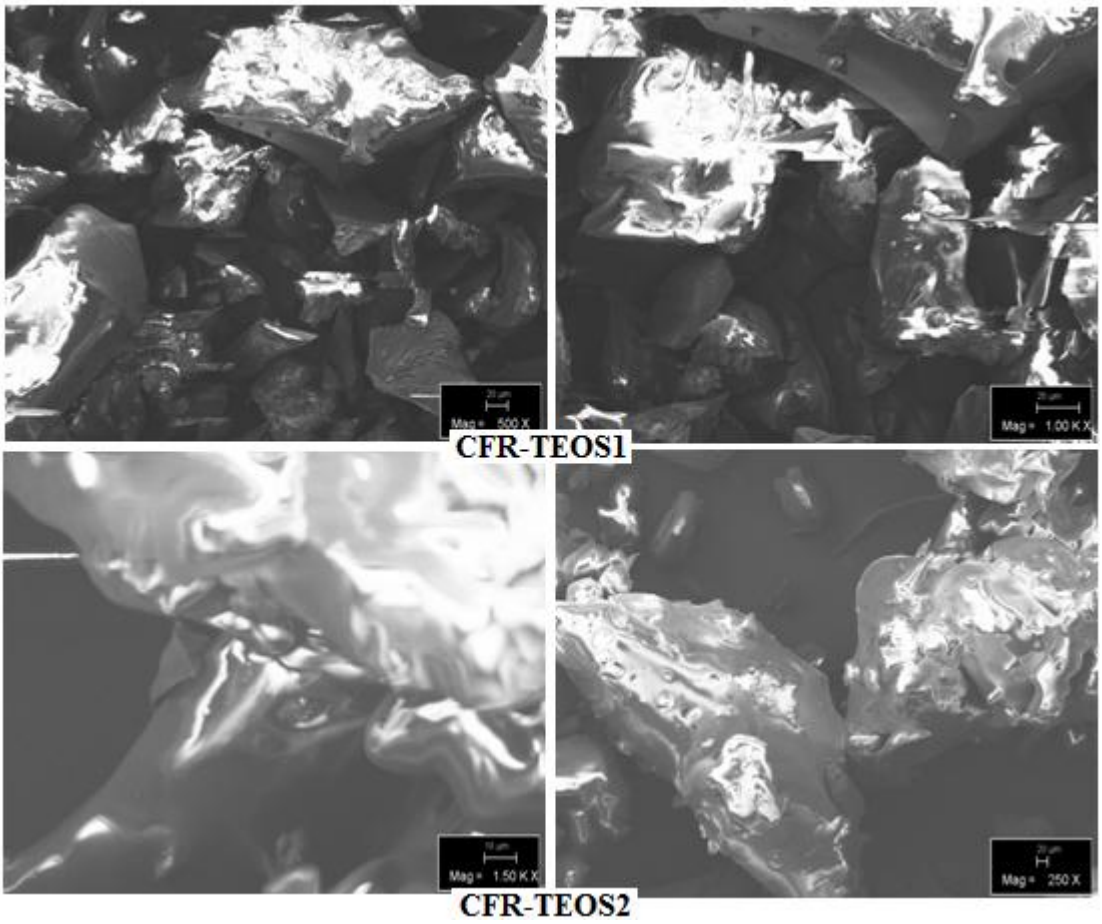

Figure 4.13 : SEM micrograps of CFR-TEOS1, CFR-TEOS2.

CONCLUSION

In this study, a new BCFR were synthesized. In the boron-containing cyclohexanone-formaldehyde resins formed from *in situ* modified method, the methylene borate linkage was mainly formed during the synthesis process. The borate linkage had better heat resistance than ether linkage, so the boron-containing ketonic resin had good thermal stability. These resins have higher T*g* and T*m* value than CFR alone and they also have thermal properties. Resulting boran containing cyclohexanone formaldehyde resins may provide an opportunity for a new breakthrough in the area of polymeric materials for advanced technologies. It can be used as reinforced laminate, heat-resistant adhesives and coating materials.

A new 3-(triethoxysilyl) propyl isocyanate modified cyclohexanone formaldehyde resins were synthesized by reaction of hydroxyl group with TEOS. These resins have higher T*g* and T*m* value than CFR alone and they also have thermal properties.

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CURRICULUM VITAE

Name Surname: Pelin DİNÇER

Place and Date of Birth: İstanbul 27.02.1987

Address: Ümraniye/İstanbul

E-Mail: pelindincer@hotmail.com

B.Sc.: Kocaeli University

M.Sc.: İstanbul Technical University

PUBLICATIONS/PRESENTATIONS ON THE THESIS

KIZILCAN, N., DİNÇER, P.,(2011). *Synthesis of Boron Containing Cyclohexanone Formaldehyde Resin*, *Eurofiller Congress*, August, 2011, Dressden, Germany.