Polymerization and Kinetic Studies of Ketonic Resin Synthesized by Environment–Friendly Method

THESIS

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by

APPALA NAIDU UTTARAVALLI

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Under the Supervision of

Prof. Srikanta Dinda

BITS Pilani
Pilani | Dubai | Goa | Hyderabad

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI
Hyderabad Campus
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Dedicated to my parents …

Birla Institute of Technology & Science, Pilani
Hyderabad Campus

CERTIFICATE

This is to certify that the thesis entitled "**Polymerization and Kinetic Studies of Ketonic Resin Synthesized by Environment–Friendly Method**" and submitted by **APPALA NAIDU UTTARAVALLI**, ID. No. **2013PHXF0005H** for award of Ph.D. of the institute embodies original work done by him under my supervision.

Signature of the supervisor : Sdinda

Name in capital letters : **Prof. SRIKANTA DINDA**

Designation : Associate Professor

Date : 14th June 2018

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Birla Institute of Technology and Science – Pilani,	***Appala Naidu Uttaravalli***
Hyderabad Campus, Hyderabad, India	***June 2018***

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Abstract

Polymerization and Kinetic Studies of Ketonic Resin Synthesized by Environment–Friendly Method

In recent years, sustainable development has become the focus of research throughout the world. It includes, among many other things, development of environment–friendly processes and products. The present research was undertaken on the same line, that is, to develop a greener product from environment–friendly raw materials. The present study deals with the development of environment–friendly product, namely, synthetic ketonic resin for paint and coating applications, from relatively less hazardous raw materials.

Based on the literature search on ketonic resins, it was observed that most of the published articles and patents have dealt with the dimerization reaction of alkyl cyclohexanone/cyclohexanone. Couple of articles is available in the literature on oligomerization or polymerization of cyclohexanone/ alkyl cyclohexanone with aldehyde (mainly formaldehyde) to obtain a ketone–aldehyde resin. As per the available literature, BASF Germany is the sole manufacturer of ketonic resin product of alkylated cyclohexanone / cyclohexanone.

In tune with this, ketonic material such as cyclohexanone was considered as model compound to prepare the ketonic resin. Cyclohexanone offers itself as an excellent candidate in the preparation of ketonic resin. Cyclohexanone is not considered as a carcinogenic material and thereby it has a potential to replace relatively more hazardous raw materials, such as, phenol and formaldehyde.

The present research deals with the development of synthetic ketonic resin from cyclic ketonic monomers such as cyclohexanone, methylcyclohexanone, and cyclopentanone using self–polymerization technique in presence of base catalyst. Two types of reactor systems namely, open system (reactions under atmospheric pressure), and closed system (reactions under autogenously developed pressure) studies were conducted to develop the ketonic resins. The

effectiveness of NaOH and KOH as base catalysts has been investigated. The entire study has been segregated into various chapters and the highlights of the chapters are as follows:

The self−polymerization reactions of cyclohexanone (CH) were carried out using open system (reactions under atmospheric pressure) in presence of KOH as a base catalyst. The reactions were carried out using a 250 mL capacity three–neck glass reactor. To investigate the effects of reaction parameters on cyclohexanone conversion and physico–chemical properties of the final products, reaction time was varied from 7 to 20 hrs, catalyst loading (expressed as 'A/K ratio') was varied between 0.05 to 0.2, and temperature was varied from 90 to 140 °C. It has been observed that the degree of polymerization of cyclohexanone depends on alkali concentration, reaction temperature, and reaction time. The degree of polymerization increased with the increase of catalyst loading and reaction time. Reaction temperature greater than 110 °C shows some detrimental effect on monomer conversion and product properties. Viscosity of the products increased substantially when the reaction time was increased from 7 to 20 hrs. A high viscous liquid resin with a hydroxyl value of around 85 mg KOH/g resin was able to prepare. The product solubility in mineral turpentine oil (MTO) was in the range of 65–90 wt% and the iodine values were in the range of 3–6 g I_2/100 g. The average molecular weight of the products was in the range of 300– 500 g/mol. The study confirmed that KOH offers better quality product than NaOH as a base catalyst under identical reaction conditions. Moreover, the liquid product with lower hydroxyl value and higher unsaturation may not be suitable for paint and coating applications.

The ketonic resin was prepared by self−polymerization reaction of cyclohexanone using a mechanically agitated batch reactor (referred as 'closed system') in presence of KOH as a base catalyst. The effect of various process parameters, such as, stirring speed, catalyst concentration, reaction time, reaction temperature, and reactor pressure on product properties have been studied and quantified. The stirring speed range of 300−1200 revolutions per minute (rpm), reaction temperature range of 130−160 °C, reaction time from 10 to 20 hrs, catalyst concentration (expressed as 'A/K ratio') range of 0.1−0.4, and reactor pressure range of 1−12 kg/cm^2(g) were considered for the study. Efforts have been made to standardize the analysis protocol, and to characterize various physico–chemical properties like hydroxyl value, viscosity, solubility, softening temperature, average molecular weight etc. of the resin products. It was observed that, for every 10 °C increase in reaction temperature, hydroxyl value and softening point of the products increased around 18 units and 9 units respectively, and solubility in MTO decreased around 12 units. Good quality resins, with hydroxyl value greater than 120 mg KOH/g, MTO solubility more than 30 wt%, iodine value less than 3.5 g I_2/100 g, and softening temperature around 80 °C, was able to prepare. The number average molecular weight of the in–house developed resins is in the range of 450–1400 g/mol. The products are adequately soluble in n–butyl alcohol, n–butyl acetate, aromatic hydrocarbons, and ketonic solvents. TGA analysis revealed that the products are thermally stable up to a temperature of around 200 ºC. Adhesive property of the solid resin was confirmed from the lap shear strength test. The study shows that >97% yield can be obtained from self–polymerization reaction of cyclohexanone. Therefore, the outcome of the present study will be very much useful to develop a desired quality of resin product and its characterization depending on specific applications.

Mathematical regression models were developed with the help of statistical analysis tools, such as, MINITAB 17 and Microsoft Excel using experimentally obtained laboratory data to optimize the reaction parameters for obtaining a desired quality resin for coating applications. An effort has been made to develop empirical models to predict the product properties like average molecular weight, solubility and softening point of resin products. The developed models were good in agreement with the experimental results.

The ketonic resin was prepared from other ketonic compounds, such as, methylcyclohexanone (MCH) and cyclopentanone (CP). The polymerization reactions of methylcyclohexanone and cyclopentanone were carried out in a high pressure reactor to develop the ketonic resins. The cross–polymerization reactions of ketonic monomers were also considered in the study. The effect of reaction parameters on various physico–chemical properties of the resin products was investigated. In the study, reaction time was varied from 15 to 20 hrs and temperature was varied from 145 to 150 °C. It was observed that the polymerization reactions with methylcyclohexanone or cyclopentanone monomers alone may not be suitable to obtain a solid resin. However, small proportion of methylcyclohexanone or cyclopentanone along with cyclohexanone can play a significant role in obtaining a product with enhanced solubility. It was observed that viscosity and hydroxyl value of the resins decreased with the increase of MCH and CP concentrations in reaction mixture. The results revealed that MCH and CP amounts in the reaction mixture can be used up to 5 wt% to obtain a solid resin product with desired hydroxyl value and MTO solubility. From the FTIR spectrum, the presence of hydroxyl group was confirmed in all the resin products. The in−house developed cyclohexanone resins are thermally stable up to a temperature of around 200 ºC. However, pure MCH and CP resins were thermally stable up to a temperature of around 170 ºC. From the overall study, it can be concluded that the in−house developed ketonic resins can be used for paint and coating applications.

In the work, the kinetics of self–polymerization reaction of cyclohexanone has been studied. From the study, it is observed that reaction order of the self−polymerization reaction varied mostly between 2 and 3 depending upon the reaction conditions. The estimated activation energy of the polymerization reaction is around 105 kJ/mol. The estimated values of entropy (ΔS^*) and free energy (ΔG^*) change of activation are around −26 J/(mol K) and 112 kJ/mol respectively.

A systematic investigation of thermal stability and decomposition kinetics of the developed resins were performed using thermogravimetric analysis (TGA). The estimated thermal stability data of the in−house developed ketonic resins was also compared with commercially available phenol−formaldehyde resin and alkyd resin. The study shows that the developed ketonic resins were thermally stable up to a temperature of around 200 °C. The apparent activation energy of the ketonic resin was in the range between 31 and 41 kJ/mol for a first−order decomposition reaction. The calculated rate constant (k) value was in between 1.07×10^{-2} and 25.36×10^{-2} 1/s at the peak temperature. The estimated values of ΔS^* and ΔG^* were in the range of −131 to −145 J/(mol K) and 101 to 125 kJ/mol respectively. The study showed that the thermal stability and apparent activation energy of the ketonic resins increased with the increase of product average molecular weights. Based on the above study, it can be concluded that the in–house developed ketonic resins were comparable with the studied phenolic resin. Therefore, the outcome of the

present work will be very much useful to get an insight on processing and application of the developed resin products.

A feasibility study was performed on the development of ketonic resin from cyclohexanone in presence of different additives. In the study, the effects of various additives, their concentration, and reaction conditions on ketonic resin properties was investigated. The study shows that the hydroxyl value of the product significantly increased in presence of Add−3. A significant increment in product solubility in MTO was observed in presence of Add−1. A resin with around 10% higher in hydroxyl value and more than 15% greater in product solubility was obtained in presence of mixed additive. Therefore, based on the present investigation, it can be concluded that it is possible to develop a good quality resin in presence of additive at optimum conditions. The conditions include a temperature range of 145−150 °C, alkali−to−ketone weight ratio of around 0.18, time between 16−18 hrs. Addition of small quantity (5 to 10 wt%) of additive to the reaction mixture can be useful to create an extra room for varying the reaction conditions to obtain a desired quality resin.

Key words: Ketonic resin, Resin characterization, Additive application, Mathematical models, Thermal decomposition, Kinetic study.

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Nomenclature

A	Pre–exponential factor, 1 / s
a	Heating rate, °C / min
AR	Alkyd resin
AV	Acid value, mg KOH / g of resin
C_{cat}	Catalyst concentration
C_{CH}	Concentration of cyclohexanone
C_{CH0}	Initial concentration of cyclohexanone
CH	Cyclohexanone
CHR	Cyclohexanone resin
CP	Cyclopentanone
cP	Centipoise
CPR	Cyclopentanone resin
CS	Closed system
E	Apparent activation energy, kJ / mol
FTIR	Fourier Transform Infrared
g	Gram
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
ΔG^*	Activation free energy change, kJ / mol
h	Planck’s constant, J s
ΔH^*	Activation enthalpy change, kJ / mol

HV	Hydroxyl value, mg KOH / g of resin
IV	Iodine value, g of I_2 / 100 g resin
k	Reaction rate constant
k_0	Pre–exponential factor, $1/(\text{mol}^{1.5}\ \text{hr})$
k_b	Boltzmann constant, J / K
kJ	Kilojoule
kV	Kilovolt
L	Liter
MALDI–TOF	Matrix Assisted Laser Desorption Ionization–Time of Flight
MCH	Methylcyclohexanone
MCHR	Methylcyclohexanone resin
$M_{n.avg}$	Number average molecular weight, g / mol
mol	Mole
MTO	Mineral turpentine oil
$M_{w.avg}$	Weight average molecular weight, g / mol
n	Order of reaction
OS	Open system
PDI	Poly–dispersity index
PR	Phenolic resin
R	Gas constant, J / (mol K)
RI	Refractive index
rpm	Revolutions per minute
s	Second

SEM	Scanning Electron Microscope
ΔS^*	Activation entropy change, J / (mol K)
ST	Softening temperature
T	Absolute temperature, K
t	Time
TGA	Thermogravimetric analysis
T_p	Peak temperature, K
W_f	Final weight, mg
W_i	Initial weight, mg
W_T	Weight at a particular temperature, mg
x	Fractional conversion
XRD	X–Ray Diffraction

Chapter 1

Introduction on Synthetic Ketonic Resins:

For paint and coating applications

1.1. Introduction

In recent years, sustainable development has become the focus of research throughout the world. It includes, along many other things, development of environment–friendly processes and products. The present research was undertaken on the same line, that is, to develop a greener product from environment–friendly raw materials. The present study deals with the development of environment–friendly product, namely, synthetic ketonic resin for paint and coating applications, from relatively less hazardous raw materials.

1.2. Synthetic Resins and Their Role in Paint and Coating Technology

Resins are basically polymeric substances which have wide range of applications including adhesives, coatings, casting, and molding materials etc. Resins play a vital role like excellent chemical resistance, good adhesion properties, heat resistance, and oxidative stability in the field of plastic, textile, paint, and construction etc. In the field of paint and coating technology, resins are used to improve adhesiveness and glossiness of paints, for dispersion of pigments, to provide resistance to water and chemical, besides acting as a dispersant (Horie, 2010).

Broadly, resins are classified as natural resins and synthetic resins based on their occurrence. Natural resins are obtained from trees which exude a viscous liquid when the bark is damaged. Commonly available natural resins are Dammar, Mastic, Rosin, Shellac and Beeswax. Natural resins are used for a wide range of applications like production of varnishes, paints, adhesives and consolidants etc. (Morgans, 1982). Natural oils such as, linseed oil, soy oil, tung oil, groundnut oil, sunflower oil, cottonseed oil, dehydrated castor oil, tall oil and fish oil are used as film forming agents.

The transformation from natural resins to the synthetic resins which are widely used today started in the early years of the 20th century. The major success of synthetic resins is due to the opportunity to tailor products to huge range of applications with a significantly high reproducibility, and their availability. Hardened resins such as copals, colophony, dammar and shellac resins were replaced by synthetic alternatives because of their unavailability in required amounts (Goldschmidt and Streitberger, 2007). A classification of film forming agents generally used in paint applications is shown in Figure 1.1.

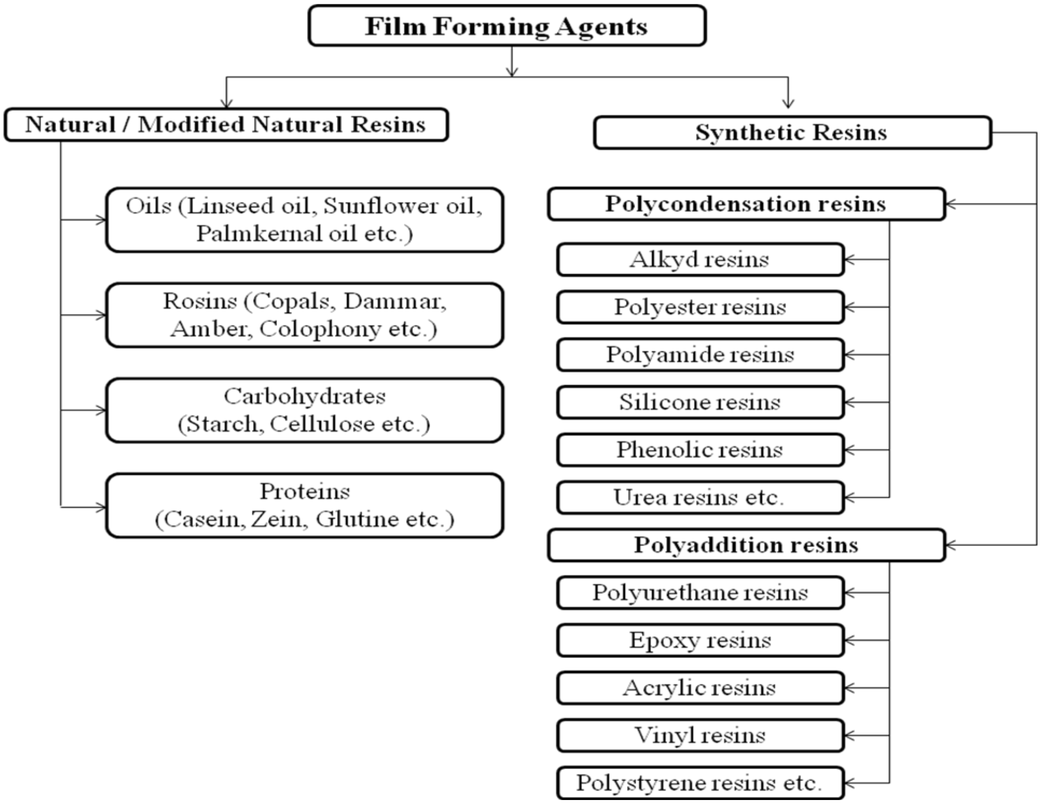


Figure 1.1. Classification of film forming agents

Synthetic resins are prepared from simple molecules called monomers by the virtue of polymerization reaction (Ebewele, 2000; Asua, 2007). Broadly, the polymerization reactions are classified as addition polymerization and condensation polymerization for the production of polymers (Gowariker et al., 2014). Various resins such as alkyd resins, epoxy resins, polyamide resins, polyurethane resins, vinyl resins, polystyrene resins, acrylic resins and phenolic resins are frequently used in paint and coating applications. (Talbert, 2008; Lambourne and Strivens, 1999). Most of the synthetic resins are insoluble in water but soluble in organic solvents like propanol, butanol, chloroform, chlorobenzene, cyclopentanone, cyclohexanone, toluene etc.

In the present study, the focus was mainly to develop suitable polymer products for paint and coating applications from ketonic monomers such as cyclohexanone, methylcyclohexanone, cyclopentanone etc. It is well known that ketones, aldehydes or their mixtures can be converted to resinous products in presence of a base or acid catalysts. Cyclohexanone and formaldehyde react to give hard resins which find uses in the coating industry (Werner et al., 2007). Cyclohexanone–formaldehyde resin plays a key role in the field of coatings since it has excellent glossy and transparent properties; wide compatibility and solubility with variety of film formers (Thakor et al., 2010; Tuba et al., 2012). It could be also used as a multifunctional additive in coatings to improve weathering resistance and as a filler dispersant in polymer matrix (Guo et al., 2015). Most of the natural resins are highly reactive with caustic potash or caustic soda. Many synthetic resins (e.g., phenol–formaldehyde resin) are also affected by strong alkali. Ketonic resins (obtained from ketonic monomer) have the ability to resist caustic alkali and even on boiling the resin with alkali (Huxham, 1924). Most of the ketonic resins are light (mostly white) in color and are useful for light color coating applications. Ketonic resins can be used in combination with high molecular weight film formers (e.g., cellulose derivatives, chlorinated rubber, vinyl esters, vinyl ethers, vinyl chloride, vinyl aromatics etc.) or chemically drying binders (e.g., alkyd resins) for the production of surface coatings (Fischer et al., 1987).

Cyclohexanone ($C_6H_{10}O$) consists of six–carbon cyclic molecule with a ketone functional group. Cyclohexanone is not carcinogenic in nature but moderately toxic, with a threshold limit value (TLV) of 25 ppm for vapor. Ketonic compound itself offers as an excellent candidate for manufacture of synthetic resin, and has the potential of replacing more hazardous materials like phenolic and aldehyde compounds.

1.3. Limitations of the existing Research

Based on the literature search on ketonic resins, it was observed that most of the published articles and patents have dealt with the dimerization reaction of alkyl cyclohexanone/cyclohexanone. Couple of articles is available in the literature on oligomerization or polymerization of cyclohexanone / alkyl cyclohexanone with aldehyde (mainly formaldehyde) to obtain a ketone–aldehyde resin. As per the available literature, BASF Germany is the sole manufacturer of ketonic resin product of alkylated cyclohexanone / cyclohexanone. A resin would be suitable for coating application, if its hydroxyl value is greater than 110 mg of KOH/g of resin, solubility is greater than 25 wt% in mineral turpentine oil (MTO), softening temperature is around 80 °C and iodine value is around 3 g of I_2/100 g resin. Though a phenolic resin is an attractive choice for high temperature applications, but the disadvantage of this resin is the toxic fumes associated with the high temperature applications, and also the yield of phenol–formaldehyde resin is lower than 75 wt%. In case of alkyd resins, the residual carbon–carbon double bonds provided by the unsaturated fatty acids raw material may lead to atmospheric oxidation under ambient conditions. The other disadvantage of alkyd resin is they required organic solvents for their synthesis and some of those solvents do not meet the volatile organic content (VOC) regulations associated with environmental restrictions. To the best of our knowledge, the studies pertaining to the thermal decomposition kinetics of ketonic resins obtained from cyclic–ketones are not reported in the literature. In the present study, cyclohexanone was considered as a model compound to develop a ketonic resin. In addition, there is scanty information in the literature about the characterization and analysis of various properties of a product.

1.4. Objective of the Present Research

Industrial revolution and the thirst for tremendous and rapid economic growth compelled the progressive human race to deliberately overlook the environmental issues. At last, people have realized that any further negligence towards the environment can lead to very serious consequences. The world has become so “synthetic” that we cannot live without chemical processes. Therefore, our aim is to make such processes safer and environment friendly, either by improving the existing methodology or by designing a safer alternative. Green Technology is looked upon to bring out better alternatives to the environmentally malignant industrial practices. In view of the commercial importance for the development of environmentally friendly processes and products, the present investigation was undertaken with the following specific objectives:

1. In terms of the principles of ‘Green Technology’, the first and foremost objective of the present research work is to develop and analyze greener routes that can replace hazardous raw materials by benign ones. In tune with this, ketonic material such as cyclohexanone was considered as model compound to prepare the ketonic resin. Cyclohexanone offers itself as an excellent candidate in the preparation of ketonic resin. Cyclohexanone is not considered

as a carcinogenic material and thereby it has a potential to replace relatively more hazardous raw materials, such as, phenol and formaldehyde.

2. Preparation of ketonic resin from cyclohexanone monomer under atmospheric pressure (referred as open system) and under pressure (referred as closed system) to study the feasibility of resin formation. The developed resin should be suitable for paint and coating applications.

3. Physico–Chemical characterization of the in–house developed resins, and comparison with the commercially available synthetic resins used for similar applications. An effort will be taken to standardize some analysis methods.

4. Feasibility study of development of ketonic resin from other ketonic monomers such as methylcyclohexanone, cyclopentanone separately or their combination.

5. Feasibility study of the effect of additives on the physico–chemical properties such as softening temperature, hydroxyl value, solubility etc. of the resin.

6. Kinetics of the polymerization reaction, thermal stability and thermal decomposition kinetics of the in–house developed resins.

In a nutshell, an attempt has been made to get the aforementioned aspects together in a coherent manner so that the information is available at a glance and is expected to be useful to the researchers and for industrial practices.

1.5. Summary of the Thesis

The present research deals with the development of synthetic ketonic resin from cyclic ketonic monomers such as cyclohexanone, methylcyclohexanone, and cyclopentanone using self–polymerization technique in presence of base catalyst. Two types of reactor systems namely, open system (reactions under atmospheric pressure), and closed system (reactions under autogenously developed pressure) studies were conducted to develop the ketonic resins. The effectiveness of NaOH and KOH as a base catalyst has been investigated. The entire study has been segregated into various chapters and the highlights of the chapters are as follows:

Chapter 2 of the thesis concerned with the detailed literature review on: (a) dimerization /oligomerization /polymerization reactions of cyclohexanone in presence of various catalysts; (b) kinetics of dimerization and trimerization reactions of cyclohexanone; (c) preparation of ketone–aldehyde resins; (d) preparation of ketonic resin in presence and absence of phase transfer catalyst; (e) effect of additives on degree of polymerization and polymer properties; and (f) thermal decomposition kinetics of different resins used in paint and coating field.

Chapter 3 of the thesis deals with the experimental details and analysis techniques adopted to characterize the in–house developed resins. The characterization technique includes, Moisture content, Gas chromatography, Fourier Transform Infrared, Viscosity, Refractive index, Gel permeation chromatography, MALDI–TOF, X–ray diffraction, Scanning electron microscope, Thermogravimetric, Softening temperature, Adhesive strength, hydroxyl value, Iodine value, Acid value and Solubility analysis.

Chapter 4 of the thesis reports a systematic study on development of synthetic resin by self–oligomerization / polymerization of cyclohexanone in presence of a base catalyst. The reactions were conducted under atmospheric pressure using a 250 mL capacity three–neck glass reactor. The effect of operating parameters on monomer conversion and physico–chemical properties of the final products has been described. For the study, the reaction time was varied from 7 to 20 hrs, catalyst loading was varied from 0.05 to 0.2, and temperature was varied from 90 to 140 °C.

Chapter 5 of the thesis reports a systematic study on self−polymerization of cyclohexanone using a high pressure reactor in presence of potassium hydroxide as a base catalyst. Various aspects like, synthesis of ketonic resin, effect of reaction parameters on product properties, and characterization of resin products have been investigated in the work. The stirring speed range of 300−1200 revolutions per minute (rpm), reaction temperature range of 130−160 °C, reaction time from 10 to 20 hrs, catalyst concentration (expressed as A/K weight ratio) range of 0.1−0.4, and reactor pressure range of 1−12 $kg/cm^2(g)$ were considered for the study.

Chapter 6 of the thesis concerned with the development of mathematical regression models to optimize the process parameters in order to get a desired product. The empirical models were also developed to predict the product properties such as solubility, softening temperature and average molecular weight.

Chapter 7 of the thesis reports the study on the preparation of ketonic resin from methylcyclohexanone and cyclopentanone. Polymerization reactions of methylcyclohexanone and cyclopentanone were carried out in a high pressure reactor to develop the ketonic resins. The cross–polymerization reactions of ketonic monomers were also considered in the study. The effect of reaction parameters on various physico–chemical properties of the resin products was investigated. In the study, reaction time was varied from 15 to 20 hrs and temperature was varied from 145 to 150 °C.

Chapter 8 of the thesis reports kinetic study of self–polymerization reaction of cyclohexanone, analysis of thermal stability, and decomposition kinetics of solid resin products. The thermal decomposition kinetics was estimated based on thermogravimetric analysis (TGA). In the study, the kinetic and thermodynamic parameters such as order of reaction (n), reaction rate constant (k), activation energy (E), activation entropy change (ΔS^*), activation enthalpy change (ΔH^*) and activation free energy change (ΔG^*) were estimated. The estimated thermal stability data of the in–house developed ketonic resins was also compared with the commercially available phenol–formaldehyde resin and alkyd resin.

Chapter 9 of the thesis reports a systematic study on the development of ketonic resin from cyclohexanone in presence of different additives. In the study, the effect of various additives on resin properties such as hydroxyl value, softening temperature, solution viscosity and solubility was investigated. In the study, reaction time was varied from 15 to 20 hrs and temperature was varied from 140 to 150 °C.

Key words: Ketonic resin, Resin characterization, Additive application, Mathematical models, Thermal decomposition, Kinetic study.

Chapter 2

Review of Status of Research on Development of Ketonic Resins

2.1. Literature Review on Polymerization Reaction of Cyclohexanone

Resins are built up from simple molecules called monomers and can be prepared by either addition polymerization or condensation polymerization. Ketones and aldehydes can be converted to resinous products by treatment with an alkali/acid through an aldol condensation reaction. The desired property of a synthetic resin greatly depends on its method of preparation and its field of application.

2.1.1. Studies on dimer and trimer formation

The most probable dimer products obtained from base–catalyzed aldol condensation of cyclohexanone are shown in Figure 2.1.

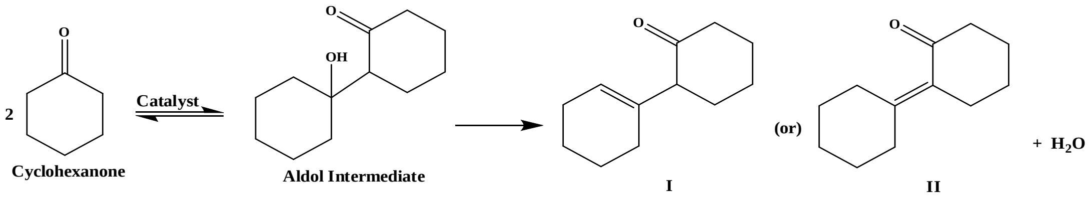


Figure 2.1. Reaction scheme of base catalyzed aldol condensation of cyclohexanone.
I= 2–(1–Cyclohexenyl) cyclohexanone, II= 2–Cyclohexylidene cyclohexanone

Melvin and Murry (1959) have studied the self–condensation of various aldehydes (e.g., propionaldehyde, crotonaldehyde, n–butyraldehyde, isobutyraldehyde, benzaldehyde etc.) and cyclohexanone in an agitated flask equipped with a condenser and water trap to remove the condensed water during the reaction. The author studied the effect of various parameters like reaction temperature, reaction time, catalyst loading, types of catalyst (e.g., Amberlite IR–120, Dowex–50), and the effect of solvent on conversion of monomer unit. The conversion was calculated based on infrared (IR) spectroscopy analysis. The effect of various parameters on the conversion of n–butyraldehyde and cyclohexanone are summarized in Table 2.1. It is observed that the maximum value of n–butyraldehyde conversion (around 75%) was achieved at a temperature of 80 °C in the presence of Amberlite IR–120 catalyst for a reaction time of 6 hrs.

Table 2.1. Effect of various parameters on monomer conversion

Reactants /monomer	Catalyst type	Catalyst loading, wt%	Temp., °C	Reaction time, hr	Estimated conversion, %
n–Butyraldehyde	Amberlite IR–120	25	30	1	58
n–Butyraldehyde	Amberlite IR–120	25	75	1	69
n–Butyraldehyde	Amberlite IR–120	10	80	6	58
n–Butyraldehyde	Amberlite IR–120	25	80	6	75
n–Butyraldehyde	Dowex–50	25	80	6	80
Cyclohexanone	Dowex–50	25	110	1	23
Cyclohexanone	Dowex–50	25	110	5	>99

The table shows that Dowex–50 offered comparatively better conversion over Amberlite IR–120 under identical reaction conditions. The result shows that the monomer conversion increased with the increase of reaction time, reaction temperature and catalyst loading. The data also shows that almost complete conversion of cyclohexanone monomer was achieved when the reaction was carried out at around 110 °C in the presence of Dowex–50 and the condensed water was continuously removed from the reactor. However, the author did not report anything about the physico–chemical properties like solubility, molecular weight, viscosity of the polymerized products of cyclohexanone.

Takashi and Kazuo (1968) have investigated the kinetics of dimerization reaction of cyclohexanone to 2–(1–cyclohexenyl) cyclohexanone. The reaction was carried out in the presence of sodium ethoxide catalyst at a temperature range of 0.6–10 °C and a pressure range of 1–2000 kg/cm^2(g) in a high pressure apparatus. The reported values of activation energy and entropy were around 53.2 kJ/mol and –0.14 kJ/°C mol respectively for a second–order reaction. However, the commercialization of any high pressure process requires more capital investment to comply with enhanced plant safety.

Harold and Gibsonia (1970) patented a process for the self–condensation of cyclohexanone to yield 2–(1–cyclohexenyl) cyclohexanone in the presence of metallic tin (Sn) as a heterogeneous catalyst. The inventor disclosed that around 27% conversion of cyclohexanone with 94%

selectivity to 2–(1–cyclohexenyl) cyclohexanone was obtained when cyclohexanone vapor mixed with hydrogen and was passed through a fixed bed reactor containing 10 wt% tin catalyst on a silica support at a temperature of 250 °C.

Tsutomu et al. (1974) studied the self–condensation of cyclohexanone at a pressure range of 20–50 kbar(g) and temperature range of 160–300 °C in absence of catalyst using a compact cubic anvil apparatus. Mass spectroscopic and IR analysis techniques were used to identify the dimer, trimer and tetramer products. The yields of various products are summarized in Table 2.2 along with reaction conditions. In the study, the reported maximum yield towards product–C was around 34%. However, a high pressure process may require enhanced safety features to avoid accidents for a large scale operation.

Table 2.2. Effect of reaction parameters on self–condensation of cyclohexanone

Reactant / monomer	Pressure, kbar(g)	Temp., °C	Time, hr	Yield[*], wt%		
				A	B	C
Cyclohexanone	20	200	0.5	5	1	negligible
Cyclohexanone	20	250	0.5	1	1	12
Cyclohexanone	35	200	0.5	7	2	negligible
Cyclohexanone	35	250	0.5	1	1	34
Cyclohexanone	45	200	0.5	1	2	10
Cyclohexanone	45	250	0.5	1	1	27

[*] A = 2–(1–Cyclohexenyl) cyclohexanone, B = 2,6–Dicyclohexenyl cyclohexanone,
C = Dodecahydrotriphenylene

Joseph et al. (1977) have patented a process for preparation of 2–(1–cyclohexenyl) cyclohexanone by self–condensation of cyclohexanone in presence of Lewatite SP–120 resin catalyst at a temperature range of 80–110 °C. The reported conversion of cyclohexanone was around 30% with a yield of around 95% of 2–(1–cyclohexenyl) cyclohexanone. However, the scope of the process disclosed in the patent was limited to the preparation of dimer products only and was silent about the polymerization products of cyclohexanone.

Muzart (1982) has studied the self–condensation reaction of ketones (cyclopentanone and cyclohexanone) in presence of basic aluminium oxide (Al_2O_3) catalyst at room temperature for a reaction time of 84 hrs. In the study, 2–cyclopentylidene cyclopentanone and 2–(1–cyclohexenyl) cyclohexanone dimer products were obtained from cyclopentanone and cyclohexanone respectively. The effect of reaction conditions on ketone conversion and yield of dimer products is shown in Table 2.3. The data shows that cyclohexanone offered lower conversion and yield towards dimer product in comparison with cyclopentanone under identical reaction conditions.

Table 2.3. Effect of reaction conditions on ketone conversion and product yield

Ketone	Catalyst loading, g/mmol	Conversion, %	Yield of dimer, %
Cyclopentanone	0.15	81	63
Cyclohexanone	0.16	60	46

Walter (1984) has disclosed a process on aldol condensation of cyclohexanone in presence of synthetic clay ($M_6N_2(OH)_{16}.A.4H_2O$ where, 'M' is a divalent metal cation (e.g. Mg^{+2}), 'N' is a trivalent metal cation (e.g. Al^{+3}), and 'A' is a mono, di, or trivalent anion (e.g. CO_3^{-2})). In the work, cyclohexanone was passed through a tubular reactor filled with in–house developed clay catalyst at a temperature of 300 °C. Gas chromatography technique was used to characterize the product compounds. The product mixture contained around 13% 2–(1–cyclohexenyl) cyclohexanone and 24% 2–cyclohexylidene cyclohexanone with the unconverted cyclohexanone.

Jose et al. (1993) have studied kinetics of self–condensation of cyclohexanone in presence of Amberlyst–15 resin catalyst at a temperature range of 70–110 °C. The experiments were carried out in a glass reactor equipped with a mechanical stirrer and reflux condenser fitted with a Dean–Stark apparatus for the removal of condensate water. The reactions were carried out under atmospheric pressure. Few set of reactions were carried out under vacuum condition to remove condensed water from the reaction mixture. A mixture of dimer and trimer products was obtained during the course of reaction. Gas chromatography (GC) was used to estimate the conversion of cyclohexanone, and the moisture content in the product was measured by Karl–Fischer instrument. The important findings of the study are summarized in Table 2.4. The data shows that the conversion of cyclohexanone increased with the increase of reaction temperature and catalyst loading. The study also shows that the water elimination from the reaction mixture plays an important role on monomer conversion.

Table 2.4. Effect of temperature and catalyst concentration on cyclohexanone conversion

Temp, °C	Catalyst loading, g/L	With water elimination, yes/no	Conversion, %
80	5	yes	33
80	10	yes	56
100	5	no	20
100	10	no	26
100	10	yes	63
110	10	no	31

Yogesh et al. (2008) have studied the self–condensation of cyclohexanone in the presence of various types of acidic ion exchange resin catalysts. The experiments were conducted in a mechanically agitated glass reactor at a temperature range of 80–100 °C under atmospheric pressure. The effects of temperature and catalyst loading on cyclohexanone conversion were investigated. Gas chromatography technique was used to identify the product compositions. Some important results obtained from the study are summarized in Table 2.5.

Table 2.5. Effect of temperature and catalyst concentration on cyclohexanone conversion

Temp., °C	Catalyst type	Catalyst loading, wt%	Estimated conversion, %
90	T–63	3	38
100	T–63	3	41
90	T–63	5	41
100	Amberlyst–15	3	36
100	Amberlyst–45	3	41

Though the conversion of cyclohexanone increased with the increase of both temperature and catalyst loading, but the increment was not so significant. From the data, it was also observed that Amberlyst–45 offered better conversion over Amberlyst–15 under identical reaction conditions. Moreover, the maximum value of cyclohexanone conversion was about 41%.

Yeqiang et al. (2011) have studied the kinetics of the dimerization reaction of cyclohexanone in presence of γ–alumina at a temperature range of 110–130 °C. Gas chromatography was used to analyze the product. The Langmuir–Hinshelwood kinetic model was used to describe the dimerization reaction of cyclohexanone. It is reported that the accumulation of condensed water within the reacting system showed a negative effect on the reaction rate. The activation energy of forward and backward reaction (shown in Figure 1.1) was around 177 and 52 kJ/mol respectively.

Ying–Ling et al. (2012) have patented a process for producing 2–(1–cyclohexenyl) cyclohexanone by self–condensation of cyclohexanone in presence of solid acidic ($Al_xS_yO_z$) catalyst at a temperature range of 130–150 °C using a stainless steel reactor. Gas chromatography was used to find the conversion and selectivity. The effect of temperature and catalyst loading on cyclohexanone conversion and selectivity towards 2–(1–cyclohexenyl) cyclohexanone are shown in Table 2.6. The data shows that the conversion and selectivity followed an opposite trend with the increase of both reaction temperature and catalyst loading. There was no information available in the article regarding the comparative study between the in–house developed catalyst and the conventional alkali catalysts like NaOH or KOH. Moreover, the scope of study was limited to dimerization reaction only.

Table 2.6. Effect of temperature and catalyst loading on conversion of cyclohexanone and selectivity of 2–(1–cyclohexenyl) cyclohexanone

Temp, °C	Catalyst loading, wt%	Conversion (approx.), %	Selectivity, %
130	4	38	100
140	4	86	92
150	4	95	83
140	8	89	80

Lorenzo et al. (2013) have studied the kinetics of dimerization reaction of cyclohexanone in presence of sodium hydroxide catalyst. The liquid phase reaction was conducted at a temperature range of 127–149 °C in a batch reactor. Gas chromatography–mass spectroscopy (GC–MS) instrument was used to quantify the dimer, trimer and tetramer products. Dimer concentration increased with the increase of both temperature and catalyst loading. Around 80% conversion of cyclohexanone was achieved in the study. 'Lumped Model' method was used to develop the kinetic rate expression. The estimated activation energy of the reaction was 132.6 kJ/mol. The article mainly deals with the formation of dimer and trimer products and no special attention was given on the formation of higher polymer compounds.

2.1.2. Studies on ketone–aldehyde resins related to coating application

Huxham (1924) has patented a process to prepare ketone–aldehyde resins from methyl acetone and formalin in the presence of caustic soda. The reaction was performed at a temperature range of 50–70 °C in a mechanically agitated jacketed vessel. After forming the brown color viscous material, the reaction was arrested by adding dilute sulphuric acid to the reacting mixture to obtain a specific product. The product was soluble in acetone, fusible in nature and its softening point was below 100 °C. When the resin was further heated at 105 °C for about 15 hrs (curing), the product became slightly infusible in nature and insoluble in acetone and alcoholic solvents.

Harold et al. (1949) have patented a process to prepare a hydroxylated ketone–aldehyde resin by condensing ketones with aldehyde (formaldehyde) at a temperature range of 40–100 °C. The reactions were carried out in a glass vessel in presence of calcium oxide (CaO) catalyst with catalyst concentration range of 0.25–0.75 mole per mole of ketone. The technical details of their invention relevant to the present study are summarized in Table 2.7. The invention shows that the hydroxyl content of the products decreased with the increase of temperature. However, the scope of the study was limited to the preparation of ketone–aldehyde resins. It is silent about the physico–chemical properties such as, molecular weight, solubility, viscosity, softening point and iodine value of the developed resin products.

Table 2.7. Effect of various parameters on hydroxyl content of a synthetic resins

Raw materials	Catalyst	Temp., °C	Time, hr	Hydroxyl content, %
Acetone and formaldehyde	CaO	50	2	27.3
Acetone and formaldehyde	CaO	90	2	13.7
Cyclopentanone and paraformaldehyde	CaO	60	0.5	27.4

Hurst et al. (1951) have disclosed a process for synthesis of ketone–aldehyde resins by reacting cyclohexanone or methyl cyclohexanone with formaldehyde in the presence of NaOH as catalyst. The objective of the study was to develop a resin which could be used for coating application. In the process, aldehyde–to–ketone molar ratio was maintained in the range of 1.4–1.6 and the catalyst concentration varied in the range of 0.25–1.0 wt%. The pH of the reaction mixture was controlled within the range of 7.0–7.5. The effects of various operating parameters on product quality are summarized in Table 2.8. The data shows that the melting point of the resin increased with the increase of reaction severity. However, the patent is silent about the average molecular weight, hydroxyl content, iodine value, and solubility of developed ketone–aldehyde resins.

Table 2.8. Effect of temperature, reflux time and aldehyde–to–ketone ratio on product quality

Raw materials	Aldehyde–to–ketone molar ratio	Temp., °C	Reaction time, hr	Product properties
Cyclohexanone–cyclohexanol mixture and formaldehyde	1.4	95	1.2	— colorless resin — melting point 90 °C
Methylcyclohexanone and formaldehyde	1.6	90	1.2	— colorless resin — melting point 78 °C
Cyclohexanone and formaldehyde	1.6	95	1.2	— colorless resin — melting point 87 °C
Cyclohexanone and formaldehyde	1.6	75	0.7	— crystal–clear resin — melting point 79 °C

Rainer et al. (1980) have disclosed a process to produce a ketone–aldehyde polymer of higher softening point. To achieve the required specification, polymerization reactions were carried out under atmospheric pressure in presence of NaOH along with various phase transfer catalysts (PTCs). In the process, organic solvents such as methanol, isobutanol etc. were used as mobile phase. The reaction was performed in a reactor with reflux facility. The reaction conditions and corresponding product properties are mentioned in Table 2.9. From the reported data, it can be said that the presence of PTC greatly influenced the reaction yield. The yield of resins and also the softening point of resins increased in the presence of PTC. In presence of TCMAC and TCMPI, the products softening points were increased to about 30 °C and 60 °C respectively. The inventor claims that the developed resins can be used in various applications, such as, making paints, adhesives, binders etc.

Table 2.9. Effect of various reaction parameters on product properties

Raw materials	PTC*	Temp., °C	Reaction time, hr	Product properties
Methyl ethyl ketone, acetone and formaldehyde	–	80	2.5	— yield of 68% — softening point 88 °C
Methyl ethyl ketone, acetone and formaldehyde	TCMAC	80	2	— yield of 79% — softening point 118 °C
Cyclohexanone and formaldehyde	–	90	1	— yield of 69% — softening point 88 °C
Cyclohexanone and formaldehyde	TCMPI	90	1	— yield of 75% — softening point 148 °C

*TCMAC = tricaprylmethylammonium chloride; TCMPI = tricaprylmethylphosphonium iodide

Dorffel (1988) has patented a process to produce a ketone–formaldehyde resin with high softening points. The condensation reaction was carried out in an agitated vessel fitted with a reflux condenser and at a temperature range of 70–100 °C in presence of NaOH catalyst for a reaction time of around 4 hrs. In the study, catalyst concentration in terms of NaOH–to–

acetophenone mole ratio was maintained at 0.25. To enhance the reaction, phase transfer catalysts (PTC) were added in the reaction. The reported conversion of acetophenone was around 96%. The softening points and molecular weights of the resins were determined by capillary method and vapor pressure osmometry method respectively. The reaction conditions and product properties are summarized in Table 2.10. Based on the reported data, it can be said that the molecular weights and softening points of the resins increased in presence of PTCs. The inventor claims that the developed resins could be used in making coatings materials, printing dyes, inks and polishes. However, no information available in the patent regarding the hydroxyl value, iodine value and acid value of the developed resin.

Table 2.10. Effect of various reaction parameters on product properties

Reactants	PTC*	PTC loading, wt%	$M_{n.avg}$, g/mol	Softening temp., °C
Acetophenone (A) and formaldehyde (F)	–	–	650	65
A and F	TMBAC	1	1060	98
A and F	TMBAC	0.5	1100	94
A and F	TEBAC	0.5	1210	98
A and F	BTPPC	0.5	830	80

*TMBAC = trimethylbenzylammonium chloride; TEBAC = triethylbenzylammonium chloride

BTPPC = benzyltriphenylphosphonium chloride

Rene de la Rie and Shedrinsky (1989) have studied the synthesis of a modified ketonic resin from Laropal K80 and MS2A for paints applications. Brittleness property is one of the drawbacks of a ketonic resin particularly for varnish applications. In the article, the author mainly focused on the synthesis of a stable and flexible resin by reduction of ketonic groups to hydroxyl groups and subsequent esterification of some of the hydroxyl groups. Various properties such as, glass transition temperature, hardness, and flexibility of the reduced resins were compared with the MS2A resin and some of important properties are given in Table 2.11.

Table 2.11. Physical and mechanical properties of the ketonic resins.

Resin	Glass transition temp., °C	Pendulum hardness, s	Flexibility, mm
Laropal K80	43	130	149
Reduced Laropal K80	58	185	199
MS2A	57	214	189

Martina et al. (1998) have disclosed a process for the preparation of ketone–aldehyde resins through condensation reaction of ketones (cyclohexanone, 4–tert–butyl cyclohexanone, methyl ethyl ketone) with formaldehyde in presence of 50% aqueous NaOH catalyst. The reaction was carried out at 85 °C for around 6 hrs. The solubility tests were performed in various solvents such as butanol, methyl ethyl ketone (MEK), xylene and mineral oil, and the results were compared with two commercially available cyclohexanone–formaldehyde resins namely, AFS resin and CA resin. According to the disclosure, the resins were brittle in nature, average molecular weight was in the range of 500–1000 g/mol, and softening point was in the range of 80–90 °C.

Mustata and Bicu (2002) have studied the preparation of cyclohexanone–paraformaldehyde resin using a laboratory glass reactor with a Dean–Stark separator. N–methylpyrrolidone and toluene (1:1) were used as solvents to dissolve the paraformaldehyde. The maintained molar ratio of ketone–to–aldehyde was one. The reactions were carried out at 95 °C for a reaction time of 3 hrs in presence of p–toluene sulfonic acid monohydrate catalyst with a concentration of 3 wt%. Finally, the reaction mass was washed with water and vacuum distilled at 120 °C. The reported melting point of the resin product was 140 °C.

Gloeckner et al. (2006) have patented a process to produce ketone–aldehyde resins by condensing cyclohexanone with formaldehyde in presence of NaOH along with benzyltributylammonium chloride as phase transfer catalyst. The reaction was performed in a three–neck flask fitted with reflux condenser at a temperature of about 60 °C for a period of 6 hrs. The reaction mass was washed with water and then the product was vacuum distilled at 165 °C. The inventor claims that the developed resin can be use in various applications such as, in making coatings, printing, and pigment materials. Some relevant properties of the developed resin are summarized in Table 2.12.

Table 2.12. Physico–chemical properties of the developed ketone–aldehyde resins

Physico–Chemical Properties		Reported values
Physical appearance	–	colorless, clear and brittle
Solubility	–	soluble in MEK, acetone, ethyl acetate and xylene
Softening temp., °C	–	106
Hydroxyl number, mg KOH/g resin	–	96
Molecular weight, g/mol	–	$M_{n.avg} = 650$; $M_{w.avg} = 1200$

Werner et al. (2007) have disclosed a process for preparing a ketone (cyclohexanone, MEK, acetophenone) – aldehyde (paraformaldehyde) resin which possesses high thermal stability and yellowing resistance. The reaction was performed in a three–neck flask equipped with a condenser in the presence of tetra–ethylammonium hydroxide catalyst at a temperature range of 60–90 °C. The reaction was continued for around 4 hrs and the condensed water was removed continuously. A light colored resin was obtained with a yield of 87%. The physico–chemical properties of the product are summarized in Table 2.13, and the simplified structure of cyclohexanone–paraformaldehyde resin is shown in Figure 2.2.

Table 2.13. Physico–chemical properties of the developed resins

Properties		Reported values / Remark
Solubility	–	soluble in ethanol and xylene
Water content, wt%	–	< 0.3
Thermal stability	–	low tendency to undergo yellowing
Non–volatile content (heating at 160 °C), wt%	–	99.4
Softening point, °C	–	50–80
Hydroxyl number, mg KOH/g resin	–	5–200
Number average molecular weight $M_{n.avg}$, g/mol	–	400–900

In the patent, the scope of the study was limited to the condensation reaction of cyclohexanone and formaldehyde mixture, and is silent about condensation of any other ketones either as a single compound or their mixtures.

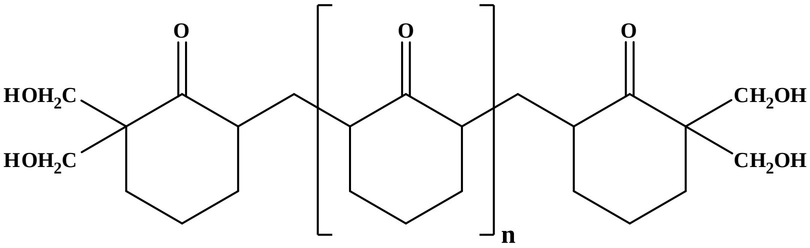


Figure 2.2. Probable structure of cyclohexanone–paraformaldehyde resin

Suparna Chemicals, an Indian chemical company, manufactures synthetic resins by reacting cyclohexanone with formaldehyde in a batch process. The resins are available in market by different trade names such as, KTR–100 and KTR–118. The available specifications of ketone–aldehyde resins are summarized in Table 2.14.

Table 2.14. Specifications of ketone–aldehyde resins

Resin Properties	Product Specifications	
	KTR–100	KTR–118
Softening temp., °C	95–105	105–115
Moisture content, wt%	3.0	3.0
Acid value , mg KOH/g resin	0.2	0.2
Hydroxyl value, mg KOH/g resin	170–200	180–210
Iodine value, g Iodine/100 g resin	2.0	2.0

2.1.3. Studies on ketonic resins related to paint and coating applications

Kocian and Antonin (1971) have disclosed a process to prepare ketonic resins by condensing the methylcyclohexanone with cyclohexanone in a Ni reactor in presence of methanolic NaOH catalyst. Initially the reactor was pretreated with 20% aqueous NaOH at a temperature of 125 °C and at around 2.5 kg/cm^2 pressure. Once pretreatment step was complete, the aqueous NaOH was drained from the reactor and the reactants were charged into the reactor for condensation reaction. The obtained resin according to the invention was having a softening point of 90 °C.

Rainer et al. (1980) have disclosed a process to prepare a ketonic resin from cyclohexanone monomer. The polymerization reactions were carried out under autogenously developed pressure in presence of methanolic NaOH along with and without phase transfer catalyst (PTC). The reaction conditions and corresponding product properties are mentioned in Table 2.15. The invention shows that the PTC was effective to boost the softening point of the resin. However, the effect of PTC on other physico–chemical properties such as, hydroxyl value, solubility, molecular weight etc. of the developed ketonic resin is not reported in the study.

Table 2.15. Effect of reaction parameters on product properties

Raw materials	PTC	Temp., °C	Pressure, kg/cm^2 (g)	Time, hr	Product properties
Cyclohexanone	–	110–125	~3	15	— hard resin — softening point ~ 115 °C
Cyclohexanone	TOMPI*	110–125	~3	15	— hard resin — softening point ~128 °C

*TOMPI = trioctylmethylphosphonium iodide

Vincent (2000) has published a report on the development of various ketonic resins such as, MS2, MS2A, AW2 and Ketone Resin–N from methylcyclohexanone and cyclohexanone mixture. MS2 and AW2 resins were used as additives in paints and varnishes to improve glossiness and hardness of paint. In 1959, Howards with the support of Garry Thompson developed MS2A resin from MS2 by reduction with sodium borohydride in presence of methanol. The probable structure of MS2A resin is shown in Figure 2.3 and the physico–chemical properties of MS2A resin are summarized in Table 2.16. In 1967, BASF developed Ketone Resin–N from cyclohexanone as a replacement of AW2.

Table 2.16. Physico–chemical properties of MS2A resin

Resin Properties	Values
Hydroxyl value, mg KOH/g resin	> 190
Softening temp., °C	85–100
Density, g/mL	1.08
Refractive index	1.505
Avg. molecular weight, g/mol	$M_{n.avg} = 769$, $M_{w.avg} = 1776$

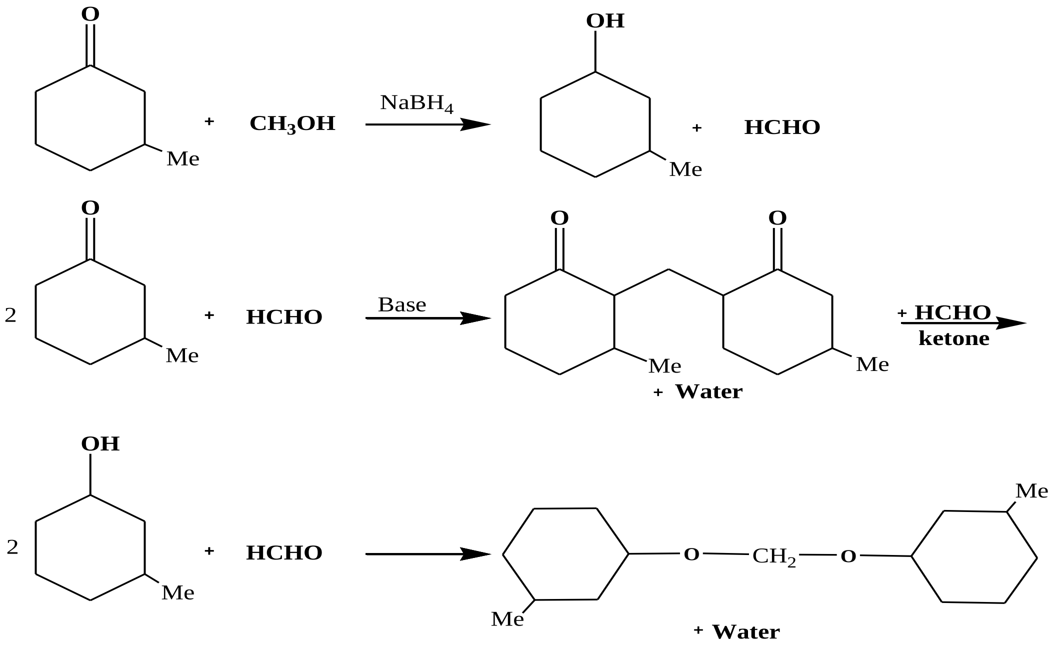


Figure 2.3. Probable structures of MS2A resin

Dinda et al. (2015) have studied the self–polymerization reaction of cyclohexanone to develop a synthetic ketonic resin. The authors have studied the effect of various operating parameters like reaction time, reaction temperature and ketone–to–alkali ratio on the polymerization reaction. The reactions were performed at a temperature range of 130–160 °C in an autoclave. Various physico–chemical properties like solubility, hydroxyl value, iodine value etc. of the resin products were analyzed in the study. The study concluded that the degree of polymerization increased with the increase of temperature and ketone–to–alkali ratio.

2.2. Kinetics of Thermal Degradation of Resins

The thermal degradation of resins/polymers is a phenomenon where the resin/polymeric material at elevated temperature undergo chemical changes. The study of thermal degradation of a resin is important for developing an efficient technology for processing the resin, and understanding its applicability at elevated temperature. Thermogravimetric analysis (TGA) method is a useful technique to evaluate the thermal decomposition behavior, and decomposition kinetics of polymer materials.

Reghunadhan et al. (2003) have studied the thermal decomposition kinetics of phenolic resins ($M_{n.avg}$ is in the range of 4000–7000 g/mol) using thermogravimetric analysis method. The TGA study was carried out within the temperature range from room temperature to 650 °C with a heating rate of 10 °C/min in presence of nitrogen atmosphere. Coats–Redfern (C–R) and Madhusudanan–Krishnan–Ninan (M–K–N) models were used to evaluate the activation energy of the thermal decomposition reaction. The estimated activation energy of the phenolic resin was around 90–106 kJ/mol for a first–order decomposition kinetics.

Andrews et al. (2017) have investigated the thermal degradation kinetics of cardanol–furfural resin (phenolic resin) using TGA technique. The analysis was carried out within the temperature range from room temperature to 800 °C at a heating rate of 20 °C/min in presence of nitrogen environment. It was reported that the resin was thermally stable up to a temperature of around 200 °C. In the study, Coats–Redfern model was used to find activation energy of the degradation reaction. The reported activation energy was around 96 kJ/mol for a first–order reaction.

Vasconcelos et al. (2014) have studied the non–isothermal decomposition kinetics of polyether–ether–ketone (PEEK) polymer using TGA technique within the temperature range of 30–1000 °C at a heating rate of 10 °C/min. The study was carried out in presence of air and nitrogen atmospheres. Coats–Redfern and Flynn–Wall–Ozawa models were used to estimate the decomposition activation energy. It was reported that the thermal stability of the material decreased in presence oxygen environment. The reported activation energy of the material was around 27 and 80 kJ/mol in presence of air and nitrogen respectively.

Mustata and Bicu (2002) have studied the thermal stability and degradation kinetics of cyclohexanone–aniline–formaldehyde and cyclohexanone–formaldehyde resins by using thermogravimetric technique. The resins were heated in the temperature range from room temperature to 500 °C. It was reported that the resins were thermally stable up to a temperature of around 200 °C. Coats–Redfern method was used to evaluate the activation energy for a first–order decomposition reaction, and the activation energy was in the range of 37–42 kJ/mol.

Singru (2011) has studied the decomposition kinetics of p–cresol–oxamide–formaldehyde resins ($M_{n.avg}$ is in the range of 4000–15500 g/mol) by TGA method within the temperature range of 20–1000 °C under nitrogen atmosphere. The reported decomposition activation energy of the resins was around 27 kJ/mol for a first–order decomposition kinetics.

Ataei et al. (2012) have studied the thermal decomposition kinetics of palm oleic acid–based alkyd resins ($M_{n.avg}$ is in the range of 1000–2100 g/mol) using TGA method under nitrogen atmosphere. It was reported that the resins were thermally stable up to a temperature of 200 °C. Kissinger model was used to find the activation energy of the thermal decomposition and the reported activation energy of the alkyd resins was in the range of 134–230 kJ/mol depending upon the oil length.

The literature shows that mostly the thermal degradation studies were carried out with phenolic resins, alkyd resins and aldehyde resins. To the best of our knowledge, the studies pertaining to the thermal decomposition kinetics of ketonic resins obtained from cyclic–ketones are not reported in the literature.

2.3. Studies on Effect of Additives on Polymer Properties

It is known that it is necessary to use the additives / short stopping agents to modify or to improve the product property in order to obtain commercially useful product. It is also known that it is necessary to control or retard the polymerization reaction from runaway process using short stopping agents in order to obtain commercially value added product (Sharaby, 1988; Lawrence, 1958; Werner, 1958; Albert, 1971; Alan, 1970).

Sharaby (1988) has studied the preparation of polyvinyl chloride resins from vinyl chloride in presence of di–secondary butyl peroxydicarbonate catalyst under autogenously developed pressure. In the invention, the polymerization reaction was stopped or controlled using alkyl substituted hydroquinone such as 2,5–di–t–amylhydroquinone as a short stopping agent. The control or stopping of polymerization reaction was measured with respect to change or drop in pressure with time.

Lawrence (1958) has studied the development of synthetic rubber from butadiene–styrene monomeric mixture in presence of short stopping agents. According to the invention, the short stopping agents such as dodecyl gallate and dodecyl pyrogallate were used in the process. The study disclosed that short stopping agents helped to improve the mechanical property of the rubber.

Werner (1958) disclosed a process to prepare polyvinyl chloride from vinyl chloride in presence of butadiene monoxide as short stopping agent. The study disclosed that product yield decreased significantly as the amount of butadiene monoxide was increased.

Albert (1971) disclosed a process to prepare synthetic rubber from butadiene–styrene copolymers in presence of different additives such as 2,5–bis(dimethylamino–methyl) hydroquinone–N,N'–dioxide, 2,5–bis(diethylamino–methyl) hydroquinone–N,N'–dioxide. The study revealed that the polymerization reaction was effectively stopped in presence of additives.

Frank and Eugene (1952) have disclosed a process to prepare polystyrene polymer from styrene monomer in presence of potassium persulfate catalyst along with stopping agents such as dihydropyridines and tetrahydropyridines. The study revealed that the yield of polystyrene was around 25% less in presence of stopping agent.

From the literature survey, it has been observed that most of the published literature on additives / short stopping agents deals with the properties of synthetic rubber, polystyrene, and polyvinyl chloride polymers. However, literature pertaining to the development of ketonic resins from cyclic ketones in presence additives / short stopping agents has yet not been reported.

2.4. Conclusions

Based on the aforementioned literature survey, it has been observed that most of the published articles and patents deal with the dimerization reaction of alkyl cyclohexanone/cyclohexanone. Couple of articles is available in the literature on the synthesis of cyclohexanone–formaldehyde resins. In the present study, the literature pertaining to the self–condensation of ketones to yield dimer, trimer and tetramer products and also the condensation of various ketone molecules with aldehydes to produce ketone–aldehyde resins are extensively reviewed, analyzed and a state–of–the–art review is written. Most of the thermal degradation studies were carried out with phenolic resins, alkyd resins and aldehyde resins. To the best of our knowledge, the studies pertaining to the thermal decomposition kinetics of ketonic resins obtained from cyclic–ketones are not reported in the literature. It is also observed that the studies related to the application of additives / short stopping agents are mostly on synthetic rubber, polystyrene, and polyvinyl chloride polymers.

The present study provides an overview of: i) effect of various operating parameters like reaction time, temperature, pressure, type of catalyst and its loading on a condensation polymerization reaction; ii) various techniques and ideas to analyze the product properties and to remove the catalyst from the reaction mass; iii) effect of phase transfer catalysts (PTC) on the resin product properties such as softening temperature, moisture content, gardener color number etc. In a nutshell, an attempt has been made to get the aforementioned aspects together in a coherent manner so that the information is available at a glance and is expected to be useful to the researchers and for industrial practices.

Chapter 3

Materials, Methods and Characterization

3.1. Experimental Details

3.1.1. Materials

Chemicals, such as, cyclohexanone, cyclopentanone, potassium hydroxide, sodium hydroxide, methyl alcohol, ethyl alcohol, iso–propyl alcohol, n–butyl alcohol, toluene, tetrahydrofuran, ethyl acetate, acetic acid glacial, acetic anhydride, chloroform, iodine trichloride, iodine resublimed, potassium iodide, potassium hydrogen phthalate, sodium thiosulphate, n–butyl acetate extrapure were procured from S D Fine–Chemicals Ltd. (India) for the resin synthesis and analysis. Other chemical such as 2–methylcyclohexanone was procured from Acros Organics (India).

n–hexane, n–heptane, m–xylene were procured from Sisco Research Laboratories Pvt. Ltd. (India). Ethyl methyl ketone was procured from Rankem (India). Pyridine and p–toluenesulfonic acid monohydrate were procured from Fischer Scientific (India) and Loba Chemie Pvt. Ltd. (India) respectively. The analytical solvent mineral turpentine oil (MTO) was procured from Hychem Laboratories (India).

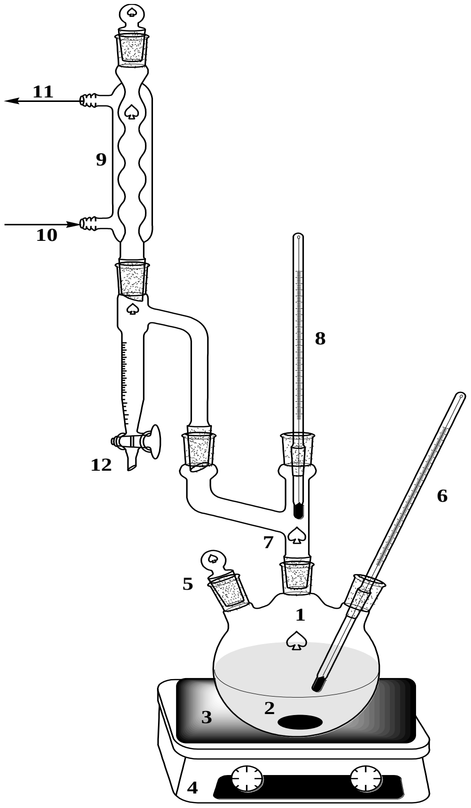
Synthetic commercial resins such as cashew nut shell liquid (CNSL)–formaldehyde viscous reddish brown resin (phenolic resin), and dehydrated castor oil (DCO) / Linseed long oil alkyd modified with cardphenol reddish brown resin (alkyd resin) were procured from Rishabh Resins and Chemicals (India).

3.1.2. Experimental setup and procedure

In the present study, two types of reactor system namely open system (under atmospheric pressure), and closed system (under elevated pressure) were considered to carry out the polymerization reaction. The experimental setup and procedure details of both the open and closed systems are described below.

3.1.2.1. Open system procedure details

Self–polymerization reactions of ketonic monomer under atmospheric pressure condition were conducted in a 250 mL capacity three–neck glass reactor, equipped with a magnetic stirrer and a Dean–Stark condenser. The reactor assembly was set in a thermostatic oil bath to maintain a constant (within ± 1 °C) temperature. A schematic diagram of the open system setup is shown in Figure 3.1. In all the runs, around 100 g of monomer was taken into the reactor and heated it to a desired reaction temperature under a stirring speed of 1000 ± 20 rev/min. Once the temperature reached to the pre–set value, calculated amount of alkali catalyst was added into the reactor, and the reaction was continued further for the desired time duration. During the polymerization reaction, the samples were withdrawn at a regular time interval to find the monomer conversion. At the end of reaction time, the reaction mass was cooled to room temperature and washed with water to remove the alkali from the liquid product. The washed material was dried using a hot air oven, and then analyzed for various physico–chemical properties.

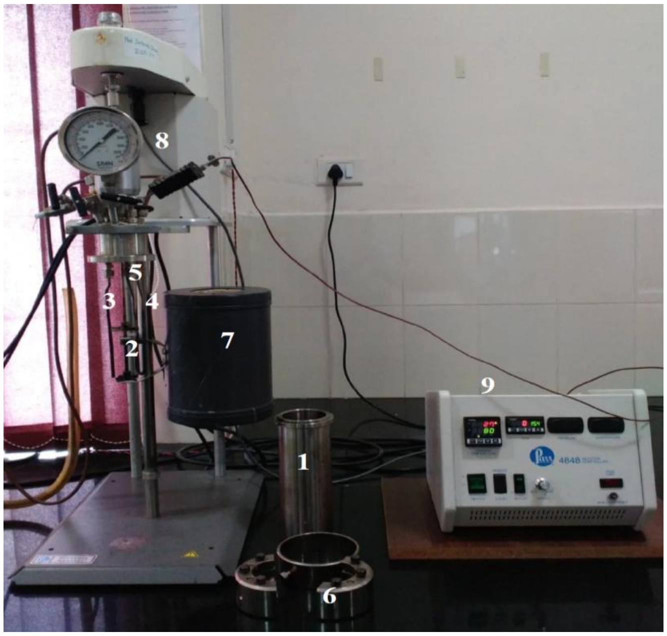


1. Three–neck round bottom flask
2. Magnetic mixture
3. Silicone–oil bath
4. Magnetic stirrer with hot plate
5. Sampling
6. Thermometer: temperature of reaction mass
7. Vapor line
8. Thermometer: temperature of vapor distillated
9. Condenser
10. Cold water
11. Hot water
12. Distillated water collector

Figure 3.1. A schematic of the open system setup

3.1.2.2. Closed system procedure details

Polymerization reactions were conducted in a 600 mL capacity high–pressure and high–temperature autoclave (Model–4568, Parr Instruments Co., USA) fitted with a stirrer, PID temperature controller, and auto cooling system. A schematic diagram of the closed system setup is shown in Figure 3.2. Around 150 g of ketonic monomer and calculated amount of methanolic alkali solution was taken into the reactor and the reaction was continued under a stirring speed of 1000 ± 20 rev/min. The reaction time and reaction temperature was varied from run–to–run as per the design of experiment. At the end of reaction time, the reaction mass was cooled to room temperature, and then collected from the reactor and powdered using a grinder. The powdered mass was washed with water to remove the alkali, and then dried using a hot air oven. The dried samples were then used for measuring its various physico–chemical properties. A typical flow sheet of experimental process is shown in Figure 3.3.



1. Stainless steel reactor
2. Stirrer
3. Sampling
4. Thermocouple
5. Cooling coil
6. Coupling
7. Heating mantle
8. Pressure gauge
9. Controller

Figure 3.2. A schematic of the closed system setup

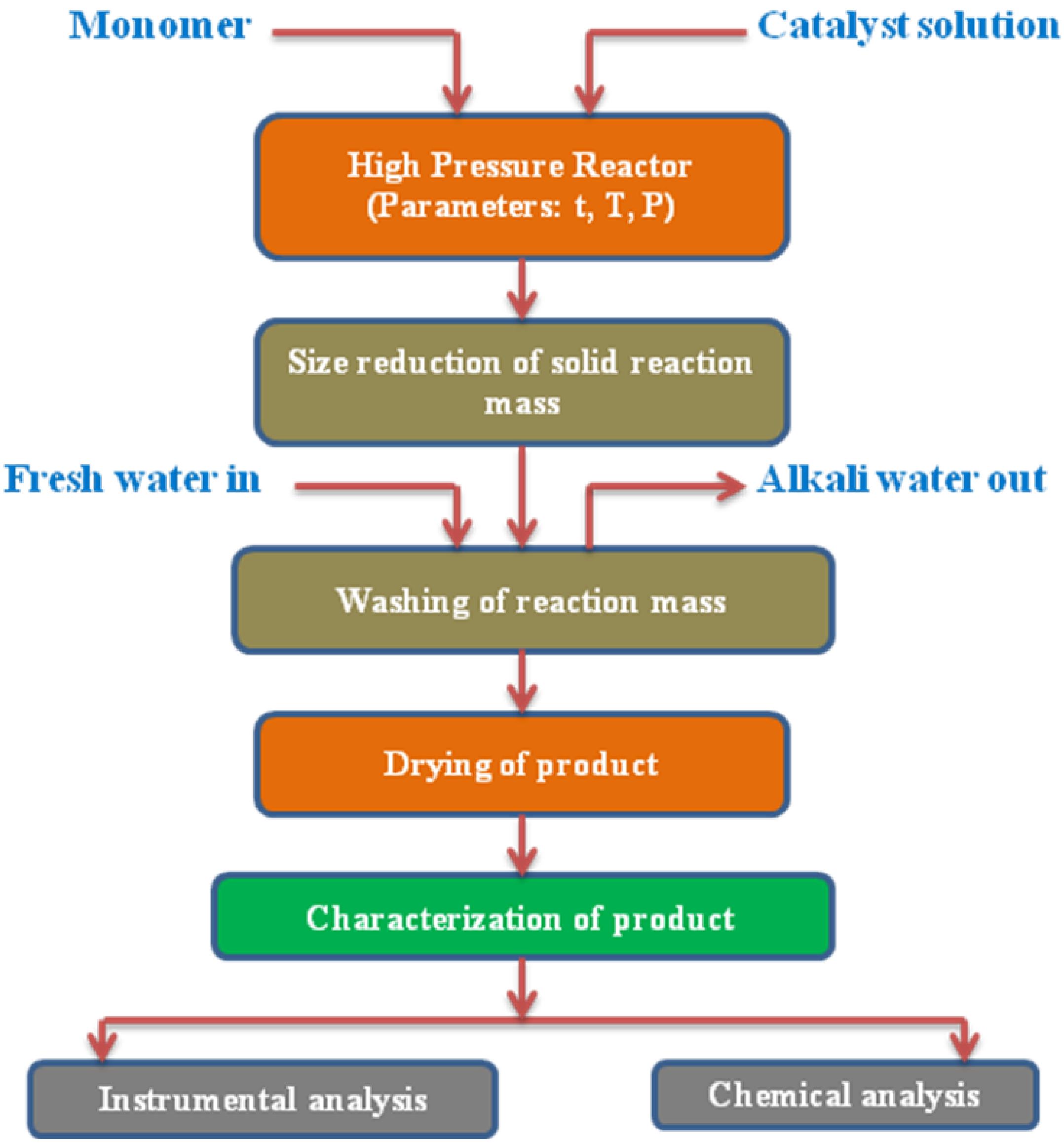


Figure 3.3. A typical flow sheet of resin preparation

3.2. Analysis Details

Chemical and instrumental analysis were carried out to investigate the various physico−chemical properties of the in−housed developed resins, and to study the kinetics of product formation and its thermal decomposition reaction. A description of each analysis procedure is given below.

3.2.1. Instrumental analysis

3.2.1.1. Moisture content analysis

The moisture content of the resin products after drying was determined using Karl−Fischer (KF) Titrator (MA−101C, Spectralab Instruments Pvt. Ltd., India). Initially 50 mL of iso−propyl alcohol (IPA) was added into the KF titrator and the moisture content present in IPA was neutralized by titrating with KF reagent. After neutralization of IPA solvent, around 50 mg of resin product was added into the titrating vessel and stirred for five minutes to dissolve the resin in IPA. Then the resin solution was titrated with KF reagent till the solution gets neutralized. The following expression was used to calculate the percentage moisture content in the resin product:

$$\text{Moisture content (wt\%)} = \frac{\text{Volume (mL) of KF reagent} \times \text{F}}{\text{Weight (mg) of resin sample}} \times 100 \qquad (3.1)$$

where, F is the KF reagent factor, mg/mL (F = wt. of water /vol. of KF reagent consumed). The estimated value of ‘F’ is 2.22 mg/mL.

3.2.1.2. Gas chromatography analysis

In the present research, a Gas Chromatography (GC) (Model No. 7820A, Agilent Technologies, USA) with flame ionization detector was used to find reactant and product conversions. A HP−5 column (30 m long × 0.32 mm ID) was used to separate the components. Iso−propyl alcohol (IPA) was used as a solvent to prepare the resin samples for GC analysis. Nitrogen gas was used as carrier gas, and the injector and detector temperature were maintained at 220 °C and 320 °C respectively during the sample analysis.

3.2.1.3. *Fourier transform infrared (FTIR) analysis*

Fourier Transform Infrared spectrometer (Model No. 4200, JASCO, Japan) was used to identify the characteristic peaks associated with different functional groups present in the resin products. The resin sample was mixed with KBr at a weight ratio of 1:100 (resin to KBr ratio) and the sample pellet was made using a die set for the FTIR analysis. The FTIR spectra of the resins were recorded in transmission mode within the wavenumber range between 4000–400 cm^{-1}.

3.2.1.4. *Viscosity analysis*

The solution viscosity and rheological properties of the resin products was measured using a Brookfield Rheometer (R/S Plus Coaxial Cylinder, Brookfield Engineering Laboratory Incorporation, USA) at a constant temperature. For the analysis of viscosity, samples were prepared by dissolving a resin in n–butyl acetate at a weight ratio of 1:1 (50% strength by weight). The measurements were carried out in forward as well as backward directions using shear rate as stimulus in the range from 0–900 and 900–0 1/s respectively. The measurements were performed for a duration of 60 s in each direction.

3.2.1.5. *Refractive index (RI) analysis*

The refractive index of the resin products was experimentally determined by using a refractometer (Model–R4, Advance Research Instruments Company, India) at a constant temperature. Samples were prepared by dissolving the resin material in THF solvent at different concentration such as 10, 30, 50 and 70% by weight. The measurements were recorded within the refractive index range between 1.3–1.7. The obtained refractive index values of resin samples at various concentrations were extrapolated to find the refractive index of the pure solid resin.

3.2.1.6. *Gel permeation chromatography (GPC) and MALDI-TOF analysis*

Average molecular weights of a polymer are very much useful to predict the degree of polymerization (DOP), and also to know the distribution of molecular weights of a polymer. For the present study, Gel Permeation Chromatography (GPC) instrument (GPC, 515 HPLC Pump, Waters, USA) fitted with Waters 2414 refractive index detector was used to determine the number–average molecular weight ($M_{n.avg}$), weight–average molecular weight ($M_{w.avg}$) and polydispersity index (PDI) of the in–house developed resin products. Samples were prepared by dissolving the resins in tetrahydrofuran (THF) solvent at a concentration of 5 mg/mL. The GPC measurement was performed at 30 °C, and with a solvent flow rate of 0.2 mL/min. Polystyrene materials were used as standards to calibrate the instrument.

For few cases, the average molecular weights of the resin products were determined by using a Matrix Assisted Laser Desorption Ionization Time–of–Flight (MALDI–TOF) Mass Spectrometer (Model No. 2.9.3.20110624, Shimadzu Biotech AXIMA Performance, UK). The observed variation in the average molecular weight of the product obtained from GPC and MALDI–TOF was around 5%.

3.2.1.7. X–Ray diffraction analysis

The X–ray diffraction (XRD) study was performed to find the degree of crystallinity of the resin products using a diffractometer (Rigaku Ultima–IV X–ray diffractometer, Japan). The diffractometer was equipped with a monochromatic Cu K_α radiation (λ=1.54 Å) light source. The diffraction angle (2–theta) was varied from 5 to 60^o at a rate of 2^o/min with a step width of 0.02°.

3.2.1.8. Scanning electron microscope (SEM) analysis

The surface morphology of the in–house developed resin samples was analyzed by using a scanning electron microscope (SEM) (FEI Quanta FEG 200, USA). Powdered resin samples were dispersed over the carbon tape which was stuck on the aluminium stub. Then the resin was sputter coated with gold and placed in the SEM instrument for the analysis. The measurements were carried out in a high vacuum mode using a voltage of 5 kV at different magnifications. In the SEM analysis, back–scattered electrons (BSE) signals were used to produce the surface morphology images of the resin materials.

3.2.1.9. Thermogravimetric analysis

To study the thermal stability and degradation characteristics of the in–house developed resin products, non–isothermal thermogravimetric analysis (TGA) was carried out using a simultaneous differential thermal analysis – thermogravimetric (DTA–TG) apparatus (DTG–60, Shimadzu, Japan). Around 5 mg of resin sample was taken into the platinum pan and heated it from 30 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The flow rate of nitrogen was maintained at 50 mL/min. The obtained TGA data was used to evaluate the decomposition kinetic and thermodynamic parameters.

3.2.1.10. Softening temperature determination

The softening temperature of the resin products were measured by using a softening point apparatus (VMP–DS, Veego Instruments Corp., India). The powdered resin sample was filled in a glass capillary tube and placed inside the oil bath. Then the temperature of the oil bath was increased gradually at a heating rate of around 2 °C/min. During the measurement, the transformation of the resin material inside the capillary was observed through the magnifying lens. The temperature at which the hard resin starts to become soft was considered as the softening temperature of the resin product.

3.2.1.11. Adhesive strength analysis

To estimate the adhesive strength of the resin products, adhesive strength tests were carried out using a lap shear strength tester equipped with 50 kg load cell (TA.XT plus Texture Analyser, Stable Micro Systems, UK). ASTM D3163 (Ebnesajjad, 2008) method was employed to determine the adhesive strength of the resin products. Cardboard material was used for testing the adhesiveness behavior of the resins. Around 0.5 g of solid resin was dissolved in 0.5 g of MTO solvent to prepare a gel of resin material. To prepare the specimen for the test, cardboard material was cut into rectangular (25.4 mm × 101.6 mm) shaped structure and then two such structures were fixed in a lap shear joint fashion with the resin sample at an overlap of 25.4 mm. The specimen was kept under 5 kg load for a duration of 24 hrs to enhance the physico–chemical interaction between the resin and the cardboard material before performing the tensile strength test. For the strength measurement, both ends of the cardboard sample were placed in the grips (jaws) of the test apparatus. One jaw was fixed and the other was allowed to move at a specific speed. The test was performed by pulling the specimen at a speed of 1.3 mm/min under auto trigger mode until the specimen breaks.

3.2.2. Chemical analysis

3.2.2.1. Hydroxyl value (HV) analysis

Hydroxyl value analysis was performed to estimate the free hydroxyl groups present in the resin products. ISO 4629 method was followed to estimate the hydroxyl value of the products (Paquot, 1979; Siggia and Hanna, 1979). The method details are as follows:

Around 2 g of resin sample was dissolved in 10 mL of chloroform in a 250 mL stopper flask, and then 5 mL of acetylating reagent (separately prepared) was added to it. Then the mixture was heated for around 20 min under reflux condition at a temperature of 50 ± 1 °C and stirred continuously. After that the reaction mass was allowed to cool to room temperature. Then 10 mL of pyridine–water mixture (3:1 ratio by volume) followed by 60 mL of toluene–butanol mixture (1:2 ratio by volume) was added to the contents and stirred for a minute. Then the mixture was titrated with 0.5 N methanolic KOH (previously standardized) solution in presence of phenolphthalein indicator. End point was identified by observing the color change from light yellowish solution to light pink solution. A blank test was carried out simultaneously without the resin sample under identical conditions. The following expression was used to calculate the hydroxyl value of the resin sample:

$$\text{Hydroxyl Value (mg KOH/g resin)} = \frac{(V_B - V_S) \times N \times 56.1}{W} \tag{3.2}$$

where, V_B is the volume of methanolic KOH solution consumed for blank test, mL;

V_S is the volume of methanolic KOH solution consumed for resin sample, mL;

N is the exact normality of methanolic KOH solution;

W is the exact weight of resin sample, g

Acetylating reagent was prepared by dissolving 4 g of p–toluenesulfonic acid monohydrate in 100 mL of ethyl acetate and then 33 mL of acetic anhydride was added to the solution.

3.2.2.2. Iodine value (IV) analysis

Iodine value analysis was performed to find the degree of unsaturation present in the product sample. Iodine value was determined according to Wij's method (Weiss, 1970). The method details are as follows:

Around 7 g of resin sample was dissolved in 10 mL of chloroform in a 250 mL stopper flask. Accurately measured 20 mL of Wij's solution (separately prepared) was added to the flask and the mixture was kept in dark for around 30 min. Then, 15 mL of 10% (by weight) potassium iodide solution and around 100 mL of distilled water were added to the mixture. Then the mixture was titrated with 0.1 N sodium thiosulphate solution (previously standardized) in presence of starch indicator. End point was identified by observing the color change from dark brown color solution to colorless solution. A blank test was carried out simultaneously without the resin sample under identical conditions. The following expression was used to calculate the iodine value of the resin samples:

$$\text{Iodine Value (g } I_2\text{/100 g resin)} = \frac{(V_B - V_S) \times N \times 12.69}{W} \qquad (3.3)$$

where, V_B is the volume of $Na_2S_2O_3$ solution consumed for blank test, mL;

V_S is the volume of $Na_2S_2O_3$ solution consumed for resin sample, mL;

N is the exact normality of $Na_2S_2O_3$ solution;

W is the exact weight of resin sample, g

Wij's solution was prepared by dissolving 9 g of iodine trichloride in 200 mL of glacial acetic acid, and 10 g of iodine in 300 mL of chloroform separately. Then the two solutions were mixed and made up to 1000 mL with glacial acetic acid.

3.2.2.3. *Acid value (AV) analysis*

Acid value test was carried out to estimate the free carboxylic acid group present in the resin sample. About 5 g of resin sample was dissolved in a neutralized mixture of 25 mL of toluene and 25 mL of ethanol. Then the solution was titrated with 0.1 N methanolic KOH solution (previously standardized) in presence of phenolphthalein indicator. End point was identified by observing the color change from light yellowish solution to light pink solution. The following expression was used to calculate acid value of the samples:

$$\text{Acid Value (mg KOH/g resin)} = \frac{V \times N \times 56.1}{W} \qquad (3.4)$$

where, V is the volume of methanolic KOH solution consumed by the resin sample, mL;

N is the exact normality of methanolic KOH solution;

W is the exact weight of resin sample, g

3.2.2.4. *Solubility analysis*

In the present study, mineral turpentine oil (MTO) solvent was used to find the solubility of resin products. To know the boiling range of the commercial MTO solvent, atmospheric distillation (ASTM D86) was carried out and the results are tabulated in Table 3.1. The estimated normal average boiling point of the MTO is around 194 °C.

Table 3.1 Boiling temperature range of the mineral turpentine oil (MTO)

Volume of distillate, ml	Boiling temperature, °C	Volume of distillate, ml	Boiling temperature, °C
IBP	138	50	189
10	164	60	198
20	171	70	207
30	178	80	214
40	182	90	230

For the analysis of solubility of the resin samples, 30 g of MTO was taken in a 100 mL conical flask and measured quantity of resin material was gradually added into the flask under stirring environment. During the test, the solution temperature was maintained at around 30 °C using a water bath. The process was repeated for several times until the solution gets saturated and the solubility of resin was expressed as weight percentage. The following expression was used to find percentage solubility of a resin sample in MTO.

$$\text{Solubility (wt\%)} = \frac{\text{Weight of resin sample}}{\text{Weight of MTO} + \text{Weight of resin sample}} \times 100 \qquad (3.5)$$

Chapter 4

Synthesis of Ketonic Resin from Cyclohexanone:

Under Atmospheric Pressure (Open System)

4.1. Introduction

Synthetic resins have been extensively used in the field of paints and coatings. In coating technology, resins are used to improve the glossiness and adhesiveness of paints, as a dispersant for pigments, and to improve weathering resistance. Synthetic resins are essentially polymers, which are built up from simple molecules called monomers by the virtue of polymerization reaction (Ebewele, 2000; Asua, 2007). Commonly used synthetic resins in coating technology are: alkyd resins, polyurethane resins, acrylic resins, phenolic resins, ketone-aldehyde resins, and ketonic resins etc. (Goldschmidt and Streitberger, 2007). It is known that ketones, aldehydes, or their mixtures can be converted to resinous materials in presence of acid or a base catalyst.

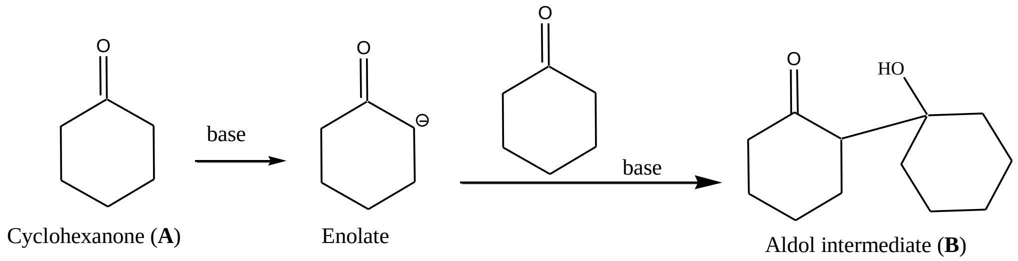
From the literature survey, it has been observed that most of the studies were carried out on dimerization reaction of cyclohexanone or alkyl cyclohexanone. Few studies are available in the literature on oligomerization or polymerization of cyclohexanone or alkyl cyclohexanone with aldehyde to obtain a ketone–aldehyde resin. It is also observed that most of the polymerization study was carried out in presence of sodium hydroxide (NaOH) as base catalyst. In addition, there is scanty information in the literature about the characterization and analysis of various properties of resin products. Therefore, in the present work, our objective is to develop a ketonic resin from cyclohexanone (as a model compound) under atmospheric pressure in presence of base catalyst. The other objective is to establish a standard analysis procedure to characterize a resin product.

4.2. Results and Discussion

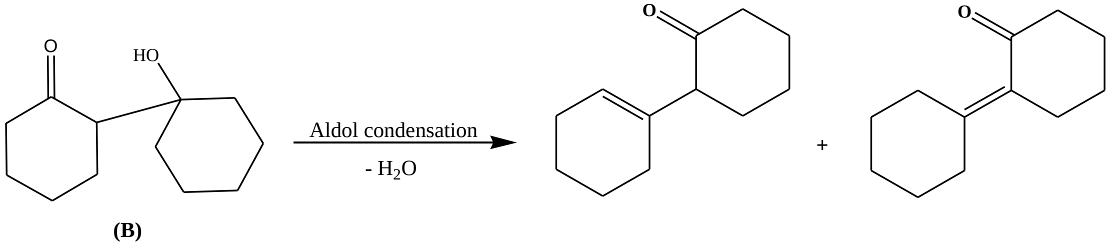
In the present work, a systematic study has been performed to develop a synthetic resin by self–oligomerization / polymerization of cyclohexanone in presence of a base catalyst. The reactions were conducted under atmospheric pressure using a three–neck glass reactor, equipped with a magnetic stirrer and a Dean–Stark condenser (referred as ‘open system’). The experimental details are mentioned in Chapter 3. To investigate the effects of operating parameters on cyclohexanone (monomer) conversion and physico–chemical properties of the final products, reaction time was varied from 7 to 20 hrs, catalyst loading (expressed as alkali–to–ketone weight ratio, ‘A/K ratio’) was varied from 0.05 to 0.2, and temperature was varied from 90 to 140 °C. In addition, an effort has been made to characterize the products by analyzing its various physico–chemical properties, such as hydroxyl content, iodine value, acid value, viscosity, solubility, and average molecular weight. The products obtained from open system are coded as ‘**OS**’ followed by a run number. The synthesis details of the products are tabulated in Table 4A at the end of the present chapter.

4.2.1. Reaction scheme

In presence of a non–nucleophilic base, cyclohexanone initially turns to enolate by losing α–hydrogen. The formed enolate then reacts with the carbonyl group of second cyclohexanone molecule and forms aldol intermediate (B). The polymerization reaction proceeds further by the reaction between the carbonyl group of third cyclohexanone molecule and the activated methylene group of the aldol intermediate. The most probable dimeric (monomer repeating unit (n) =1) and polymeric (n ≥2) structures of base-catalyzed polymerization of cyclohexanone are shown in Figure 4.1.



(a) Condensation route (undesired path):



(b) Polymerization route (desired path):

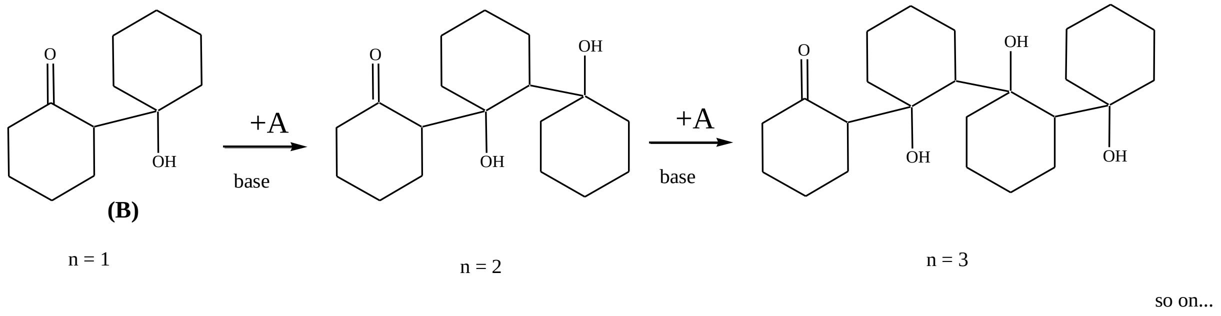


Figure 4.1. Probable reaction scheme of base–catalyzed aldol condensation, and polymerization of cyclohexanone

4.2.2. Effect of alkali loading on monomer conversion and product properties

To find the effect of alkali loading on monomer conversion and product properties, a set of reactions were carried out with four different A/K ratios at 110 °C for a fixed duration of 10 hrs, and the results are shown in Figure 4.2 and Table 4.1. The figure shows that both monomer conversion (Figure 4.2a) and hydroxyl value (Figure 4.2b) increased with the increase of alkali concentration. Around 1.6 fold increment in hydroxyl value was observed when the A/K ratio was increased from 0.05 to 0.2. Although there was no significant variation in iodine values but a decreasing trend was observed when the alkali concentration was increased from 0.05 to 0.2 (Figure 4.2c). The increasing trend of hydroxyl values of the products indicates that the rate of polymerization reaction increased with the increase of alkali concentration. A decreasing trend in acid values (Table 4.1) with alkali concentration was observed, though there was no significant change in acid values of the products. The decrease in acid values with the increase of A/K ratio may be due to the availability of more hydroxyl ions to the reactants for the polymerization reaction compared to thermal oxidation. The solubility of the products in MTO decreased with the increase of alkali concentration, and the viscosity of the products increased with the increase in alkali concentration. The decreasing trend of solubility and an increasing trend of viscosity confirmed that the degree of polymerization increased with the increase of A/K ratio. Therefore, based on the experimental observation it can be said that, A/K ratio may be a critical parameter to obtain a desirable quality of product.

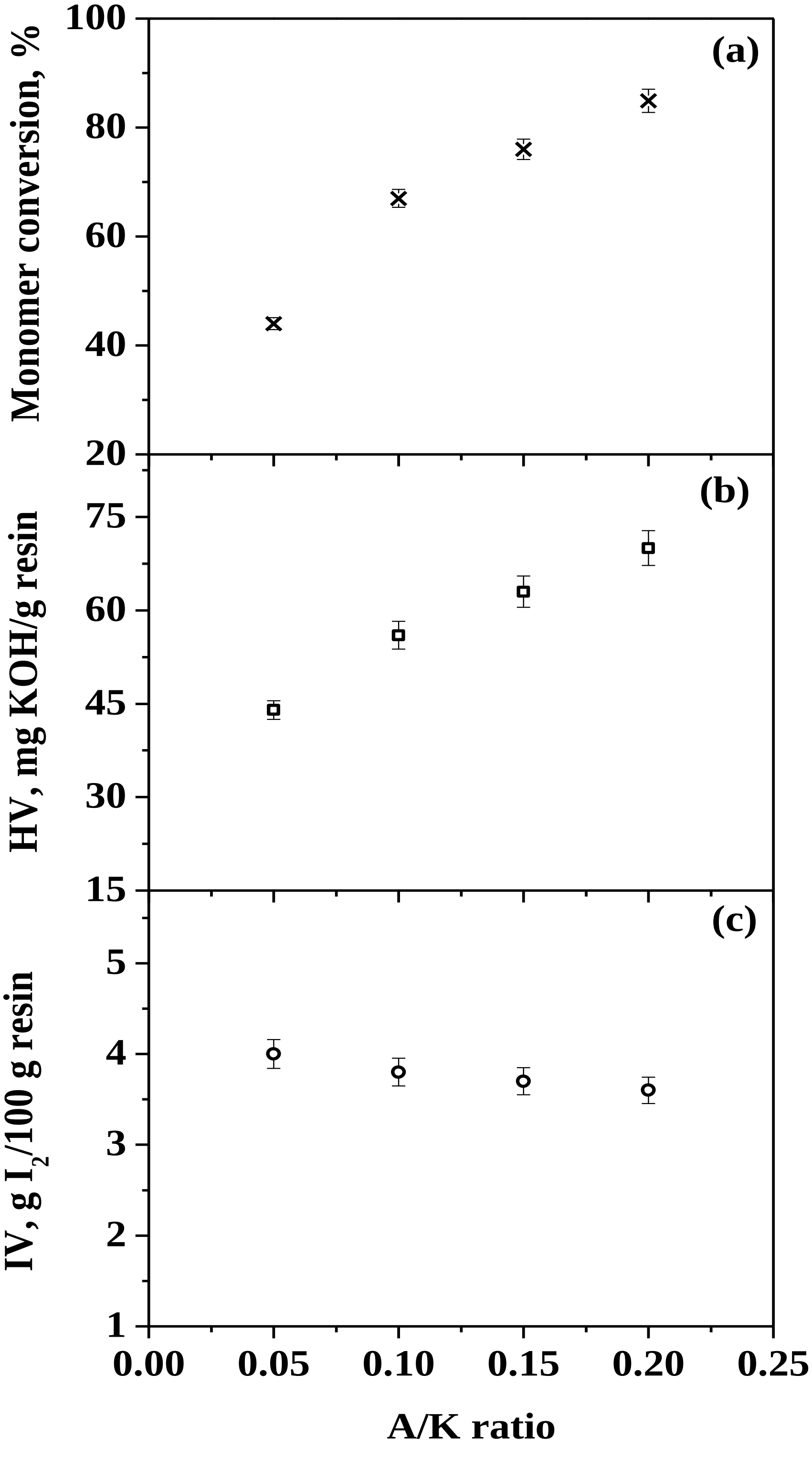


Figure 4.2. Effect of alkali loading on **(a)** monomer conversion, **(b)** hydroxyl value, and **(c)** iodine value (IV) of the products (reaction conditions: reaction temp. = 110 °C, time = 10 hrs) (Product ID: OS–5, OS–6, OS–7, OS–8)

Table 4.1. Effect of alkali loading on physico–chemical properties of the products*

Product ID	OS–5	OS–6	OS–7	OS–8
A/K ratio, wt/wt	0.05	0.1	0.15	0.2
Physical state	VL	VL	VL	VL
Acid value, mg KOH/g resin	0.53	0.48	0.4	0.31
Solubility in MTO at 30 °C, wt%	88	87	85	82
Viscosity at 30 °C, cP	22	29	43	52

*Reaction conditions: reaction time = 10 hrs, reaction temp. = 110 °C

4.2.3. Effect of reaction temperature on monomer conversion and product properties

To investigate the effect of reaction temperature on monomer conversion and physico–chemical properties of the products, polymerization reactions were carried out at different temperatures ranging from 90 to 140 °C at a fixed A/K ratio. The effect of temperature on monomer conversion, hydroxyl value, and iodine value is shown in Figure 4.3. The figure (Figure 4.3a) shows that monomer conversion increased with the increase of reaction temperature from 90 to 110 °C. However, a decreasing trend of monomer conversion was observed when the temperature increased from 110 to 130 °C. The decrease of conversion at higher temperature may be due to the elimination of water molecule from aldol intermediate at an enhanced rate, and the presence of water in the reaction medium helps to setup equilibrium at early stage. Similar kind of observation was reported by other research groups too (Yogesh et al., 2008; Yeqiang et al., 2011). The water content in the reaction mixture was confirmed from the Karl–Fisher titration. The presence of C=C bond (from FTIR analysis) also supports the elimination of water molecule during the course of reaction. The plot shows that when the temperature was further increased from 130 to 140 °C, monomer conversion slightly increased. The reason behind the fact may be due to the escaping of water molecules from the reaction medium at higher temperature. Under the present experimental environment, the obtained monomer conversion was around 85% at 110 °C.

Figure 4.3b shows that hydroxyl value of the products increased with the increase of reaction temperature from 90 to 110 °C. However, a drop in hydroxyl value was observed when the temperature was increased from 110 to 130 °C. When the temperature was further increased from 130 to 140 °C, an increasing trend of hydroxyl values was observed. The reason for increase in hydroxyl value at higher temperature (130−140 °C) is due to the slight increase in monomer conversion with temperature. The variation in hydroxyl value with temperature was further confirmed from the iodine value analysis results. The result shows that no remarkable difference in iodine values of the products was observed below 110 °C (Figure 4.3c). However, an increasing trend in iodine value was observed when the temperature was increased from 110 to 140 °C. The iodine value was around 1.6-fold higher when the temperature was increased from 130 to 140 °C. The result indicates that the rate of condensation is more in comparison with the rate of polymerization with the increase of reaction temperature under present experimental conditions. Product with higher iodine value is not a favorable for the present objective. From the present study, it can be concluded that higher temperature (>110 °C) may not be a good option to carry out the self–polymerization reaction. Therefore, most of the successive runs were carried out at 110 °C.

The effect of temperature on other physico−chemical properties such as acid value, solubility, and viscosity of the products are shown in Table 4.2. The data shows that, though there was no significant variation in acid values among the products, but an increasing trend was observed with reaction temperature. The average value of acid value of the products was around 0.35 mg KOH/g resin. The solubility of the products in MTO solvent decreased with the increase of temperature from 90 to 110 °C. The decrease of solubility was due to the increase of extent of polymerization with temperature. However, an increasing trend in solubility was observed when the temperature was further increased from 120 to 140 °C. The variation of solubility with temperature was confirmed from the analysis of product viscosity. The result shows that viscosity followed an inverse trend of solubility, and which is quite true for polymeric materials. Sample with higher viscosity indicates that the average molecular weight of the sample is relatively higher and consequently the solubility is lower. Therefore, based on the experimental results, it can be said that selection of temperature is another important parameter for the present polymerization reactions to obtain a desirable product.

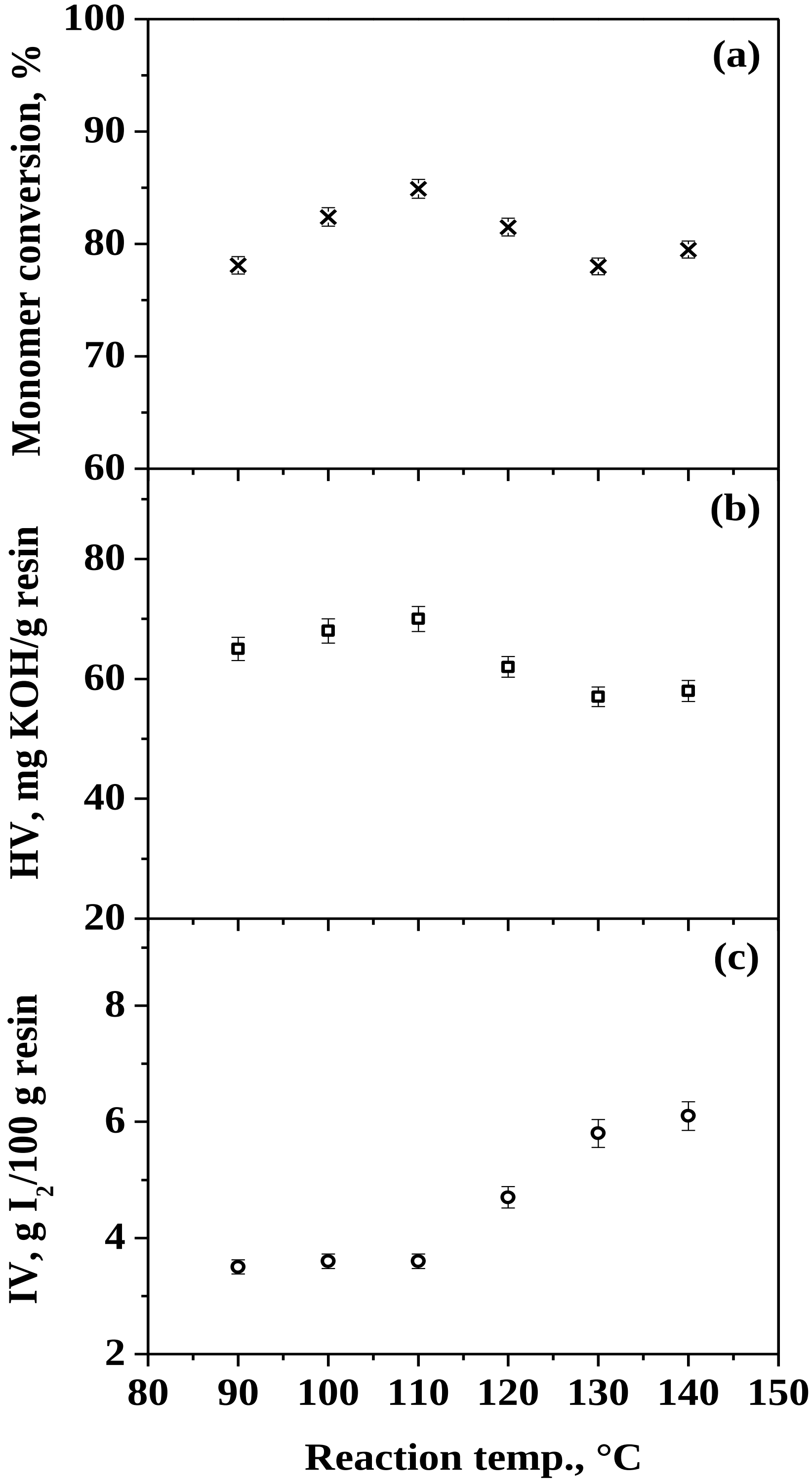


Figure 4.3. Effect of temperature on **(a)** monomer conversion, **(b)** hydroxyl value, and **(c)** iodine value of products (reaction conditions: reaction time = 10 hrs, A/K ratio = 0.2)

(Product ID: OS−4, OS−18, OS−8, OS−20, OS−12, OS−24)

Table 4.2. Effect of temperature on physico–chemical properties of the products*

Product ID	OS−4	OS−18	OS−8	OS−20	OS−12	OS−24
Reaction temp., °C	90	100	110	120	130	140
Physical state	VL	VL	VL	VL	VL	VL
Acid value, mg KOH/g resin	0.29	0.29	0.31	0.34	0.37	0.40
Solubility in MTO at 30 °C, wt%	86	85	82	83	85	86
Viscosity at 30 °C, cP	42	45	52	50	44	42

*Reaction conditions: time = 10 hrs, A/K ratio = 0.2

4.2.4. Effect of reaction time on monomer conversion and product properties

To find the effect of reaction time on monomer conversion, and physico−chemical properties of the final product, a set of reactions were carried out for different time duration at a fixed temperature and alkali concentration. The conversion of monomer was calculated from the GC analysis results. A typical chromatogram of GC analysis of a sample is shown in Figure 4.4. Total five peaks were found from the GC analysis. Peak−1 corresponds to solvent, peak−2 corresponds to cyclohexanone monomer, peak−3 corresponds to dimer product, peak−4 and peak−5 are corresponds to oligomer products. The effect of reaction time on monomer conversion and product properties such as hydroxyl value, iodine value is shown in Figure 4.5. The plot (Figure 4.5a) shows that monomer conversion increased with the increase of reaction time from 7 to 13 hrs at a fixed temperature and A/K ratio. However, when the reaction time was further increased from 13 to 20 hrs, no significant change in monomer conversion was observed. The estimated monomer conversion after 13 and 20 hrs was around 86% and 87% respectively. The small variation in monomer conversion after 13 hrs indicates that the reaction reached towards the equilibrium state under present experimental conditions. Figure 4.5b shows that hydroxyl value of the products increased with the increase of reaction time. The increase of hydroxyl value indicates that the extent of polymerization increased with reaction time. The experimentally obtained hydroxyl values of the products after 13 and 20 hrs are around 74 and 83 mg KOH/g resin respectively. Figure 4.5c shows that there was no significant change in iodine value of the samples with reaction time. However, a decreasing trend of iodine value was observed. The experimentally determined average iodine value of the products was around 3.5 g I_2/100 g sample.

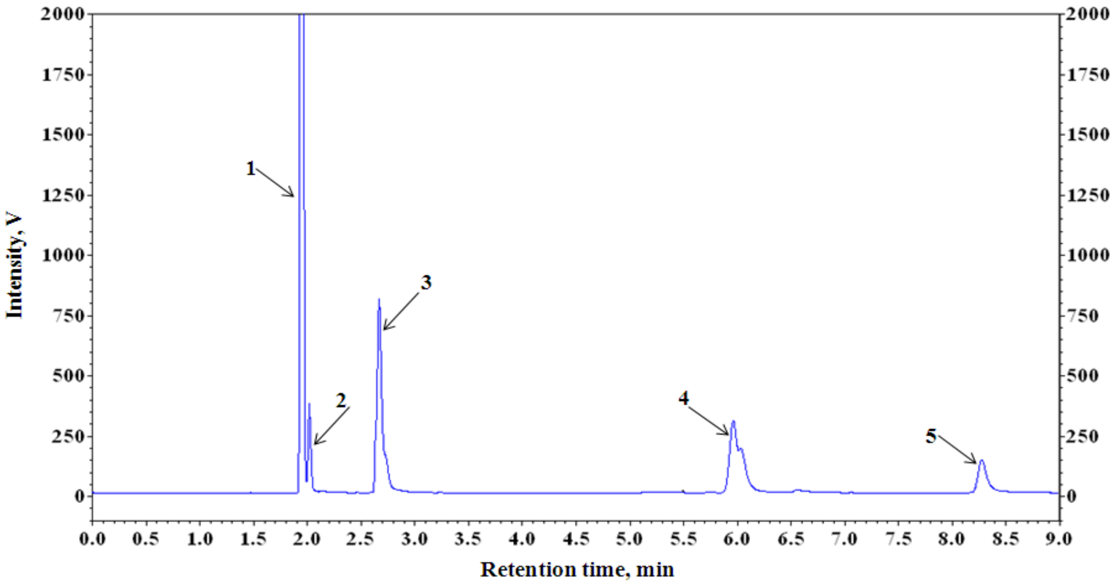


Figure 4.4. GC plot of a product sample (reaction conditions: time = 20 hrs, temp. = 110 °C, A/K ratio = 0.2) (Product ID: OS–28)

The variation of other physico–chemical properties such as acid value, solubility, viscosity, and moisture content of the products with reaction time are shown in Table 4.3. The result shows that there was no significant change in acid values of the products with reaction time. The average acid value of the product samples was around 0.3 mg KOH/g resin. The data shows that solubility of the products in MTO decreased with the increase of reaction time. The reason for the gradual decrease in solubility was due to the increase in average molecular weight of the products with time. The measured solubility of 20 hrs sample was around 66 wt%. The data also shows that viscosity of the products increased with the increase of reaction time. Both the phenomena (i.e. decrease of solubility and increase of viscosity with time) clearly indicates that the extent of polymerization increased with reaction time. The average value of moisture content in the products was around 1.8 wt%.

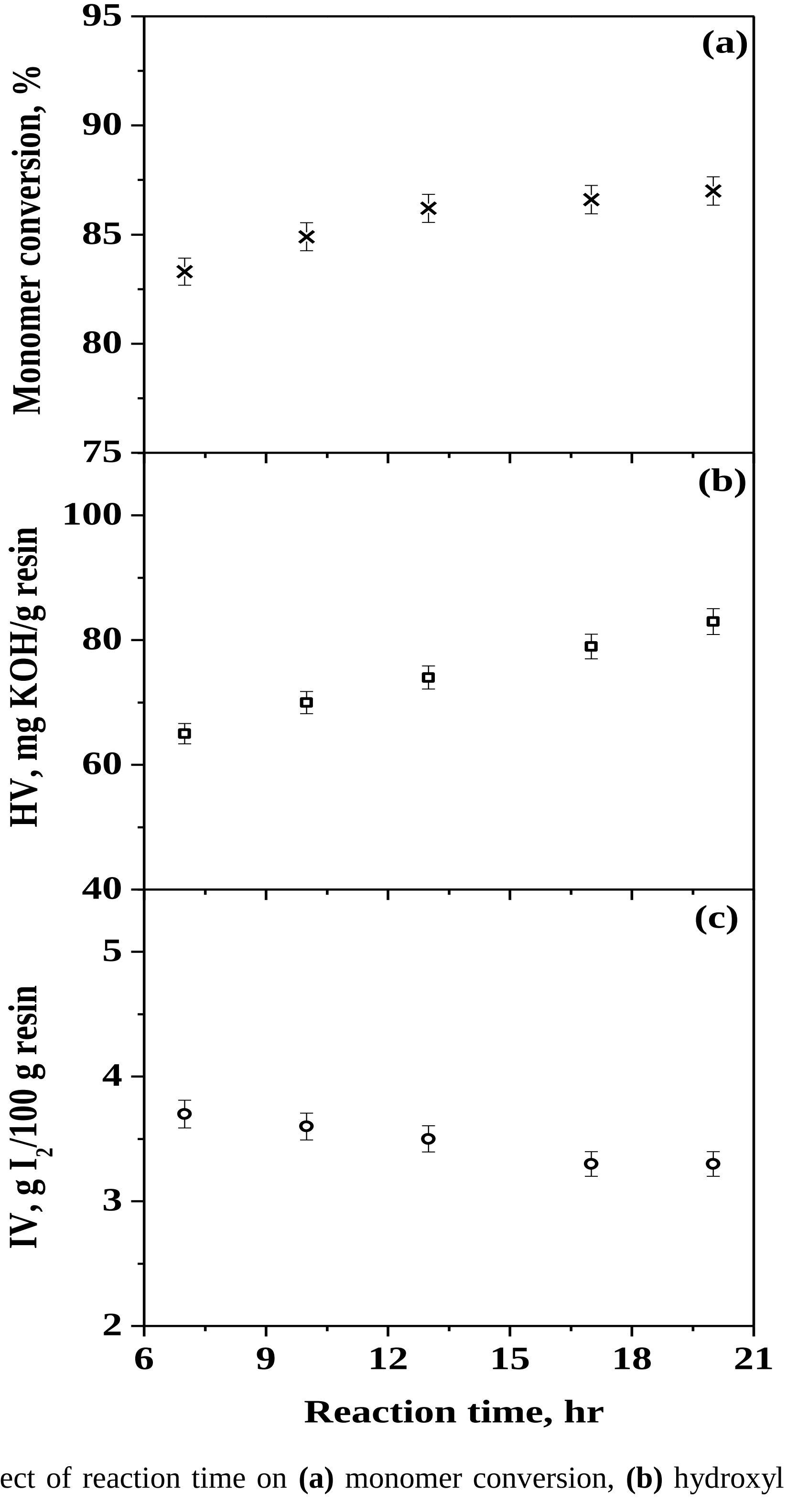


Figure 4.5. Effect of reaction time on **(a)** monomer conversion, **(b)** hydroxyl value, and **(c)** iodine value of products (reaction conditions: temp. = 110 °C, A/K ratio = 0.2)

(Product ID: OS–25, OS–8, OS–26, OS–27, OS–28)

Table 4.3. Effect of reaction time on physico–chemical properties of the products*

Product ID	OS–25	OS–8	OS–26	OS–27	OS–28
Reaction time, hr	7	10	13	17	20
Physical state	VL**	VL	VL	VL	VL
Acid value, mg KOH/g resin	0.28	0.31	0.30	0.28	0.28
Solubility in MTO at 30 °C, wt%	86	82	72	69	66
Viscosity at 30 °C, cP	44	52	83	153	171
Moisture content, wt%	1.6	1.8	1.7	1.9	1.8

*Reaction conditions: temp. = 110 °C, A/K ratio = 0.2.

**VL = viscous liquid

To know the rheological behavior of the resin samples, rheology study was performed using a Brookfield make Rheometer. Typical rheogram of a product sample is shown in Figure 4.6. The figure shows that shear stress increased linearly with shear rate. Based on the nature of plot it can be said that the sample behaves like a Newtonian fluid under the present experimental condition.

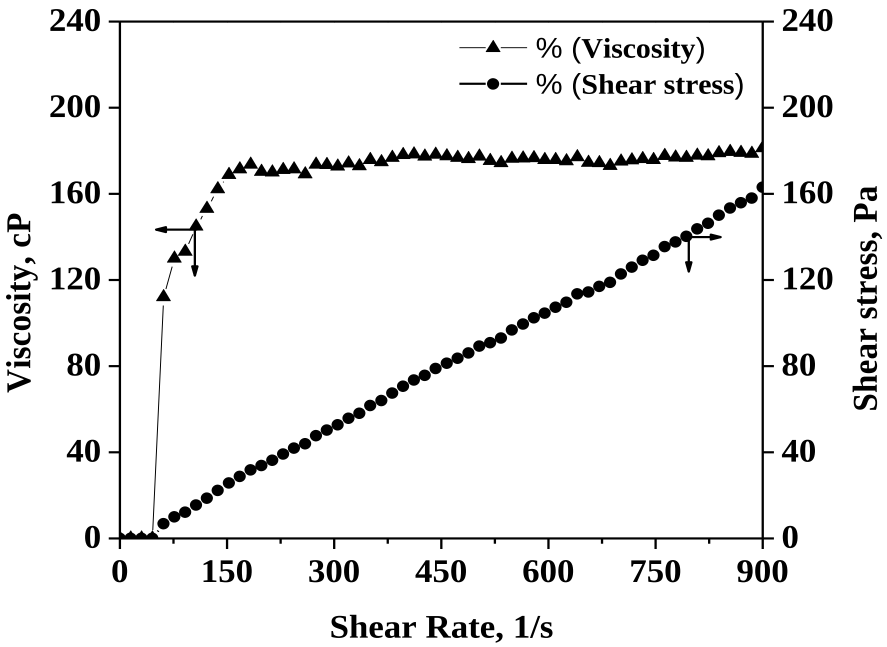


Figure 4.6. Rheogram of a product (reaction conditions: temp. = 110 °C, A/K ratio = 0.2, reaction time = 20 hrs) (Product ID: OS–28)

The presence of a specific functional group in a polymer is useful to modify the physico–chemical properties like adhesiveness, solubility, and film–forming ability of the polymer. Hydroxyl content in a polymer is also an important characteristic to analyze the degree of polymerization. The reactivity of the hydroxyl group plays a vital role on film formation properties of a resin (Solomon and Hopwood, 1966). To identify the functional group present in the monomer and product samples, FTIR analysis was performed for both the monomer and product samples. A typical FTIR spectrum of monomer and product is shown in Figure 4.7. The figure shows that, no characteristic band corresponding to O–H stretching at around 3430 cm^{-1} was observed for cyclohexanone monomer. On the other hand, a broad band at 3429 cm^{-1} and a peak at 1648 cm^{-1} indicates the presence of O–H group and C=C bond respectively in the product. The other characteristic bands at 2928 cm^{-1} and 1714 cm^{-1} corresponds to C–H stretching and C=O stretching respectively. The presence of O–H group in the product confirms the progress of polymerization reaction of cyclohexanone.

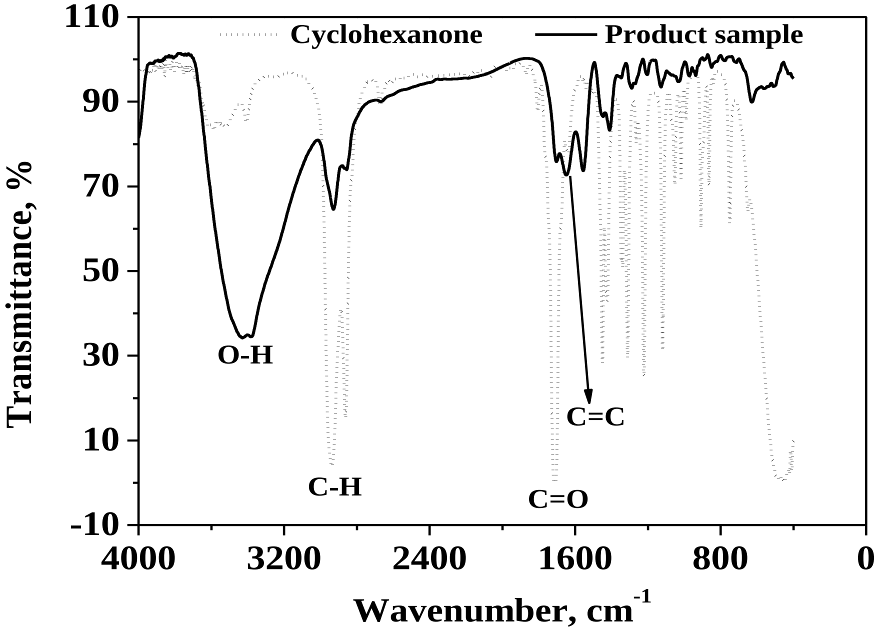


Figure 4.7. FTIR spectra of cyclohexanone monomer and a product sample (reaction conditions: temp. = 110 °C, A/K ratio = 0.2, reaction time = 20 hrs) (Product ID: OS–28)

In this study, it was observed that the hydroxyl value of the products increased with the increase of reaction time, temperature and catalyst loading. Hydroxyl content in a polymer can also provide information on the degree of polymerization. In the present study, the qualitative variation of hydroxyl value with reaction conditions was also confirmed from the FTIR analysis. The variation of hydroxyl content with reaction time from FTIR analysis is shown in Figure 4.8. From the figure, it was observed that the area under the curve of the hydroxyl (O–H) group increases with the increase of reaction time for a fixed reaction time and temperature. The increase in area of O–H group indicates the increase of hydroxyl value in the product. Therefore, from the results it can be concluded that FTIR analysis can be used to get a qualitative insight on hydroxyl value and degree of polymerization.

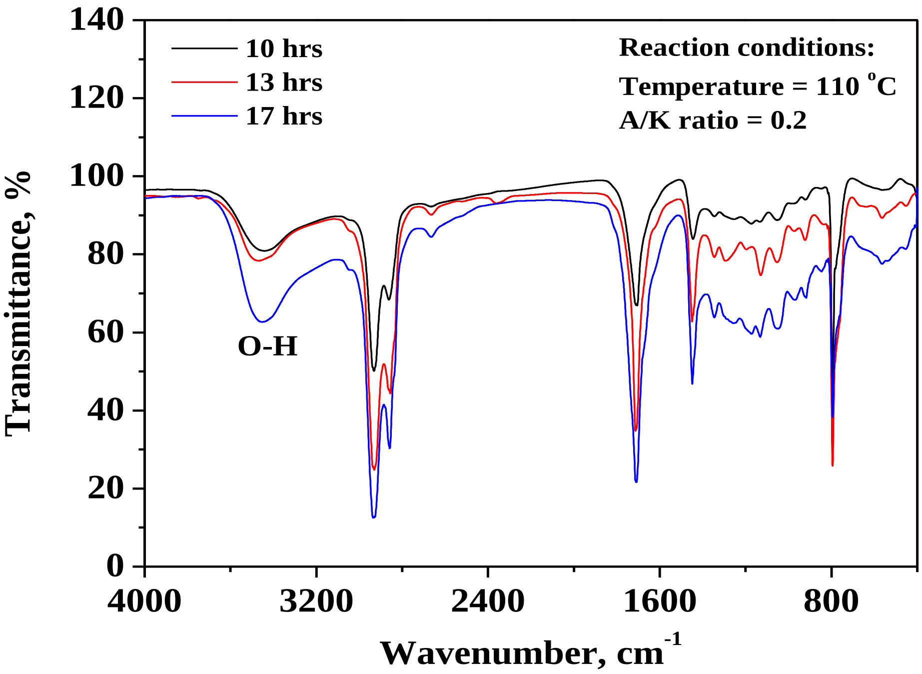


Figure 4.8. FTIR spectrums of resin products with respect to reaction time (Product ID: OS–8, OS–26, OS–27)

4.2.5. Comparison between KOH and NaOH as base catalysts

The cost of NaOH is relatively cheaper than KOH, and it can also act as a base catalyst. Therefore, to investigate the effectiveness or suitability of NaOH for the present study, few experiments were conducted with NaOH as a substitute of KOH under identical conditions. A comparison between NaOH vis–a–vis KOH on monomer conversion and product properties are shown in Table 4.4. The result shows that the monomer conversion was relatively higher with KOH compared to NaOH as base catalyst for the same mole ratio. Lower value of hydroxyl content and lower viscosity of the products in presence of NaOH indicates that the progress of polymerization was relatively poor in presence of NaOH catalyst. Therefore, based on the results, it can be concluded that KOH offered comparatively better performance over NaOH under present experimental conditions.

Table 4.4. Comparison between KOH and NaOH on monomer conversion and product properties

	KOH	NaOH
Product ID	OS–29	OS–30
Reaction temp., °C	110	110
Reaction time, hr	10	10
A/K mole ratio, mol/mol	0.3	0.3
Monomer conversion, %	78	62
Solubility in MTO at 30 °C, wt%	83	89
Viscosity at 30 °C, cP	45	32
Hydroxyl value, mg KOH/g resin	65	54
Iodine value, g I_2/100 g resin	3.7	4.1

4.2.6. Determination of molecular weight of the product

MALDI−TOF mass spectrometry analysis was performed to find the average molecular weight of the products, and also the distribution of molecular weights. Typical MALDI−TOF mass spectrum of a specific sample is shown in Figure 4.9. The spectrum shows that the molecular weight distribution of a product obtained from open system was in the range of 200−700 g/mol. The calculated average molecular weights of the products lie in the range of 300–500 g/mol.

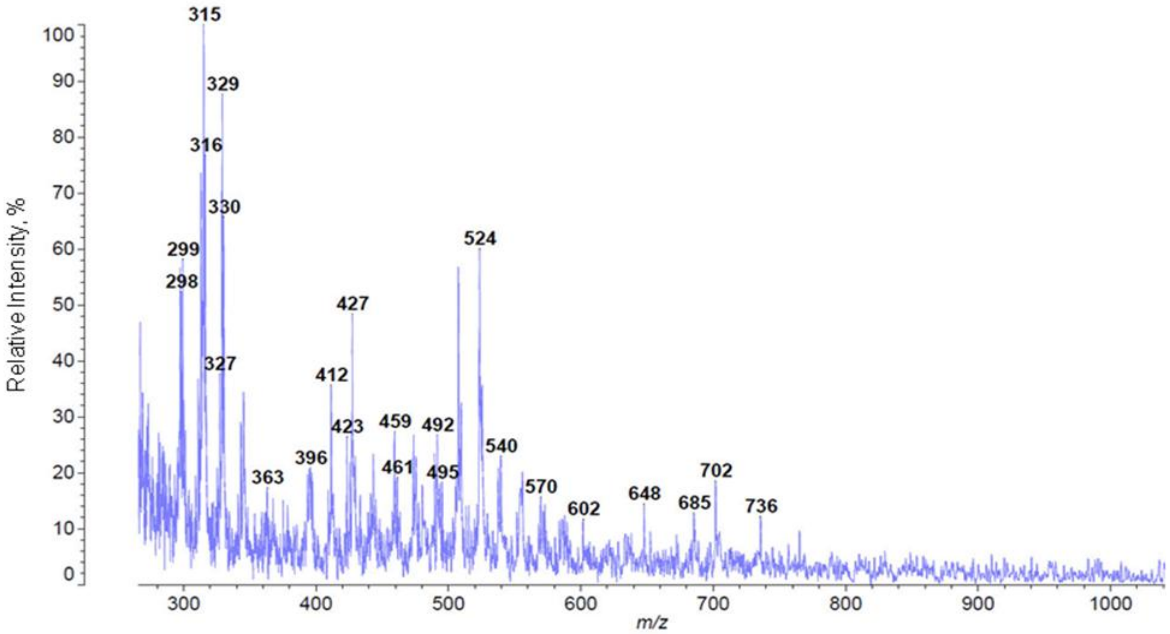


Figure 4.9. MALDI–TOF mass spectrum of a product (reaction conditions: time = 20 hrs, temp. = 110 °C, A/K ratio = 0.2) (Product ID: OS–28)

4.3. Conclusions

In the present work, a systematic study has been performed to develop a ketonic resin from cyclohexanone monomer in presence of a base catalyst. In addition, an effort has been made to characterize a product by analyzing its various physico–chemical properties such as hydroxyl content, iodine value, acid value, solubility, viscosity and average molecular weight. The self–polymerization reaction was carried out under atmospheric pressure using a glass reactor. It has been observed that the progress of polymerization of cyclohexanone depends on alkali concentration, reaction temperature, and reaction time. The degree of polymerization increased with the increase of catalyst loading and reaction time. Reaction temperature greater than 110 °C shows some detrimental effect on monomer conversion and product properties under atmospheric pressure. Viscosity of the products increased substantially when the reaction time was increased from 7–20 hrs. The study confirmed that KOH offers better quality product than NaOH as a base catalyst. The average molecular weight of the products lies in the range of 300–500 g/mol. The above findings will be very much useful in obtaining insight on polymerization reaction with respect to process parameters to obtain a good quality of oligomer/polymer product for paints and coating applications. The summary of the product properties obtained at various reaction conditions is shown in Table 4.5.

Table 4.5. Summary of the product properties obtained from open system study

Physical state of the product	Viscous liquid
Hydroxyl value, mg KOH/g resin	40 – 85
Iodine value, g I_2/100 g resin	3.0 – 6.0
Acid value, mg KOH/g resin	0.25 – 0.55
Solubility in MTO at 30 °C, wt%	65 – 90

From the results, it can be concluded that open system study offered viscous liquid product with a maximum hydroxyl value of around 85 mg KOH/g resin. Moreover, the liquid product with lower hydroxyl value and higher unsaturation may not be suitable for paint and coating applications. Therefore, it is a necessary requirement to select a suitable system to develop a solid resin product with desired property which could be suitable for paint and coating applications. Hence, the objective of the forthcoming study is to find the suitability of the closed system to carry out the polymerization reactions.

Table 4A. Synthesis details of the open system products

Product ID	Reaction time, hr	Reaction temp., °C	A/K ratio, wt/wt
OS–4	10	90	0.2
OS–5	10	110	0.05
OS–6	10	110	0.1
OS–7	10	110	0.15
OS–8	10	110	0.2
OS–12	10	130	0.2
OS–18	10	100	0.2
OS–20	10	120	0.2
OS–24	10	140	0.2
OS–25	7	110	0.2
OS–26	13	110	0.2
OS–27	17	110	0.2
OS–28	20	110	0.2
OS–29	10	110	0.3[*]
OS–30	10	110	0.3[*]

[*] A/K ratio was in terms of mol/mol instead of wt/wt

<u>Chapter 5</u>

Preparation of Ketonic Resin from Cyclohexanone

Using Pressurized System (Closed System)

5.1. Introduction

It was observed that the resin obtained from the open system study (in Chapter 4) was in the form of viscous liquid. The maximum value of hydroxyl content of the resin was around 85 mg KOH/g resin. A liquid product with lower hydroxyl value and higher iodine value may not be a suitable material for paint and coating applications. A resin would be suitable for coating application, if its hydroxyl value is greater than 110 mg of KOH/g of resin, solubility is greater than 25 wt% in MTO, softening temperature is around 80 °C and iodine value is around 3 g of I_2/100 g resin. Therefore, the objective of the present study is, to develop a desired quality synthetic resin at elevated temperature and pressure from a ketonic monomer (cyclohexanone) for paint and coating applications. An autoclave reactor (closed system) was used to carry out the self–polymerization reaction at elevated temperature and higher pressure. The other objective is to establish a standard analysis protocol to characterize various properties like hydroxyl value, iodine value, viscosity, solubility, softening temperature, average molecular weight, refractive index, thermal stability, crystallinity and surface morphology and adhesive strength etc. of the resin products. The third objective is to quantify the effects of various parameters on physico–chemical properties of a resin product.

In the present study, around 150 g of cyclohexanone (CH) and calculated amount of methanolic alkali solution was taken into the reactor and the reaction was continued under stirring condition. The experimental details are mentioned in Chapter 3. The reaction time and reaction temperature was varied from run–to–run according to the experimental planning. At the end of reaction time, the reaction mass was cooled to room temperature and powdered. The powdered mass was washed with water to remove the alkali, and then dried using a hot air oven. The dried sample was then used for analysis of its various physico–chemical properties.

5.2. Results and Discussion

Self–polymerization of cyclohexanone was carried out in presence of potassium hydroxide (KOH) as a base catalyst. Various aspects like, synthesis of ketonic resin, effect of reaction parameters on product properties, and characterization of resin products has been investigated in the present work. The stirring speed range of 300−1200 revolutions per minute (rpm), reaction temperature range of 130−160 °C, reaction time from 10 to 20 hrs, catalyst concentration (expressed as A/K weight ratio) range of 0.1−0.4, and reactor pressure range of 1−12 kg/cm^2(g) were considered for the preset study. The products obtained from closed system are coded as '**CS**' followed by a run number. The synthesis details of the resin products are tabulated in Table 5A at the end of the present chapter.

5.2.1. Effect of solvent / autogenously developed pressure on polymerization reaction

In the previous study (Chapter 4), the reactions were carried out in a glass reactor by adding solid KOH directly to the cyclohexanone; and the obtained products were in the form of viscous liquid (VL) with lower hydroxyl values. Therefore, in the present study, to enhance the catalytic activity of KOH and to reduce the mass transfer resistance, few set of experiments were conducted by dissolving the solid alkali in an inert solvent (methanol) prior to mix with cyclohexanone and the reaction was carried out in a closed system (Parr reactor) under autogenously developed pressure. Parr reactor was used to restrict the evaporation loss of reactants and products at higher temperature. A comparison of product properties under atmospheric pressure (open system) and autogenously developed pressure (closed system with and without solvent) are shown in Table 5.1.

The result (Table 5.1) shows that products (CS−2 and CS-4)) obtained from the closed system possess higher viscosity and hydroxyl value compared to the product obtained from the open system (OS−12) under identical temperature, time and alkali concentration. The viscosity and hydroxyl value of the product (CS−4) further increased in presence of methanol solvent. The reasons for the improved product properties may be due to the autogenously developed pressure effects, and enhanced utilization of the catalyst. The autogenously developed pressure helped to retard the water elimination reaction (Figure 4.1a) and enhanced the polymerization reaction (Figure 4.1b). The inert solvent helped to solubilize the catalyst and to minimize any deposition of polymer material on the catalyst. The increased accessibility of reactant molecule favored the polymerization reaction. The other advantages of inert solvent are: it reduces the medium viscosity, offers better mixing, and better heat and mass transfer effect within the reaction medium. All these effects have a positive role to enhance the degree of polymerization reaction. The improvement in degree of polymerization was further confirmed from the iodine value data. Therefore, based on the above results it can be said that solvent has positive effect on the polymerization reaction to obtain a better quality product.

Table 5.1. Comparison of product properties between open system and closed system

	Open system	Closed system without solvent	Closed system with solvent
Product ID	OS–12	CS–2	CS–4
Reaction temp., °C	130	130	130
Reaction time, hr	10	10	10
A/K ratio, wt/wt	0.2	0.2	0.2
Reactor pressure, kg/cm^2(g)	-	1.1	1.9
Physical state of product	VL	VL	Semi solid
Solution viscosity at 30 °C, cP	2.9	3.4	9.5
Solubility in MTO at 30 °C, wt%	85	70	57
Hydroxyl value, mg KOH/g resin	57	65	81
Iodine value, g I_2/100 g resin	5.8	4.2	3.6

5.2.2. Effect of stirring speed on physico−chemical properties of the resin products

In the work, to investigate the effect of stirring speed on physico−chemical properties of the products, the polymerization reactions were carried out at four different stirring speeds ranging from 300 to 1200 rpm for a fixed time of 10 hrs, temperature of 130 °C and catalyst loading of 0.3. Stirring is useful to reduce/eliminate the diffusional mass transfer resistance and to enhance the heat and mass transfer rates. The effect of stirring speed on physico−chemical properties of the products is shown in Figure 5.1. The figure shows that hydroxyl value and softening temperature of the product increased with the increase of stirring speed. Around 6 units increase in hydroxyl value and 4 units increase in softening temperature were observed when the stirring speed was increased from 300 to 900 rpm. The increasing trend of hydroxyl value and softening temperature of the products indicates that the degree of polymerization slightly increased with the increase of stirring speed. It was also observed that beyond a stirring speed of 900 rpm, there was no significant improvement in the product properties. Therefore, all the successive studies were carried out at a constant stirring speed of 1000 ± 20 rpm.

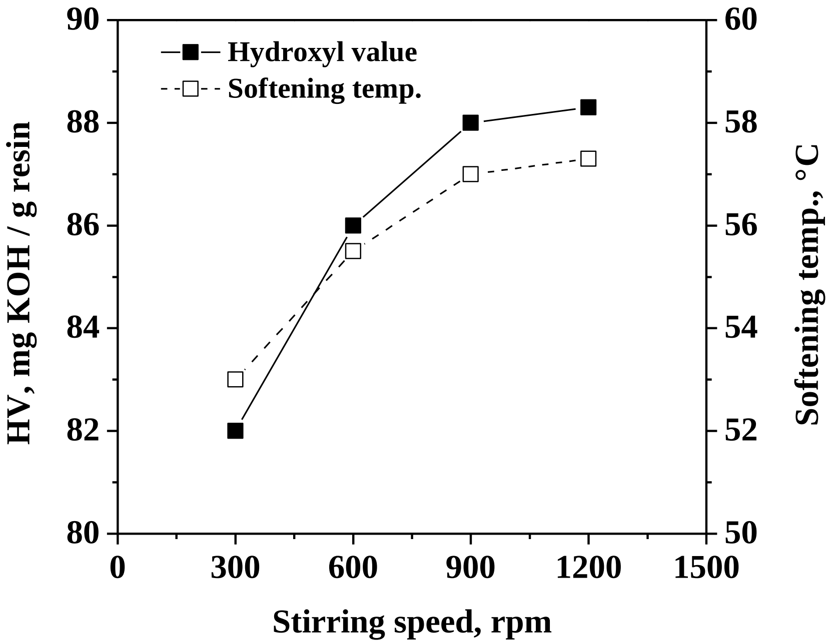


Figure 5.1. Effect of stirring speed on Hydroxyl value and Softening temperature (Product ID: CS–5, CS–6, CS–7, CS–8)

5.2.3. Effect of catalyst loading on physico–chemical properties of the resin products

To study the effect of catalyst loading on product properties, the reactions were conducted with four different A/K ratios ranging between 0.1–0.4 at a fixed temperature of 130 °C. In each run, the reaction was continued for a time duration of 10 hrs. The effect of catalyst loading on hydroxyl value, softening temperature, solution viscosity and solubility in MTO are shown in Figure 5.2 and 5.3. The figure (Figure 5.2) shows that both hydroxyl value and softening temperature of the products increased with the increase of catalyst loading. Around 20 units increase in hydroxyl value and 30 units increase in softening temperature were observed when the A/K ratio was increased from 0.1 to 0.4. The physical state of the products obtained at 0.1

and 0.2 A/K ratio were high−viscous liquid and semi−solid state respectively, whereas solid state products were obtained with A/K ratio of 0.3 and 0.4. The change of state of the products from high−viscous liquid state to solid state, with the increase of catalyst concentration indicates that the degree of polymerization increased with catalyst loading.

Figure 5.3 shows that solubility of products in MTO decreased with the increase of catalyst concentration. Approximately 25 units decrease in product solubility was observed when the A/K ratio was increased from 0.1 to 0.4. From the iodine value analysis, it was observed that degree of unsaturation decreased with the increase of alkali concentration. About one−unit decrease in iodine value was observed when the A/K ratio was increased from 0.1 to 0.4. The increasing trend of hydroxyl value, softening temperature, and viscosity of the products indicates that the degree of polymerization increased with the increase of catalyst loading.

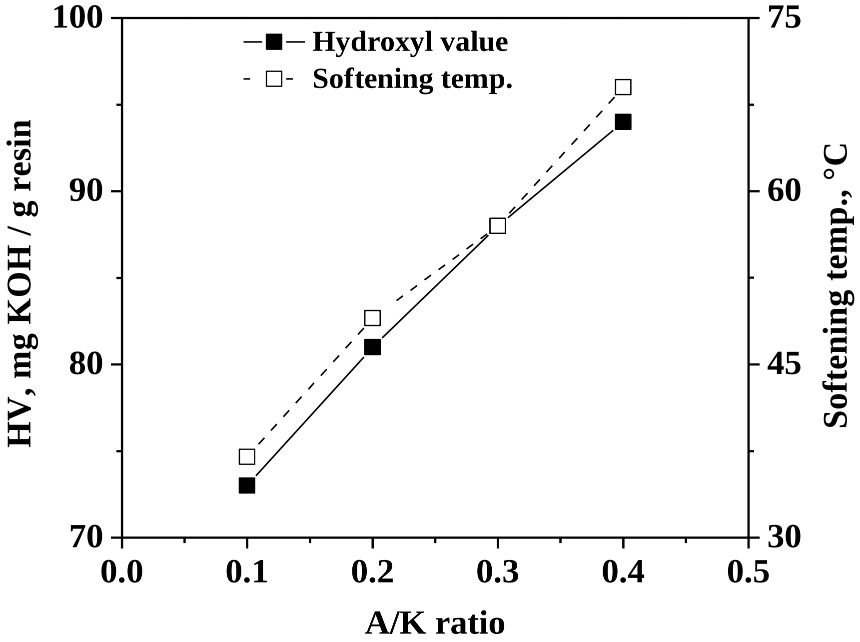


Figure 5.2. Effect of catalyst loading on Hydroxyl value and Softening temperature (Product ID: CS−3, CS−4, CS−5, CS−9)

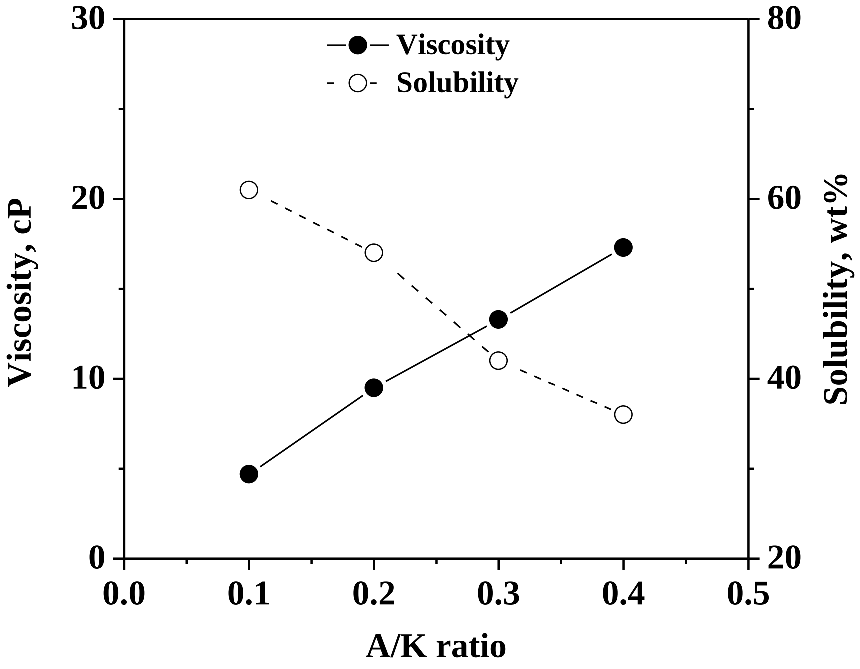


Figure 5.3. Effect of catalyst loading on Viscosity and Solubility value (Product ID: CS−3, CS−4, CS−5, CS−9)

5.2.4. Effect of reaction time on physico−chemical properties of the resin products

To find the effect of reaction time on product properties, experiments were carried out for different time duration ranging from 10 to 19 hrs at a fixed temperature of 130 °C and with an A/K ratio of 0.3. The effects of reaction time on hydroxyl value, softening temperature, viscosity, and solubility are shown in Figure 5.4 and 5.5. The results show that both hydroxyl value and softening temperature of the products increased with the increase of reaction time (shown in Figure 5.4) for a fixed temperature and fixed catalyst concentration. It was observed that for 9 hrs increment in reaction time, hydroxyl value and softening temperature of the product increased by around 1.5 and 1.4 fold respectively.

Figure 5.5 shows that, viscosity of the products increased with the increase of reaction time, whereas solubility in MTO decreased with reaction time. Increase of viscosity indicates that the average molecular weight of the products increased with reaction time and consequently solubility decreased. Around 35% reduction in product solubility was observed when the reaction time was increased from 10 to 19 hrs.

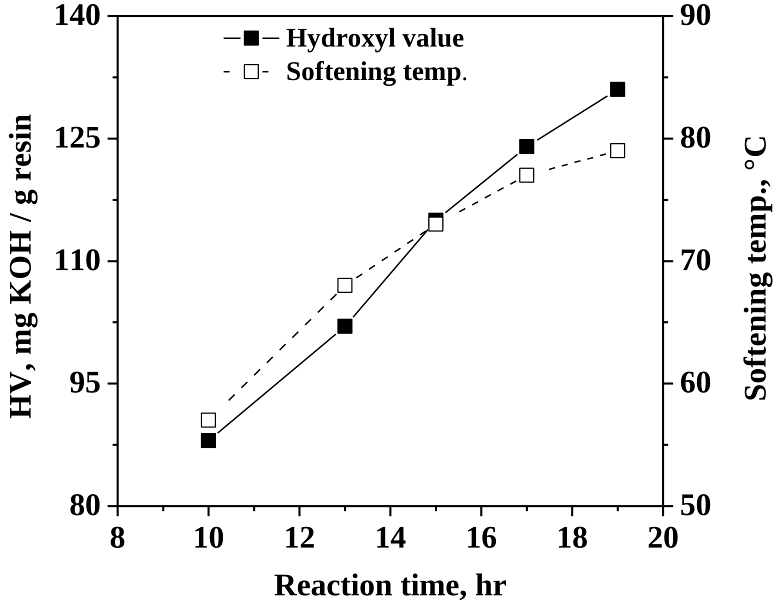


Figure 5.4. Effect of reaction time on Hydroxyl value and Softening temperature

(Product ID: CS–5, CS–12, CS–13, CS–14, CS–15)

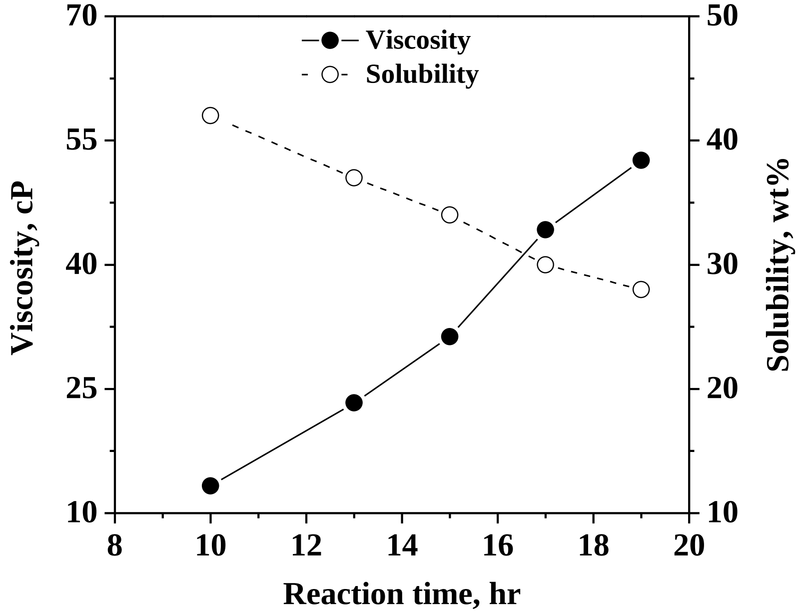


Figure 5.5. Effect of reaction time on Viscosity and Solubility

(Product ID: CS–5, CS–12, CS–13, CS–14, CS–15)

Though, a decreasing trend in iodine value of the products was observed, but the reduction of iodine value was not so significant. The iodine value of the products was between 2.5–3.2 g

I_2/100 g resin. The experimentally obtained moisture content of the products was in the range of 2–3% by weight. The increase of hydroxyl value and softening temperature of the products indicates that the extent of polymerization increased with the reaction time.

5.2.5. Effect of temperature on physico−chemical properties of the resin products

To study the effect of reaction temperature on resin properties, reactions were carried out at four different temperatures ranging from 130 to 160 °C for a fixed reaction time of 15 hrs. In each run, 20 g KOH was added with 100 g cyclohexanone to maintain an alkali loading of 0.2. The effect of temperature on hydroxyl value, softening temperature, solution viscosity and solubility in MTO are shown in Figure 5.6 and 5.7. The plot (Figure 5.6) shows that both hydroxyl value and softening temperature of the products increased with the increase of reaction temperature. It was observed that for every 10 °C increase in reaction temperature from 130 to 150 °C, hydroxyl value increased around 18 units. However, when temperature was further increased from 150 to 160 °C, around 35 units increment in hydroxyl value was observed. Around two−fold increment in hydroxyl value at 160 °C may be due to partial vapor−phase polymerization reaction. The boiling point of the monomer is around 155 °C. For every 10 °C increment in reaction temperature, softening point increased around 9 °C.

Figure 5.7 shows that viscosity of the products increased with the increase of reaction temperature, and solubility of the products in MTO decreased with the increase of reaction temperature. The iodine value of the products obtained at 130, 140, 150 and 160 °C temperature are around 3.6, 3.8, 4.1 and 4.5 g I_2/100 g resin respectively. Though the effect of reaction temperature on iodine value variation was not so significant but an increasing trend was observed. The increase of iodine value with reaction temperature may be due to the increase of aldol condensation rate (undesired reaction) at elevated temperatures.

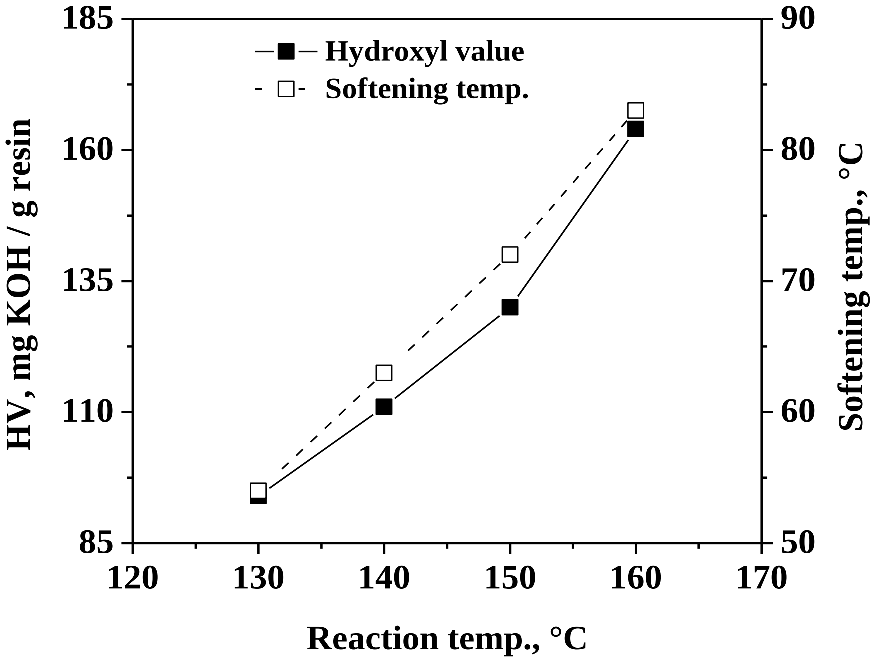


Figure 5.6. Effect of reaction temperature on Hydroxyl value and Softening temperature (Product ID: CS−41, CS−39, CS−25, CS−40)

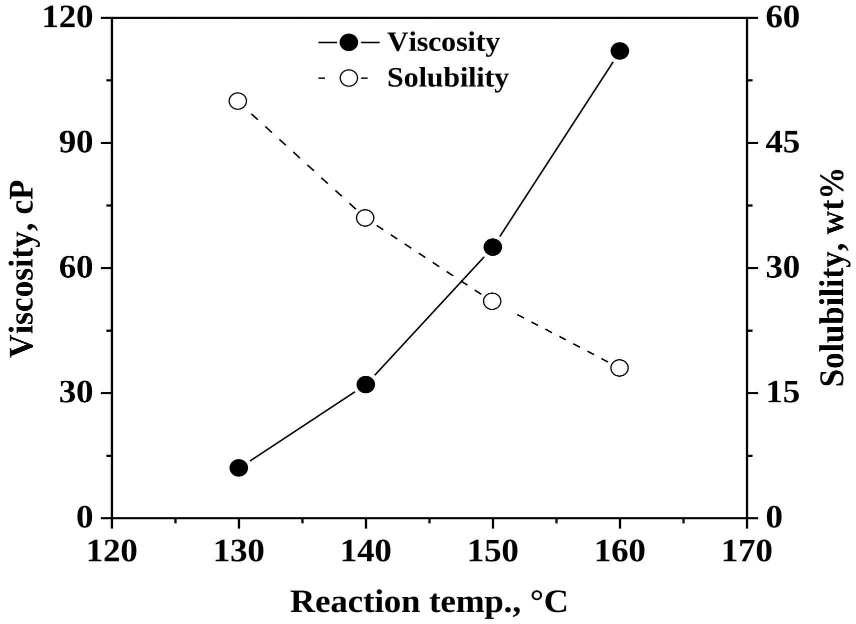


Figure 5.7. Effect of reaction temperature on Viscosity and Solubility (Product ID: CS−41, CS−39, CS−25, CS−40)

5.2.6. Effect of pressure on physico–chemical properties of the resin product

To study the effect of reactor pressure on resin properties, reactions were carried out at four different reactor pressures ranging from 2.1 to 12.0 kg/cm^2(g) at a fixed temperature of 130 °C, and with an A/K ratio of 0.3. The closed system (Parr reactor) was pressurized by introducing inert nitrogen gas into the reactor at the beginning of reaction. The total pressure obtained from the pressure indicator at the operating temperature is the sum of autogenously developed pressure by the reacting mass, and pressure exerted by nitrogen gas. The reactions were carried out for a duration of 13 hrs under pressurized condition. The important physico–chemical properties of the reaction products are shown in Table 5.2.

Table 5.2. Effect of reactor pressure on resin properties

Product ID	Reactor pressure, kg/cm^2(g)	HV, mg KOH/g	Softening temp., °C	Viscosity, cP	Solubility, wt%
CS–12	2.1	102	68	23.3	37
CS–23	6.1	107	66	14.5	40
CS–24	8.5	109	65	13.8	41
CS–22	11.9	112	64	13.1	42

Table 5.2 shows that as the reactor pressure was increased from 2.1 to 12.0 kg/cm^2(g), an increasing trend of hydroxyl value, and a decreasing trend of softening temperature was observed. However, the increment in hydroxyl value was not so significant with the increase in reactor pressure. The data also shows that the product viscosity decreased by approximately 40% with the increase in reactor pressure from 2.1 to 6.1 kg/cm^2(g), and beyond a pressure value of 6.1 kg/cm^2(g), no substantial change in viscosity was observed up to 12 kg/cm^2(g) pressure. The solubility of the products in MTO increased with the increase of reactor pressure. However, the rate of increment of solubility slowed down beyond a pressure value of 6.1 kg/cm^2(g). The pressure value of 2.1 kg/cm^2(g) in the reactor was basically an autogenously developed pressure at the operating temperature. When the reactor pressure was increased by introducing nitrogen, the vapor fraction of reacting mixture partially/fully converted to liquid phase where the polymerization reaction occurred. The decreasing trend of softening temperature and viscosity of

the products with the increase of reactor pressure indicates that degree of polymerization reduced with the increase of reactor pressure. Therefore, based on the experimental results, it can be said that an excess pressure has no significant role to improve the degree of polymerization. Hence, for the present study, most of the experiments were conducted under autogenous pressure only.

5.2.7. Solubility of resin in various solvents

Varieties of solvents are used to dissolve a particular resin depending on specific applications. Therefore, it is important to check the compatibility of a solvent for a specific resin material. In the present study, to investigate the solvent compatibility for the in–house developed resins, different types of aliphatic and aromatic solvents were chosen to find the extent of solubility of the ketonic resins. The resin used for testing the solubility in various solvents was prepared at 145 °C, and with an A/K ratio of 0.18. The properties of the resin are: HV = 127 mg KOH/g, IV = 2.9 g I_2 /100 g and softening temperature = 75 °C. Solubility value of the resin in the studied solvents at 30 ± 1 °C are given in Table 5.3.

Table 5.3. Solubility of the in–house developed resin (CS–75) in various solvents at 30 °C

Solvent	Solubility, wt%	Solvent	Solubility, wt%
Methyl alcohol	insoluble*	Ethyl acetate	28
Ethyl alcohol	< 5	n–Butyl acetate	52
Iso–propyl alcohol	15	Toluene	48
n–Butyl alcohol	46	m–Xylene	51
Acetone	insoluble*	Carbon tetrachloride	43
n–Hexane	insoluble*	Methyl ethyl ketone	54
n–Heptane	insoluble*	Mineral turpentine oil	34

* Solubility less than 2 wt%

The result shows that the resin is almost insoluble in low molecular weight alcohols (methyl and ethyl alcohols) and aliphatic hydrocarbons (acetone, hexane and heptane). However, the product is sufficiently soluble in n–butyl alcohol, n–butyl acetate, aromatic hydrocarbons, carbon tetrachloride, and ketonic solvents.

5.2.8. Determination of molecular weight and polydispersity index of the products

Molecular weight distribution of a resin can have a profound effect on coating performance. To obtain same solution viscosity, a high molecular weight resin requires more solvent than that of a low molecular weight resin for a similar resin composition. Number–average and weight–average molecular weight of a polymer is very much useful to predict the degree of polymerization and distribution of molecular chains. In the present study, Gel Permeation Chromatography (GPC) instrument was used to determine number–average molecular weight ($M_{n\cdot avg}$), weight–average molecular weight ($M_{w\cdot avg}$), and polydispersity index (PDI) of the resin products. The GPC chromatograms of four resin samples are shown in Figure 5.8. The figure shows that the samples eluted between the elution time of 28–48 min. Based on the elution time information, it can be said that, CS–3 sample consist of short chain polymer molecules compared to other three samples. The negative peaks at around 49.5 min correspond to solvent (THF) peak.

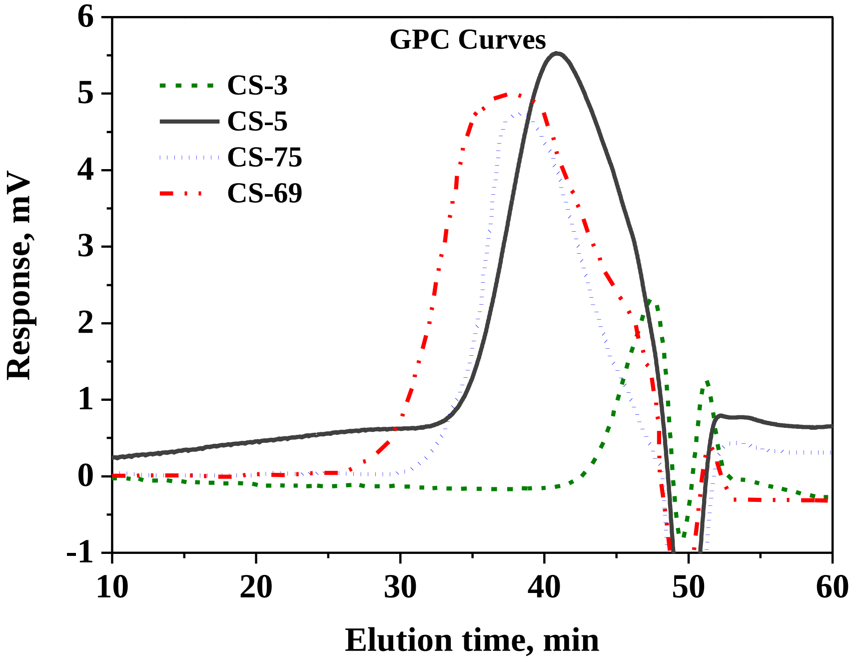


Figure 5.8. Gel Permeation Chromatography curves of four product samples

For few resin samples, the average molecular weight was estimated using a MALDI–TOF instrument, and a typical mass spectrum of a product sample (CS–69) is shown in Figure 5.9.

The estimated values of number–average and weight–average molecular weights of four samples are given in Table 5.4 along with their other properties.

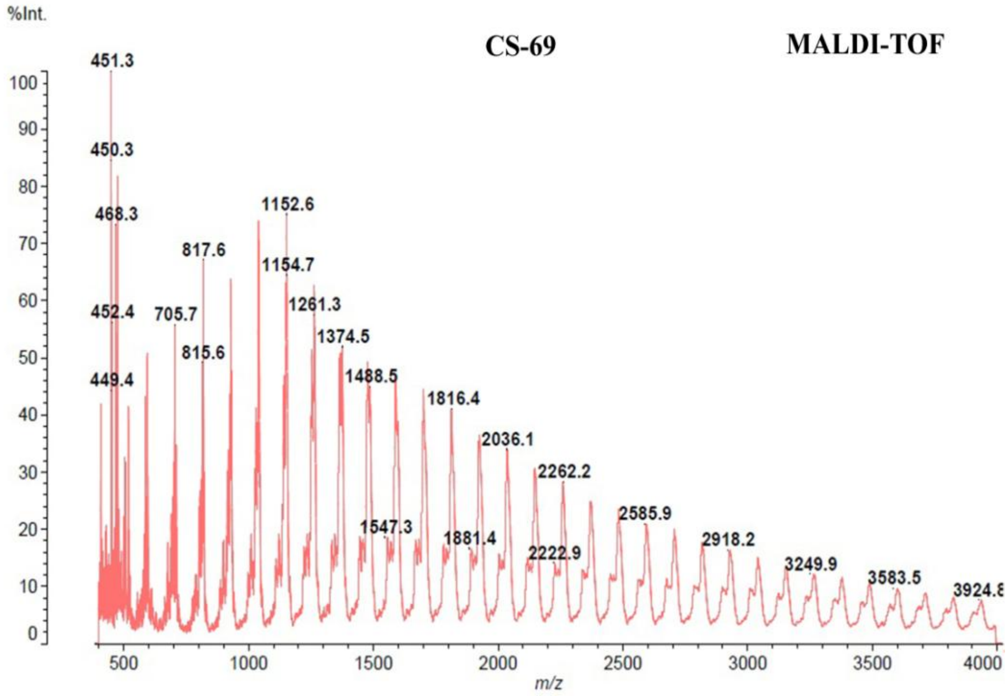


Figure 5.9. MALDI–TOF mass spectrum of a product samples

Table 5.4. Average molecular weights and polydispersity index values of resin samples

Product ID	HV, mg KOH/g	Viscosity, cP	$M_{n.avg}$, g/mol	$M_{w.avg}$, g/mol	PDI
CS–3	73	5	480	498	1.03
CS–5	88	14	668	1080	1.61
CS–75	127	86	1176	1605	1.36
	From MALDI–TOF		1220	1671	1.37
CS–69	134	580	1332	1785	1.34
	From MALDI–TOF		1371	1810	1.32

The data (Table 5.4) shows that, the degree of polymerization increased with the increase in product viscosity and hydroxyl value. The narrow range distribution in the chromatography for CS–3 sample confirmed that its $M_{w \cdot avg}$ is very close to $M_{n \cdot avg}$ value. The data also shows that the deviation in molecular weight obtained from GPC and MALDI−TOF analysis for the same products (CS−75 and CS−69) is below 5%.

5.2.9. Refractive index analysis of the resin samples

Refractive index (RI) analysis is an important characterization technique for a polymer material to know the extent of light that can pass through the material. A resin with higher refractive index enables to provide higher degree of opacity in paint films. In the present study, a refractometer instrument was used to find the refractive index of the polymers. The test samples were prepared by dissolving the resins in tetrahydrofuran (THF) solvent at various concentrations by weight. The refractive index of a pure resin was estimated from the plot (shown in Figure 5.10) by extrapolating the RI data obtained at various concentrations. The average value of RI of the in–house developed resin products was approximately 1.52.

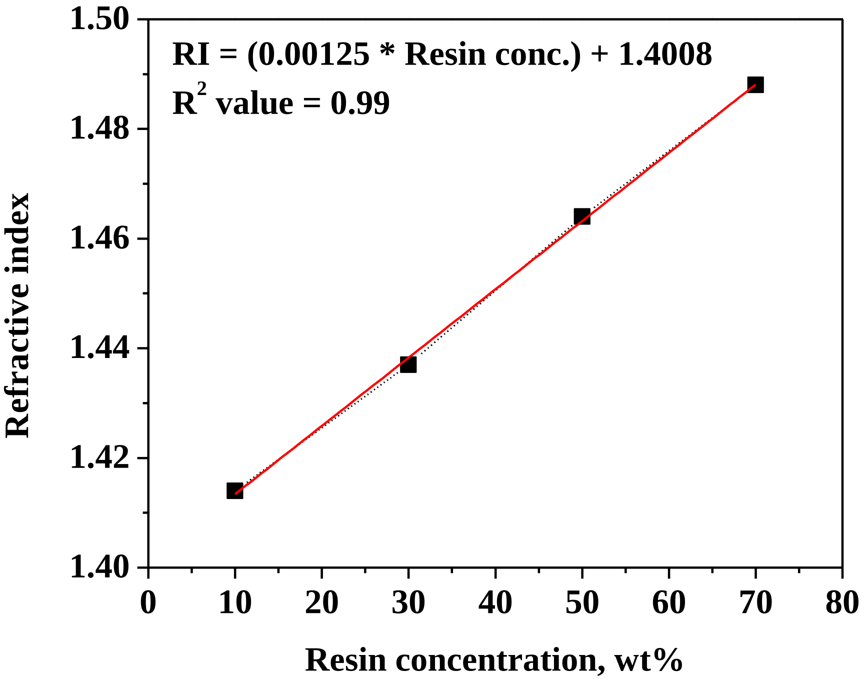


Figure 5.10. Resin concentration vs refractive index (RI) plot of product CS−75

The estimated refractive index values of the four products are given in Table 5.5. The data shows that the refractive index of the resin samples were greater than the individual refractive index of

THF and cyclohexanone monomer. The data also shows that, the value of refractive index increased with the increase of product viscosity and which means that the light propagating capacity of the material decreased with the increase of product viscosity. The refractive index values of the in–house developed resins were also compared with few commercial resins reported by various authors and are tabulated in Table 5.6. The data shows that the refractive index value of in–house developed resins are comparable with other resins used in coating technology.

Table 5.5. Refractive index value of THF, cyclohexanone and resin samples

Product ID	HV, mg KOH/g	Viscosity, cP	Solubility, wt%	Refractive index
THF	–	–	–	1.399
Cyclohexanone	–	–	–	1.448
CS–3	73	5	61	1.518
CS–5	88	14	42	1.521
CS–75	127	86	34	1.525
CS–69	134	580	10	1.528

Table 5.6. Refractive index values of various resin products

Resin	Refractive index	Reference
In–house developed ketonic resins	1.510 – 1.530	–
MS2A ketonic resin	1.505	Vincent, 2000
Aldehyde resin	1.494	Bradford, 1996
Polyester resins	1.523 – 1.540	Lambourne and Strivens, 1999
Long oil alkyd resin	1.530 – 1.550	
Epoxy resins	1.550 – 1.600	
Phenolic resins	1.660 – 1.700	
Shellac	1.510 – 1.530	Brydson, 1999
Dammar	1.530	Horie, 2010

5.2.10. Thermogravimetric analysis of the resin products

Thermal stability study can be useful to know the behavior of a material in presence of high temperature environment. To study the thermal stability of the in–house developed resin products, thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer. The obtained TGA–thermograms of four resin samples are shown in Figure 5.11. The weight loss percentage of the products for different temperature range are tabulated in Table 5.7 along with their important physico–chemical properties.

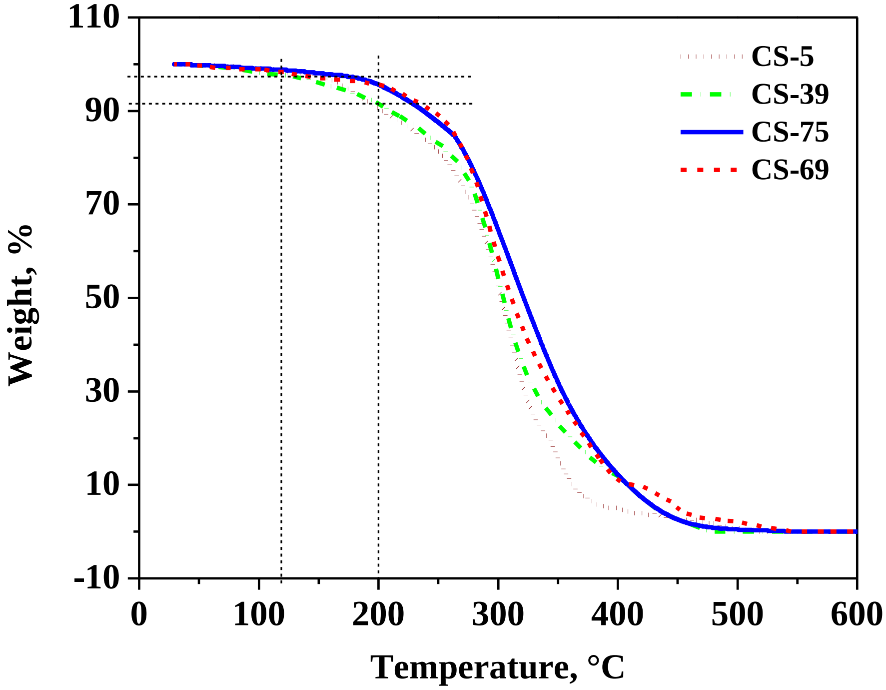


Figure 5.11. TGA thermograms of resin samples

The thermogram shows that, order of thermal stability of the products is CS–69 > CS–75 >CS–39 > CS–5. It was observed that the thermal stability of the products increased with the increase of product viscosity. The lower thermal stability of CS–5 and CS–39 was confirmed from viscosity and softening temperature values. The data also shows that, around 2.5% weight loss of the material was observed when the samples were heated up to 120 °C. This loss of weight was mainly due to the evaporation of moisture and solvent molecules from the product sample. Less than 8% weight loss was observed when the products were heated from 120–200

°C and which may be due to the evaporation of unconverted monomer trapped inside the products. The normal boiling point of cyclohexanone is around 155.6 °C. The decomposition of products started at around 200 °C and mostly completed at around 500 °C. Around 90% thermal decomposition occurred between 200–450 °C. Therefore, based on the thermogravimetric analysis, it can be said that the in–house developed resins are thermally stable up to a temperature of around 200 °C.

Table 5.7. Physico–chemical properties and weight loss data of the resin products

Product ID	HV, mg KOH/g	Viscosity, cP	Softening temp., °C	Weight loss, %		
				till 120 °C	120–200 °C	200–500 °C
CS–5	88	14	57	1.6	8.1	89.6
CS–39	111	28	68	2.4	6.1	91.3
CS–75	127	86	75	1.4	3.1	95.0
CS–69	134	580	101	1.7	2.7	93.7

5.2.11. X–ray diffraction analysis of the resin products

To identify the nature (amorphous or crystalline) of the resin products, X–ray diffraction (XRD) measurements were performed using a diffractometer equipped with monochromatic Cu K_α radiation (λ=1.54 Å). Diffraction angle (2 Theta) was varied from 5 to 60^o with a rate of 2^o/min and with a step width of 0.02°. The XRD patterns of the four resin products (CS–5, CS–39, CS–75 and CS–69) are shown in Figure 5.12.

The figure shows that, the XRD patterns are quite similar for all four (CS–5, CS–39, CS–75 and CS–69) resin products with some variation in their intensity levels. The difference in intensity levels among the products may be due to their morphology variation (Inoue and Hirasawa, 2013). A broad peak was observed in XRD pattern between the 2–Theta value range of 10–25° for all the resin products, corresponding to highly disordered carbon atoms. Based on the XRD analysis, it was confirmed that the in–house developed resin products were amorphous in nature.

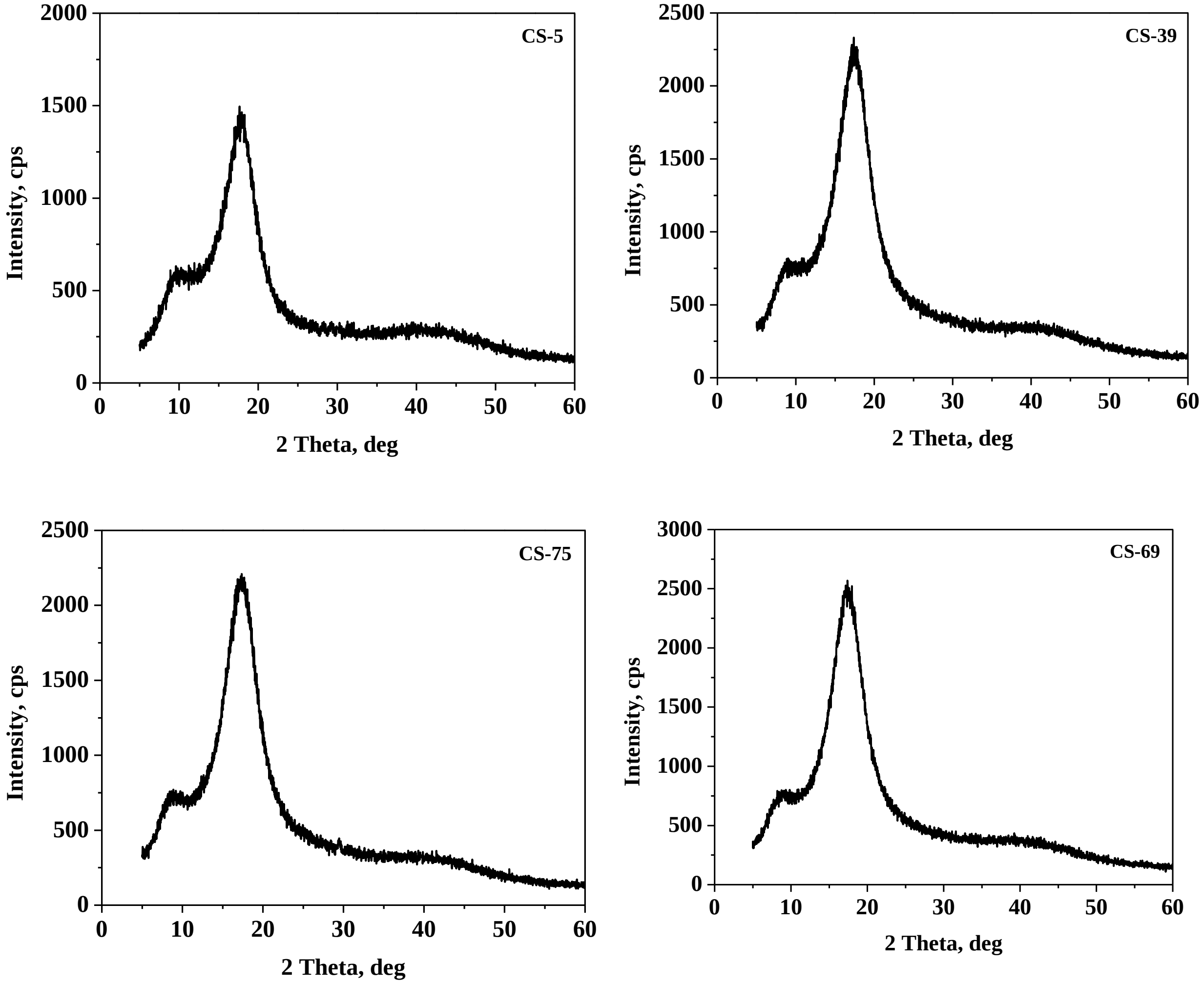


Figure 5.12. X–ray diffraction patterns of CS–5, CS–39, CS–75 and CS–69 products

5.2.12. Morphology studies of the product samples

Scanning electron microscopy (SEM) analysis is one of the efficient techniques used to investigate surface morphology of the materials. In the present work, SEM analysis was performed to know the surface morphology of the in–house developed resin samples, and the SEM images of the two products (CS–75 and CS–69) are shown in Figure 5.13. The images show that surface of the resin materials are rough in nature. The CS–75 sample shows cluster formation with less agglomeration. However, lumpy appearance with more agglomeration was observed for CS−69 product. Therefore, based on SEM analysis, it can be said that product morphology varied with product properties like, viscosity and hydroxyl value.

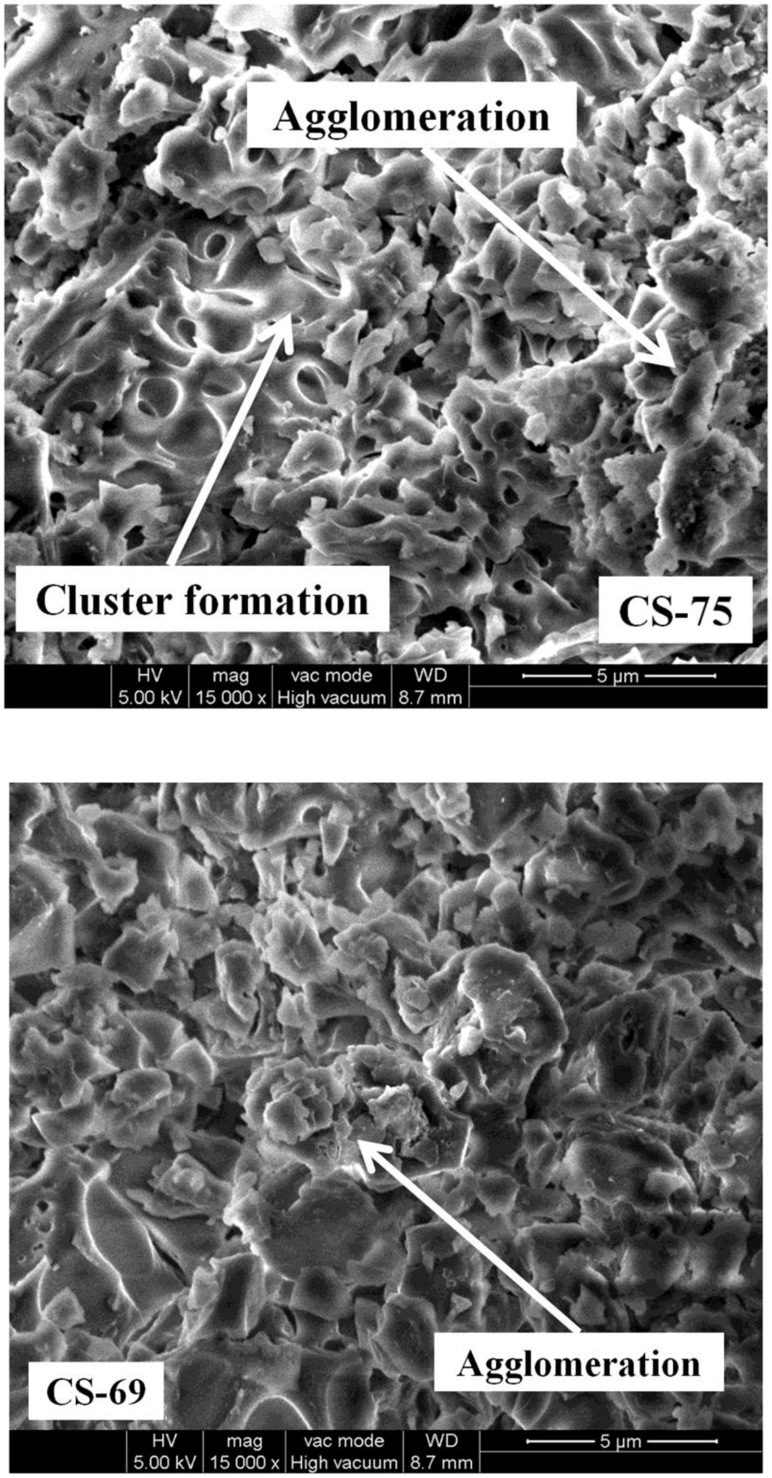


Figure 5.13. SEM images of CS−75 and CS−69 products

5.2.13. Testing of adhesive strength of the resin products

The adhesive property of a resin plays an important role in paint and coating technology in different ways, such as: to bind the pigment particles, to adhere the coating material to the substrate, to increase the durability of the coating material and to avoid peeling of the paint from the surface. To investigate the adhesive property of the developed resin products, adhesive strength tests were performed using a TA.XT plus instrument. The testing procedure details have been mentioned in Chapter 3. The obtained adhesive strength results are shown in Figure 5.14. In addition, the results were compared with the adhesive strength of commercial fevistick material under similar conditions.

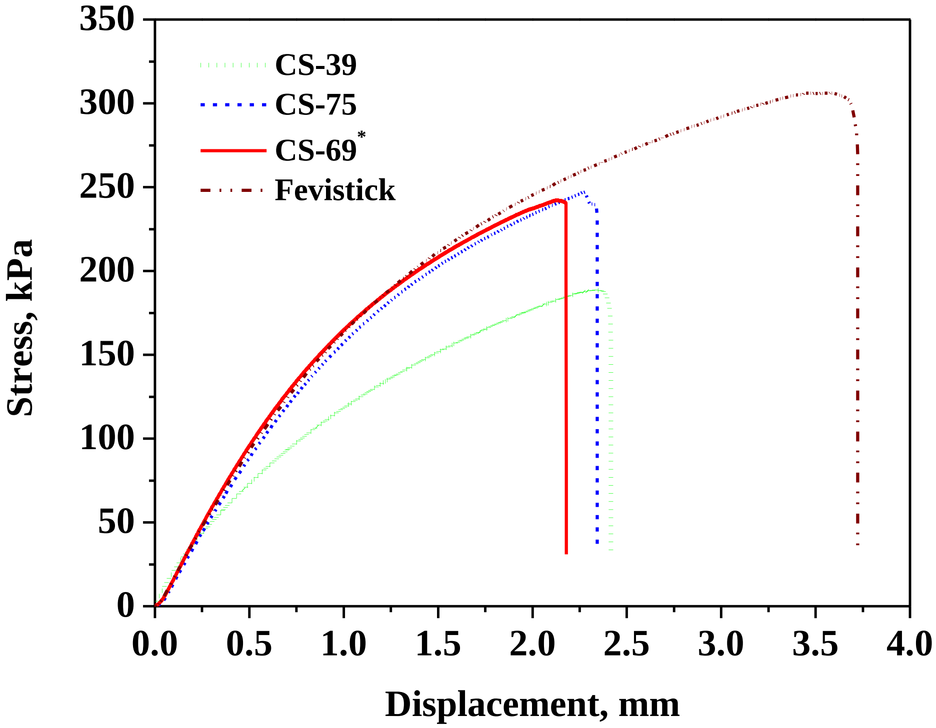


Figure 5.14. Adhesive strength analysis of two resin products and fevistick material (*MTO–to–resin wt ratio was 2)

The figure shows that adhesive strength of the resin products increased with the increase of hydroxyl value and viscosity of the resin. Slightly lower value in adhesive strength of CS−69 product in comparison with CS−75 was due to its more dilution in MTO (MTO–to–resin wt ratio was 2) since its solubility was less in MTO. The order of adhesive strength was CS−39 < CS−75

< CS−69 < Fevistick. The data shows that the adhesive strength of the resin products (CS−75 and CS−69) was around 0.2 folds lower than the adhesive strength of the fevistick material under present analysis conditions. However, the adhesive strength of the products CS−39 was around 0.38 folds lower than the adhesive strength of the fevistick material. The ultimate stress required to break the cardboard joint was around 188, 247, 242, and 306 kPa for CS−39, CS−75, CS−69, and fevistick material respectively. The present study confirms that the resin products could be used as an adhesive material for different applications.

5.2.14. Material balance of the polymerization reaction

In the study, material balance has been carried out for each reaction based on quantity of feed (input) material into the reactor and product (output) material from the reactor. The percent losses during the polymerization reaction and product yield were estimated from the material balance analysis. The estimated material balance of few products obtained at various reaction conditions is shown in Table 5.8. The data shows that >97% product yield was obtained from self−polymerization reaction of cyclohexanone monomer.

Table 5.8. Material balance of the polymerization reaction

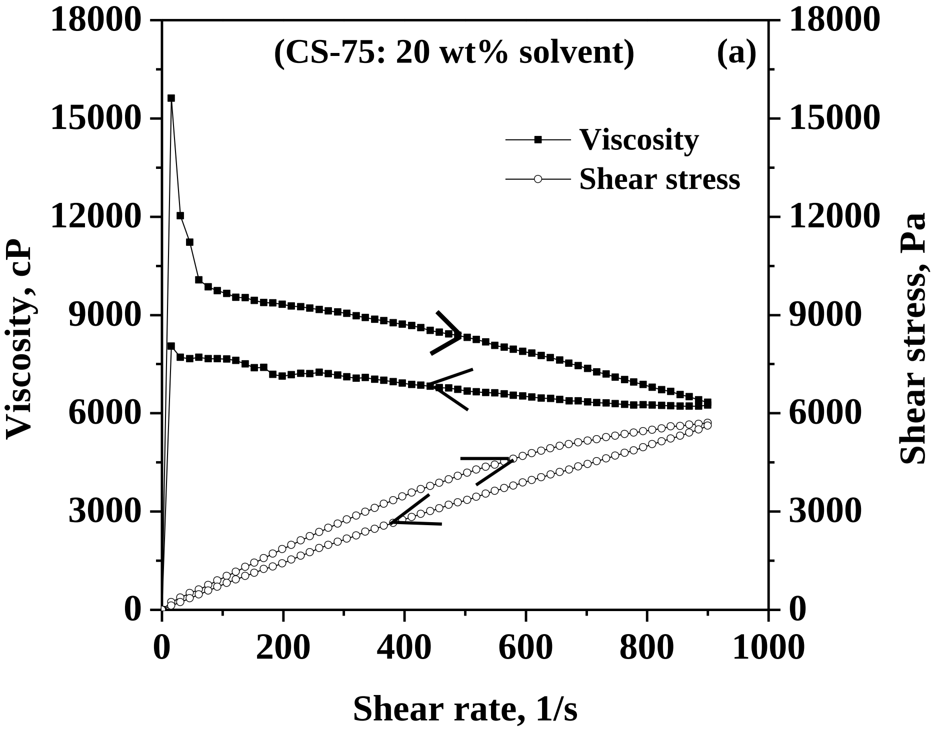
Product ID	Weight of feed, g				Weight of product, g	Loss of material, %	Yield of product, %
	Monomer	Catalyst	Solvent	Total			
CS−5	150	45	90	285	277	2.8	97.2
CS−6	150	60	120	330	321	2.7	97.3
CS−13	150	45	90	285	279	2.1	97.9
CS−25	150	30	60	240	235	2.0	98.0
CS−39	150	30	60	240	233	2.9	97.1
CS−75	150	27	54	231	225	2.6	97.4
CS−69	150	27	54	231	224	3.0	97.0

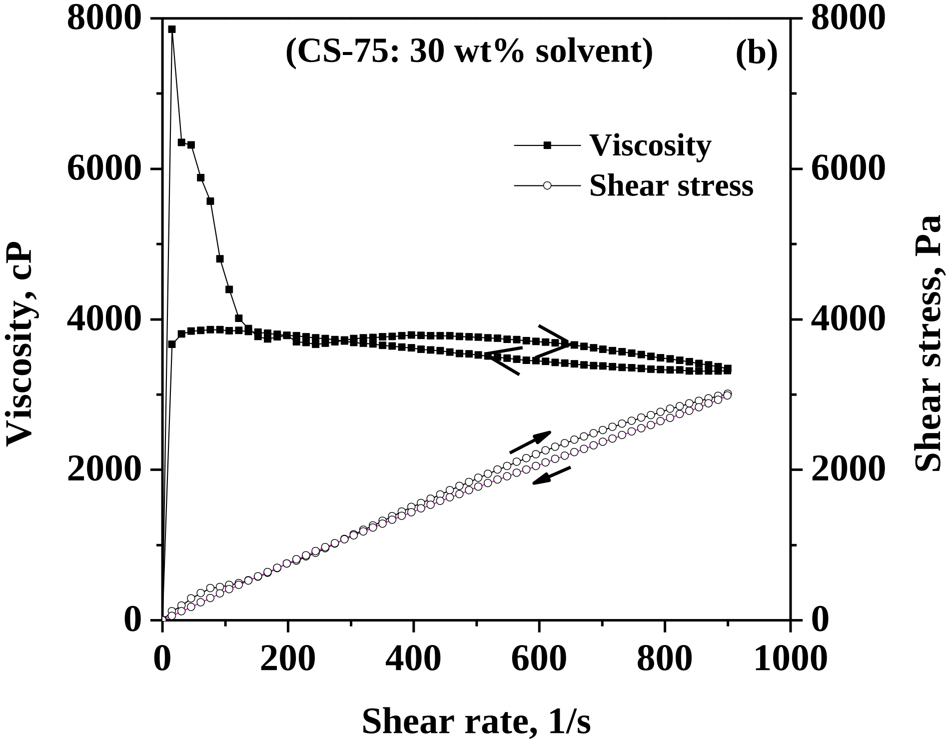
5.2.15. Rheology of the resin product

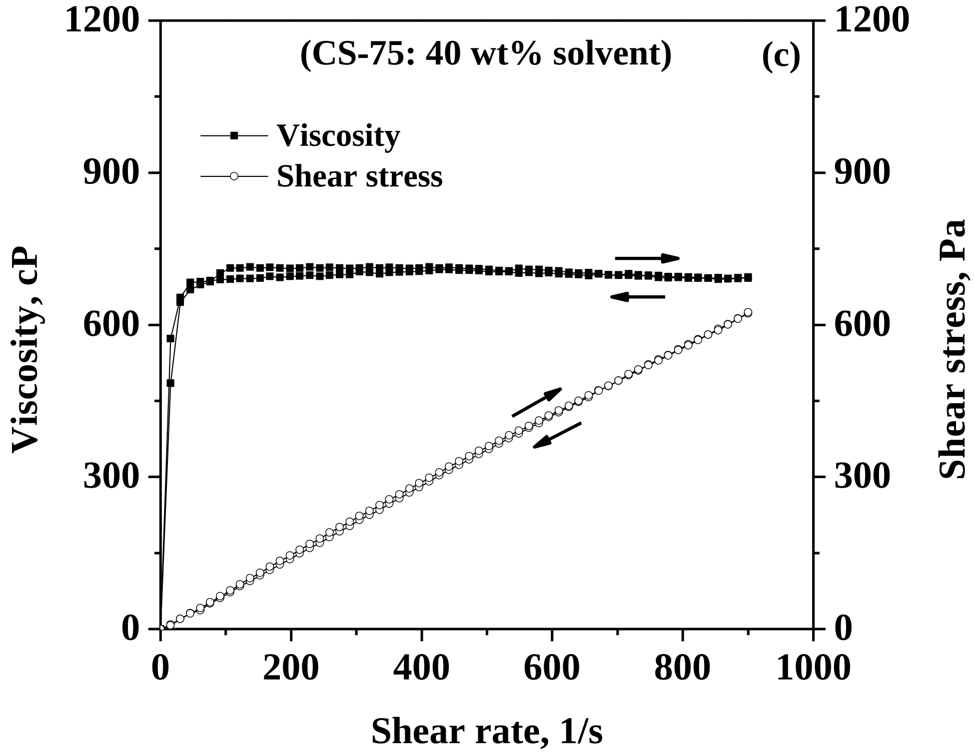
The rheology of paints mainly depends on the nature and concentration of the polymer. It is known that thixotropy is a time–dependent phenomenon and it brings about a reduction in viscosity during the high level of shear rate. It is usually evaluated by measuring the area enclosed between the forward measurement and backward measurement curve obtained in a hysteresis loop (Armelin et al., 2006; Goldschmidt and Streitberger, 2007).

To study the rheological characteristics of the ketonic resin products, the resin solution viscosity was measured at different concentrations under identical conditions using Brookfield Rheometer for a controlled shear rate range (0–900 1/s). The viscosity measurements were carried out for the resin products starting from low shear rate to high shear rate (forward measurement) as well as from high shear rate to low shear rate (backward measurement) to observe the thixotropic behavior of the resins.

The rheological behavior of ketonic resin (CS–75) at different concentrations of the resin is shown in Figure 5.15. The rheograms show that the viscosity of the product decreased with the increase in shear rate at lower solvent concentration (20 and 30 wt% of solvent). At lower dilution, shear thinning behavior was obtained for the product. The figure further shows the formation of a loop between forward and backward viscosity measurements at lower dilution. The obtained area of the formed loops at 20 and 30 wt% solvent concentrations are around 486.6 and 74.7 kPa/s respectively. The study shows that the resin shows thixotropic behavior at higher concentration of the resin in solution. It was also observed that the thixotropic behavior decreased with the increase of solvent concentration. The forward and backward direction viscosity curves overlapped to each other when the solvent concentration was increased to 50 wt%, and the resin solution behaves like a Newtonian fluid. It is also evident from the literature that a polymer can behaves like a Newtonian fluid at dilute solutions (Joseph, 1995).


(CS-75: 20 wt% solvent)
(a)
Viscosity
Shear stress
Viscosity, cP
Shear stress, Pa
Shear rate, 1/s
0
3000
6000
9000
12000
15000
18000
0
200
400
600
800
1000


(CS-75: 30 wt% solvent)
(b)
Viscosity
Shear stress
Viscosity, cP
Shear stress, Pa
Shear rate, 1/s
0
2000
4000
6000
8000
0
200
400
600
800
1000



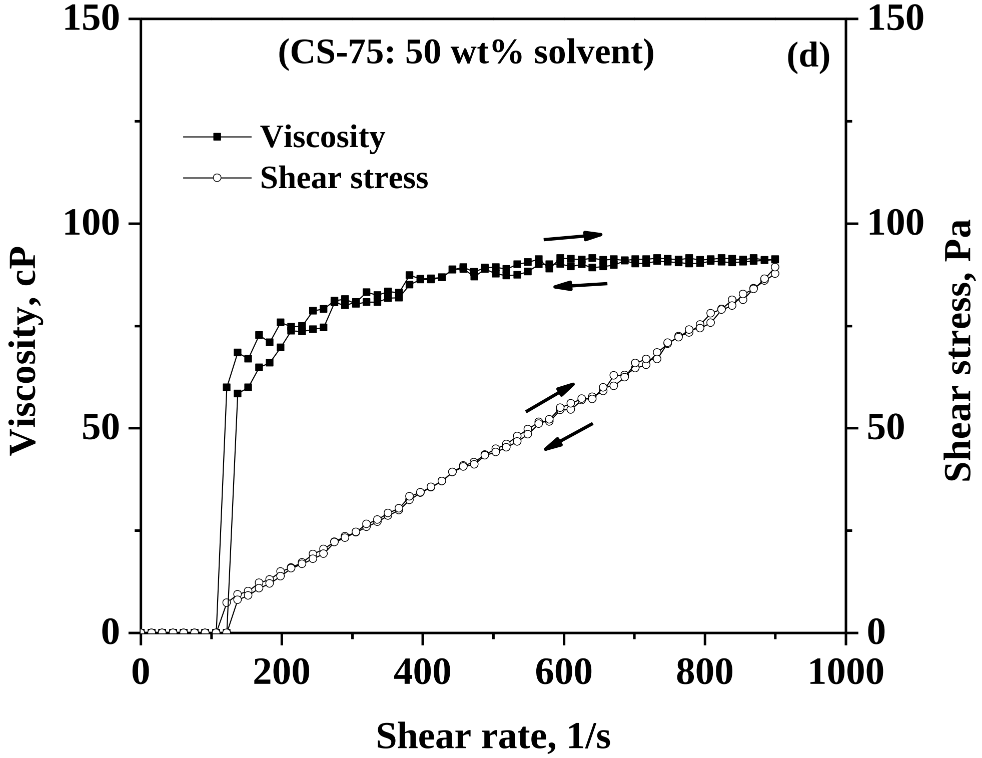


Figure 5.15. Rheology plots of ketonic resin at different concentrations

5.3. Conclusions

In the present study, ketonic resin was prepared by self–polymerization of cyclohexanone using a mechanically agitated batch reactor. Effects of various process parameters such as, stirring speed, catalyst concentration, reaction time, reaction temperature, and reactor pressure on product properties have been studied and quantified. Efforts have been made to standardize the analysis protocol, and to characterize various physico–chemical properties like hydroxyl value, viscosity, solubility, softening temperature, average molecular weight etc. of the resin products. It was observed that, for every 10 °C increase in reaction temperature, hydroxyl value and softening point of the products increased around 18 units and 9 units respectively, and solubility in MTO decreased around 12 units. Around 8 units increase in hydroxyl value, and 16 units decrease in solubility were observed when the A/K ratio was varied from 0.2 to 0.3 at a constant reaction temperature and time. It was also observed that for five hours increase in reaction time, hydroxyl value increased around 22 units and solubility value decreased around 8 units at a constant reaction temperature and alkali loading. The number average molecular weight of the in–house developed resins is in the range of 450–1400. The weight–average molecular weights of the products were in the range of 500–1800. The products are adequately soluble in many commercial solvents like n–butyl alcohol, n–butyl acetate, aromatic hydrocarbons, and ketonic solvents. TGA analysis revealed that the products are thermally stable up to a temperature of around 200 ºC. Amorphous nature of the resins was confirmed from XRD analysis. Morphological properties like surface roughness, lumpy appearance, and surface agglomeration of the resins were established from SEM analysis. Adhesive property of the solid resin was confirmed from the adhesive strength test. The study shows that >97% yield obtained from self–polymerization reaction of cyclohexanone. The results also show that the in–house developed resin can be used for paint and coating applications. Therefore, the outcome of the present study will be very much useful to develop a desired quality of resin product and its characterization depending on specific applications.

Table 5A. Synthesis details of the closed system products

Product ID	Reaction time, hr	Reaction temp., °C	A/K ratio, wt/wt
CS–2	10	130	0.2
CS–3	10	130	0.1
CS–4	10	130	0.2
CS–5	10	130	0.3
CS–6	10	130	0.3
CS–7	10	130	0.3
CS–8	10	130	0.3
CS–9	10	130	0.4
CS–12	13	130	0.3
CS–13	15	130	0.3
CS–14	17	130	0.3
CS–15	19	130	0.3
CS–22	13	130	0.3
CS–23	13	130	0.3
CS–24	13	130	0.3
CS–25	15	150	0.2
CS–39	15	140	0.2
CS–40	15	160	0.2
CS–41	15	130	0.2
CS–69	20	150	0.18
CS–75	16	145	0.18

Chapter 6

Development of Mathematical Models to Predict Various Properties of Resins

6.1. Introduction

In the present work, mathematical regression models were developed to know the sensitivity of various reaction parameters on the properties of the final product, and also to retrofit the experimental conditions to obtain a desire quality product for coating application. The mathematical model approach has the advantage of fast, less expensive and provide insight into parametric sensitivity (Tsivilis and Parissakis, 1995; Zelic et al., 2004).

6.2. Optimization of reaction parameters with the help of regression models

After quantifying the effects of individual parameters on product properties, the focus was extended to optimize the reaction parameters to obtain a desired quality resin for coating applications. Mathematical regression models were developed with the help of statistical analysis tools, such as, MINITAB 17 and Microsoft Excel using experimentally obtained laboratory data to predict the product properties. Reaction time (X_1), reaction temperature (X_2), and A/K ratio (X_3) were considered as independent input variables. The product properties such as, hydroxyl value (Y_1) and solubility (Y_2) were chosen primarily as dependent output variables. The following expression was used to find the response of the product property ‘Y’:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \tag{6.1}$$

Where, β_1, β_2, β_3, are the coefficients of linear effects, β_{11}, β_{22}, β_{33} are the coefficients of squared effects, and β_{12}, β_{13}, β_{23} are the coefficients of interaction effects. The term β_0 is constant coefficient. The model developed to predict hydroxyl value and solubility of the resin products are shown by Equation 6.2 and 6.3 respectively.

$$\begin{aligned} Y_{1\,\text{predicted}} = {} & 1312 + 2.3\,X_1 - 17.21 X_2 - 1727\,X_3 - 0.549\,X_1^2 + 0.052\,X_2^2 + 102\,X_3^2 \\ & + 0.116\,X_1 X_2 + 4.9\,X_1 X_3 + 13.07\,X_2 X_3 \end{aligned} \tag{6.2}$$

$$\begin{aligned} Y_{2\,\text{predicted}} = {} & 310 + 15.2\,X_1 - 4.84\,X_2 + 749\,X_3 - 0.328\,X_1^2 + 0.019\,X_2^2 - 51\,X_3^2 \\ & - 0.037\,X_1 X_2 - 14.07\,X_1 X_3 - 5.27\,X_2 X_3 \end{aligned} \tag{6.3}$$

The estimated R^2 values of the Equation 6.2 and 6.3 are 0.97 and 0.98 respectively. The developed models were used to find the set of operating parameters to obtain a desired quality product. Four set of experiments were carried out based on the model output information to check the deviation between the experimental results and model predicted responses. The results of experimental and predicted hydroxyl value and solubility value of the products shown in Figure 6.1 and 6.2 respectively.

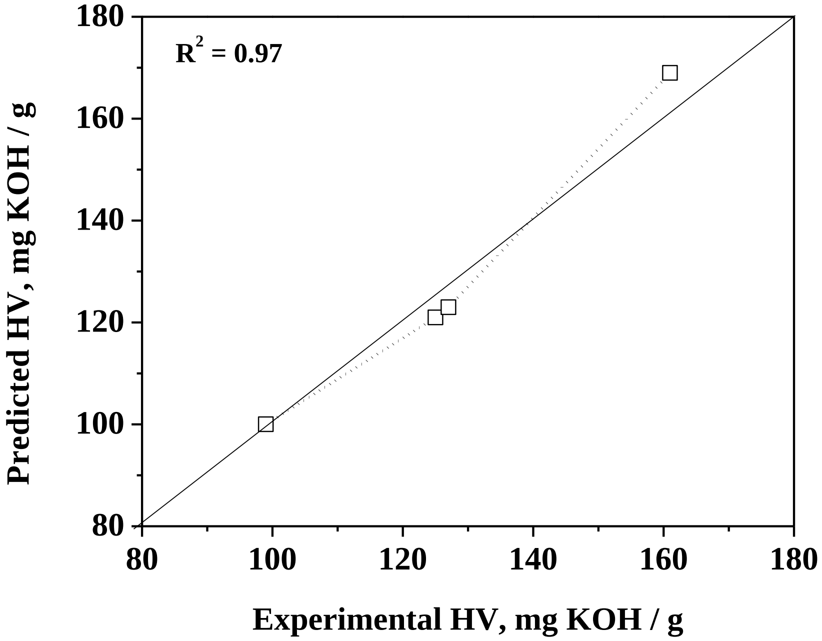


Figure 6.1. Experimental vs Model predicted hydroxyl values of the products

The data shows that the experimentally obtained hydroxyl and solubility values of the resins were comparable with the model predicted values for a fixed reaction conditions. In case of hydroxyl value, the maximum deviation between experimental and predicted value was around 5%. However, the deviation between experimental and predicted solubility was in the range of 3–15%. From the results, it can be concluded that the developed models can be used to get preliminary information on product property prior to carry out the reaction. Based on the preliminary information of product property, the experimental planning can be done to get desired property product.

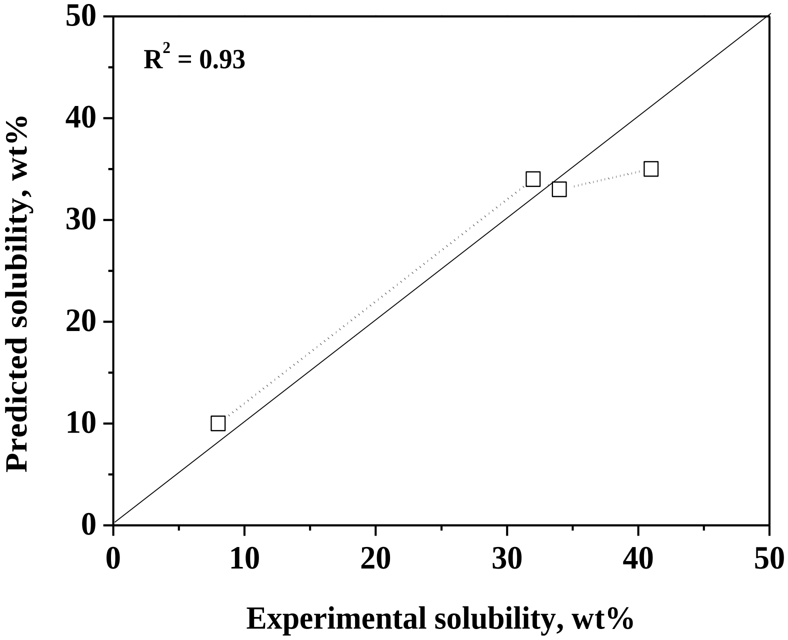


Figure 6.2. Experimental vs Model predicted solubility values of the products

6.3. Development of empirical models to predict solubility and softening temperature

In the present study, the focus was further extended to develop the empirical models to predict solubility and softening temperature of the resin products from the viscosity data. Empirical models were developed using the experimental data of product viscosity, solubility, and softening temperature. The developed models were used to test the new set of values. The developed models from experimental viscosity, solubility and softening temperature data to predict product solubility and softening temperature is shown in Figure 6.3 and 6.4 respectively. The experimental solubility and softening temperature values of the resins along with the corresponding predicted values with the help of the developed models are shown in Figure 6.5 and 6.6 respectively. The Figure 6.3 shows that the solubility of the products decreased logarithmically with the increase in resin viscosity which means that product solubility decreased with the increase in degree of polymerization. The developed models were good in agreement with the experimental data with an average deviation of around 10%. It was also observed from Figure 6.4 that softening temperature of the products increased logarithmically with the increase of resin viscosity. The developed models were good in agreement with the experimental data with an average deviation of around 5%.

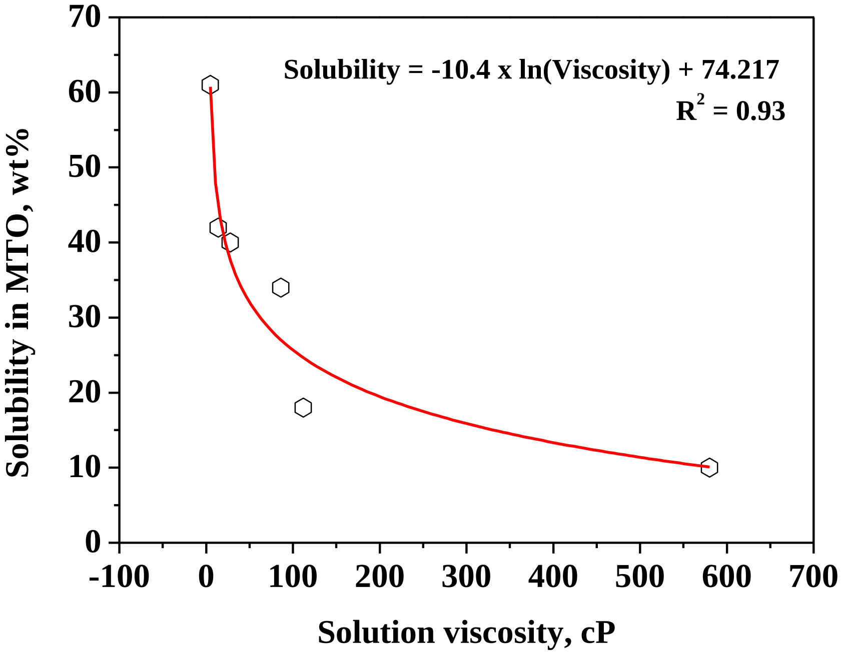


Figure 6.3. Empirical model to predict product solubility from viscosity data

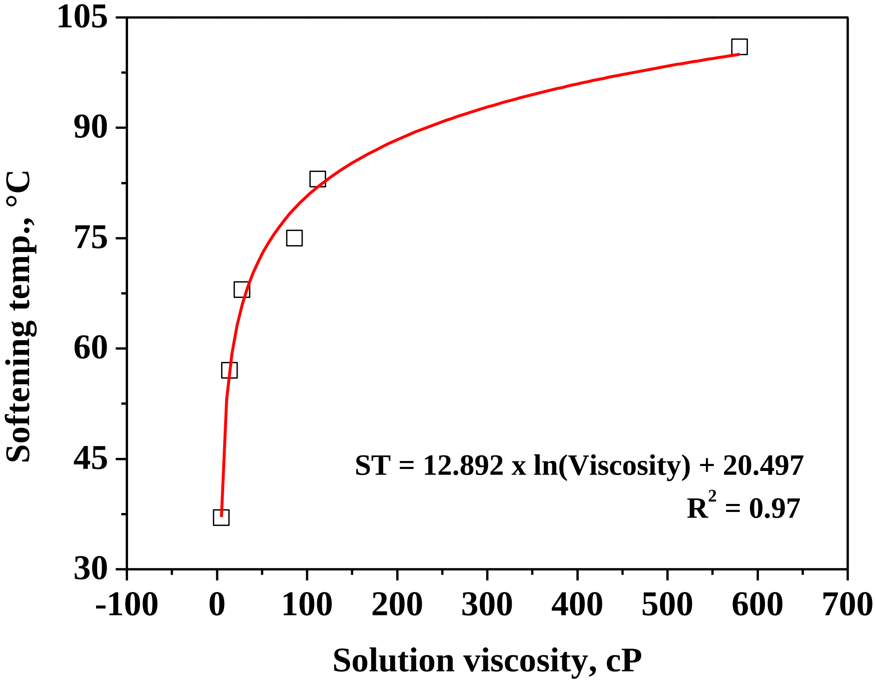


Figure 6.4. Empirical model to predict softening temperature of product from viscosity

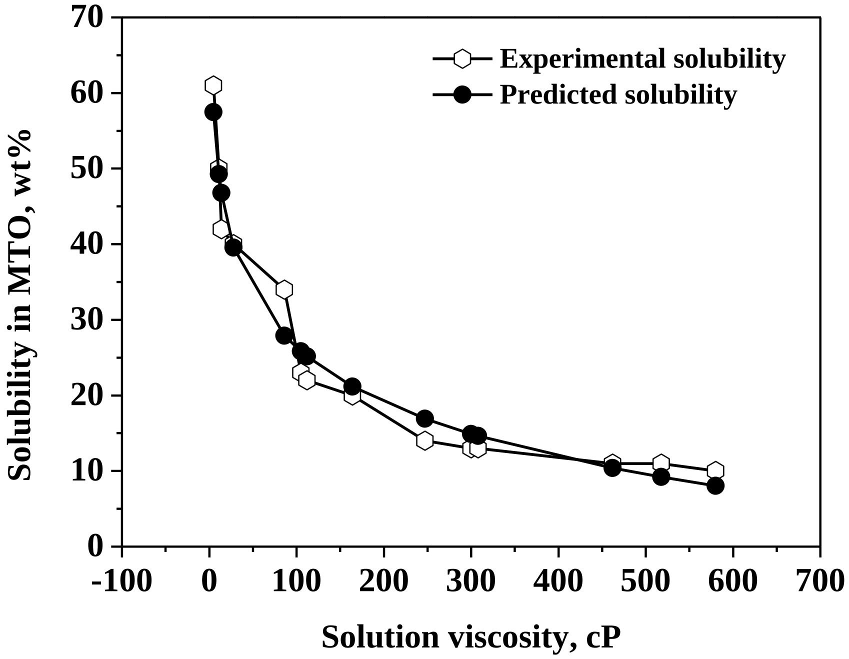


Figure 6.5. Experimental and predicted values of product solubility in MTO

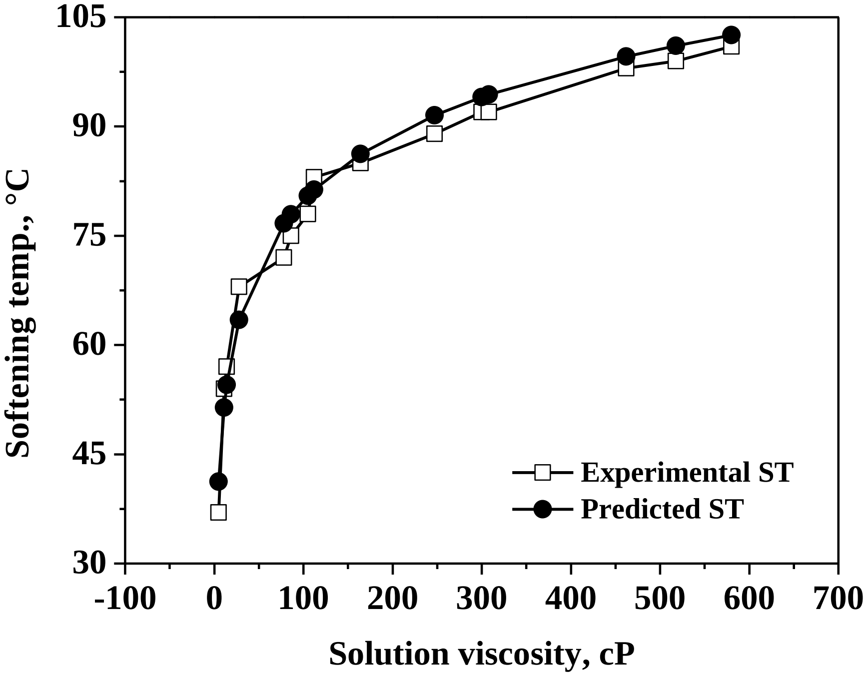


Figure 6.6. Experimental and predicted values of product softening temperature

6.4. Mathematical model to predict average molecular weight of the resin product

Refractive index (RI) is an important property of a polymer material. The light passing capacity decreases with the increase of molecular weight of the polymers, and these changes have been used in GPC analysis for the determination of molecular weight after calibration (Charles, 2003). In the work, number–average molecular weights of the resins were determined using GPC analysis. The refractive index of resins of known molecular weight was measured to develop a correlation between the resin refractive index and molecular weight. The obtained calibration data between the experimental values of refractive index and number–average molecular weight ($M_{n \cdot avg}$) is shown in Figure 6.7. The figure shows that the number–average molecular weight of the resins follows nearly a linear relationship with the refractive index values. The molecular weights of new resin samples were predicted with the help of the developed model and the values are shown in Figure 6.8.

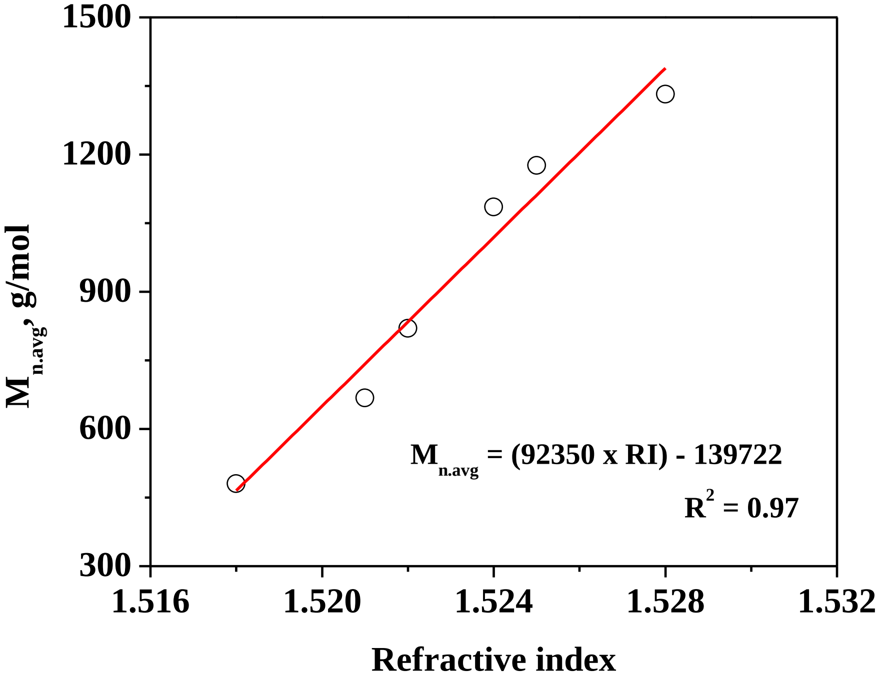


Figure 6.7. Experimentally obtained refractive index and $M_{n \cdot avg}$ values of the resins

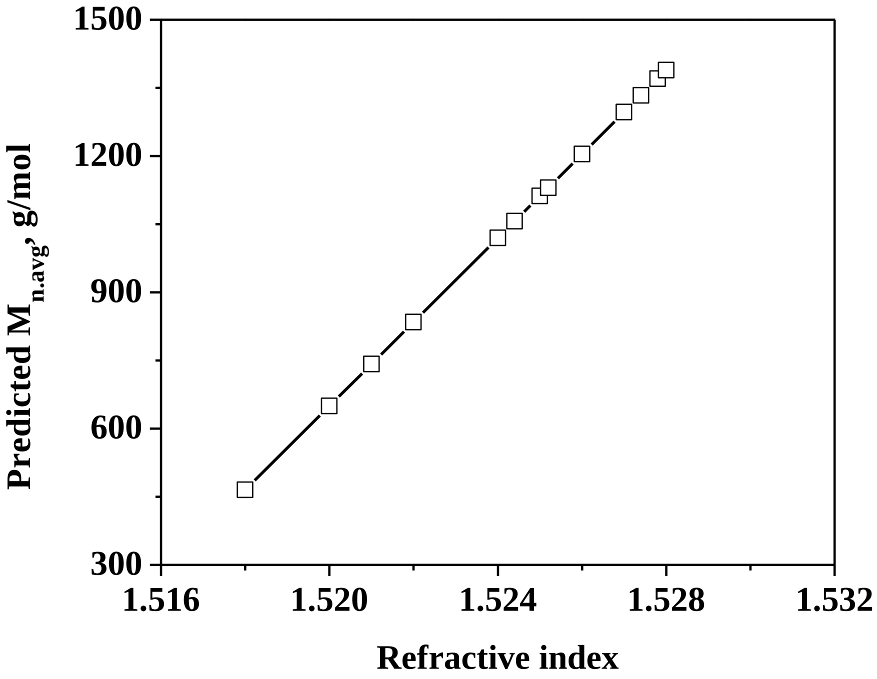


Figure 6.8. Refractive index and predicted $M_{n.avg}$ values of the resins

In the study, the average molecular weights of the resins were also predicted with the help of Mark–Houwink (M–H) relation. The Mark–Houwink relation $[\eta] = K\,(M_{w.avg})^{\alpha}$ (where $[\eta]$, and $M_{w.avg}$ are the intrinsic viscosity and weight–average molecular weight respectively, and K and α are Mark–Houwink constants), was used to predict the average molecular weight of the in–house developed resins (Wagner, 1985). The experimentally obtained viscosity and weight–average molecular weight of the products were used to find the value of Mark–Houwink constants, and the methodology is shown in Figure 6.9. The constant α is a function of three–dimensional polymer configuration and its value varies between 0.5 and 2 (Sousa et al., 2015). The estimated Mark–Houwink constants ($K = 2.120\times10^{-7}$ and $\alpha = 2.858$) were used to predict the unknown molecular weight of the resin samples based on the viscosity data, and the corresponding values are plotted in Figure 6.10. The figure shows that the predicted weight–average molecular weight of the resins increased with the increase of viscosity, and were in the range between 500–1800.

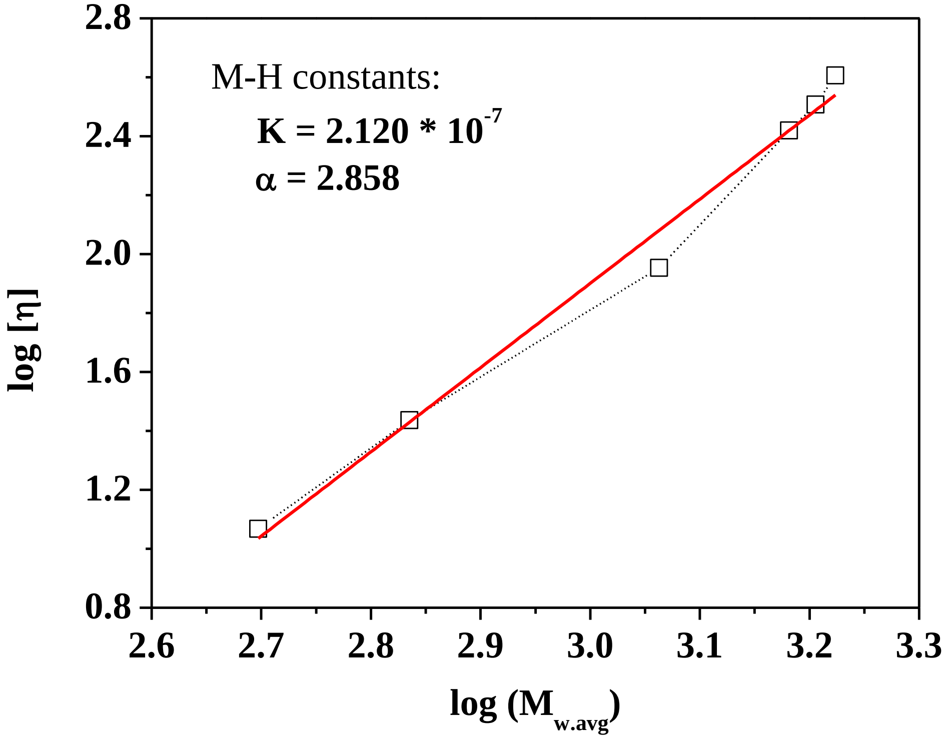


Figure 6.9. $M_{w.avg}$ and solution intrinsic viscosity of the resin products

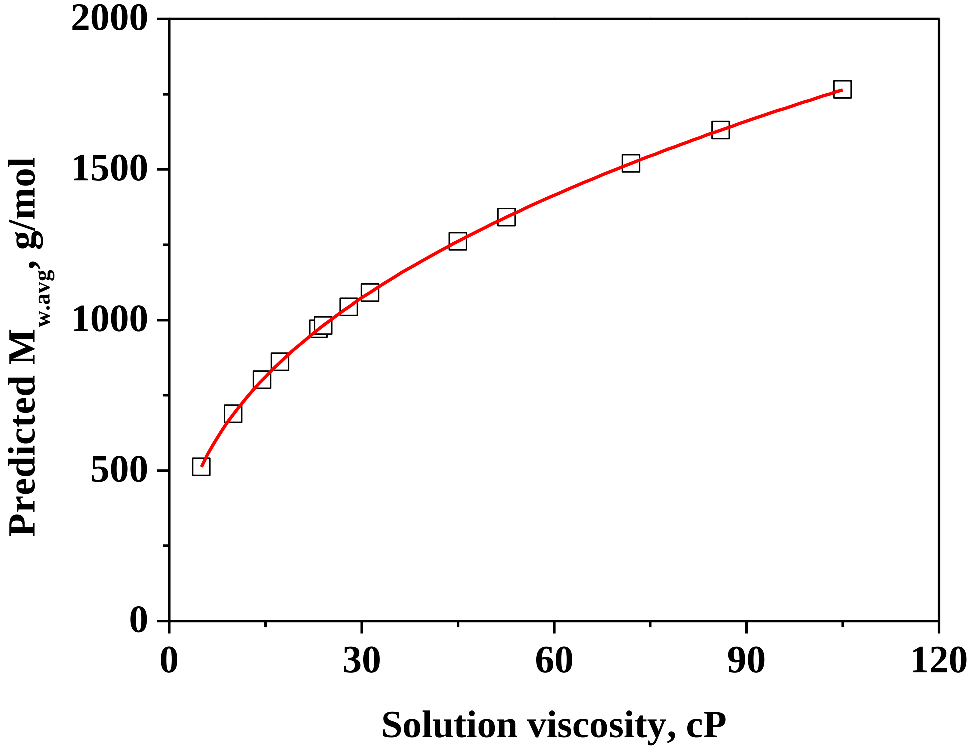


Figure 6.10. Solution viscosity and predicted $M_{w.avg}$ of the resin products

6.5. Conclusions

Mathematical regression models were developed with the help of statistical analysis tools, such as, MINITAB 17 and Microsoft Excel using experimentally obtained laboratory data to optimize the reaction parameters for obtaining a desired quality resin for coating applications. An effort has been made to develop empirical models to predict the product properties like average molecular weight, solubility and softening point of resin products. The developed models were good in agreement with the experimental results.

<u>Chapter 7</u>

Preparation of Ketonic Resins from Methylcyclohexanone and Cyclopentanone

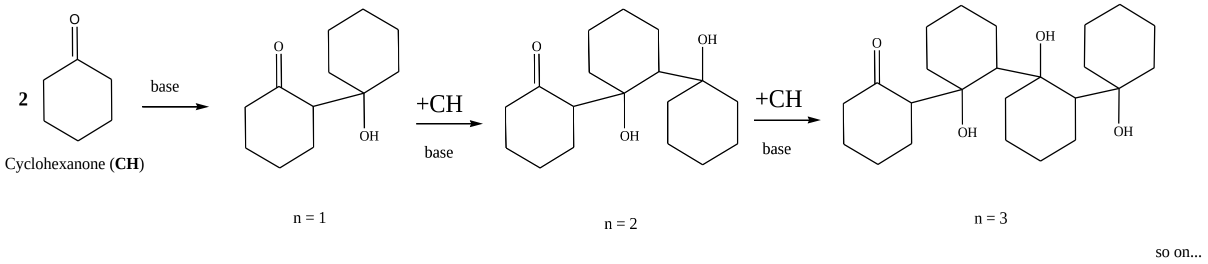
7.1. Introduction

From the literature, it has been observed that most of the studies were carried out on dimerization, trimerization and tetramerization reactions of cyclohexanone or alkyl cyclohexanone (Yogesh et al., 2008). Few studies are available in the literature on oligomerization or polymerization of ketones (mainly cyclohexanone) with aldehyde (mainly formaldehyde) to obtain a ketone–aldehyde resin (Werner et al., 2007). It is quite clear that the comprehensive study on self–polymerization reaction of cyclic ketones such as cyclohexanone (CH), cyclopentanone (CP), and alkyl ketone such as methylcyclohexanone (MCH) is not available in open literature. Therefore, the objective of the present study is to develop synthetic resins from cyclic ketones such as MCH and CP for paint and coating applications. The other objective of the study is to compare the MCH and CP resin properties with CH resin properties.

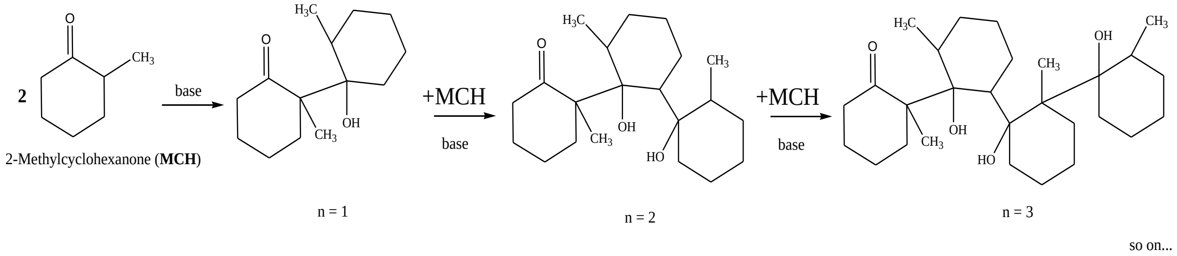
7.2. Results and Discussions

After successful preparation of ketonic resin from cyclohexanone monomer, another cyclic ketone, namely, cyclopentanone and alkyl ketone such as 2–methylcyclohexanone were considered for the present study to investigate the feasibility of resin formation. Polymerization reactions of cyclopentanone and 2–methylcyclohexanone were carried out in a high pressure reactor (the detailed experimental procedure is mentioned in Chapter 3) to develop the ketonic resins. The cross–polymerization reactions of ketonic monomers were also considered in the present study. The effect of reaction parameters and monomer concentration on various physico–chemical properties of the resin products were investigated. In the study, reaction time was varied from 15 to 20 hrs and temperature was varied from 145 to 150 °C. The synthesis details of the resin products are tabulated in Table 7A at the end of the present chapter. The probable reaction schemes of self–polymerization reactions of cyclohexanone, methylcyclohexanone and cyclopentanone are shown in Figure 7.1.

(a) Self–polymerization of cyclohexanone:



(b) Self–polymerization of methylcyclohexanone:



(c) Self–polymerization of cyclopentanone:

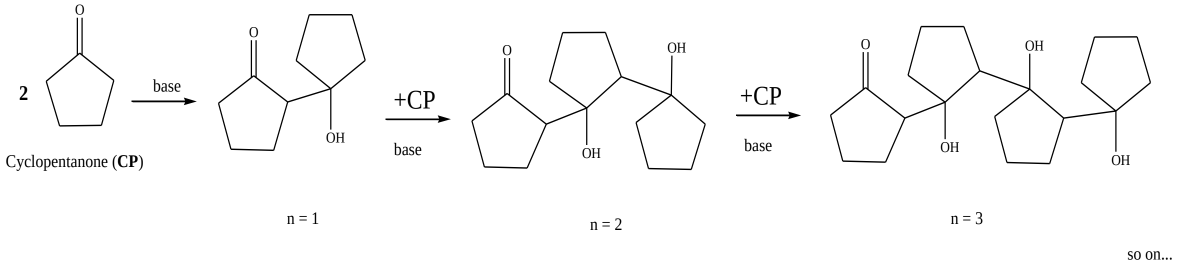


Figure 7.1. Probable reaction schemes of base–catalyzed self–polymerization reactions of cyclohexanone, methylcyclohexanone and cyclopentanone

7.2.1. Preparation of methylcyclohexanone and cyclopentanone resins

In the study, the ketonic monomers such as methylcyclohexanone (MCH) and cyclopentanone (CP) were used to prepare the ketonic resins namely methylcyclohexanone resin (MCHR) and cyclopentanone resin (CPR) respectively. The properties of MCHR and CPR were compared with cyclohexanone resin (CHR) prepared under similar conditions. The reaction conditions and the physico–chemical properties of the resin products are shown in Table 7.1. The data shows that methylcyclohexanone and cyclopentanone produced liquid resin in comparison with solid resin obtained from cyclohexanone monomer under similar reaction conditions. In addition, cyclopentanone offered brown colour product, whereas methylcyclohexanone yielded yellowish white colour resins. The data also shows that MCH and CP resins offered lower hydroxyl value and viscosity over CH resin. Around 63% and 70% decrease in hydroxyl value was observed for MCH and CP resins respectively in comparison to CH resin. However, the solubility of MCHR and CPR in MTO was relatively more compared to CH resin. It was also observed that the solubility of MCH resin was more than the CP resin obtained under identical conditions. The iodine values of MCH and CP resins was relatively higher than the CH resin. Therefore, based on the experimental results, it can be said that methylcyclohexanone or cyclopentanone alone may not be suitable raw materials to obtain a desire quality (hydroxyl value should be greater than 110 mg KOH/g resin and solubility should be greater than 25 wt% in MTO) of solid resin for paint and coating applications. Therefore, an attempt was taken to carry out cross–polymerization reactions between CH–MCH and CH–CP with different proportions to investigate the feasibility of resin formation with a desired property.

Table 7.1. Reaction conditions and physico–chemical properties of the resins

Product ID	CS–75	CS–70	CS–98
Resin type	CHR	MCHR	CPR
Reaction time, hr	16	16	16
Reaction temp., ºC	145	145	145
A/K ratio, wt./wt.	0.18	0.18	0.18
Product colour	White	Yellowish	Brown
Physical state	Solid	Viscous liquid	Viscous liquid
Hydroxyl value, mg KOH/g resin	127	46	37
Viscosity at 30 ºC, cP	86	6.9	3.1
Solubility in MTO, wt%	34	63	58
Iodine value, g I_2/100 g resin	2.9	3.8	4.3

7.2.2. Effect of methylcyclohexanone concentration on resin properties

In the study, it was observed that self–polymerization of methylcyclohexanone offered viscous liquid resin product. Therefore, the study was extended to carry out the cross–polymerization reactions of CH and MCH at various concentrations of MCH to find the feasibility for preparation of desired quality of CH–MCH resin and the preparation details are given in Table 7.2. The effect of MCH concentration on physico–chemical properties of the resin is shown in Figure 7.2 and 7.3. The results (in Table 7.2) show that a white color resin product was obtained from the cross–polymerization of CH and MCH. The physical state of the resin products varied from solid to soft–solid with the increase of MCH concentration and which indicates that the degree of polymerization decreased with MCH.

Table 7.2. The effect of MCH concentration on physico–chemical properties of the resins

Product ID	CS–75	CS–72	CS–71	CS–74
Resin type	CHR	CH–MCHR	CH–MCHR	CH–MCHR
Concentration of MCH	0	5	10	25
Concentration of CH	100	95	90	75
Reaction temp., °C	145	145	145	145
Reaction time, hr	16	16	16	16
A/K ratio, wt/wt	0.18	0.18	0.18	0.18
Product color	White	White	White	White
Physical state	Solid	Solid	Solid	Soft–solid

The variation in hydroxyl value and iodine value of the products with methylcyclohexanone concentration is shown in Figure 7.2. The figure shows that a decreasing trend in hydroxyl value and an increasing trend in iodine value were observed with the increase of methylcyclohexanone concentration. Figure 7.3 shows that viscosity of the resins decreased with the increase in methylcyclohexanone concentration. However, a remarkable increase in product solubility in MTO was observed with the increase of methylcyclohexanone concentration. From the results it can be said that methylcyclohexanone can play an important role to obtain a resin with higher solubility values by compromising hydroxyl value.

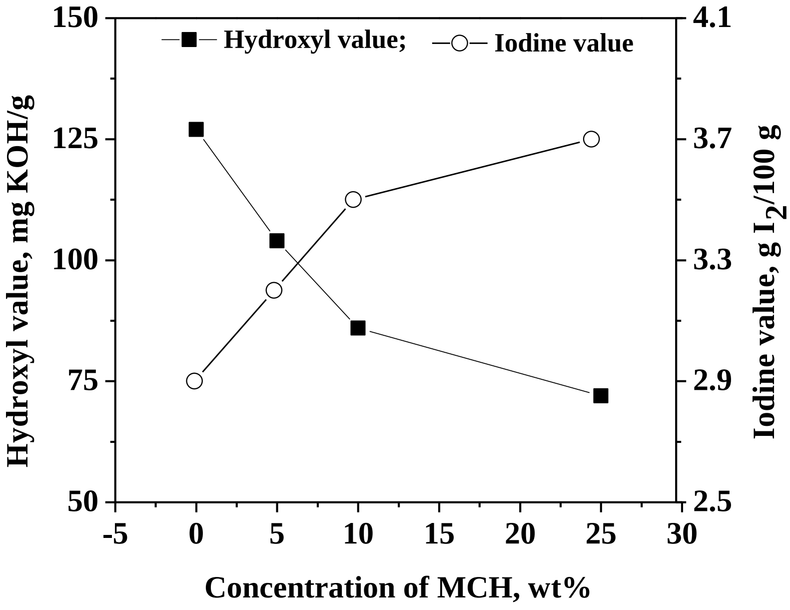


Figure 7.2. Effect of MCH concentration on Hydroxyl value and Iodine value of the resin

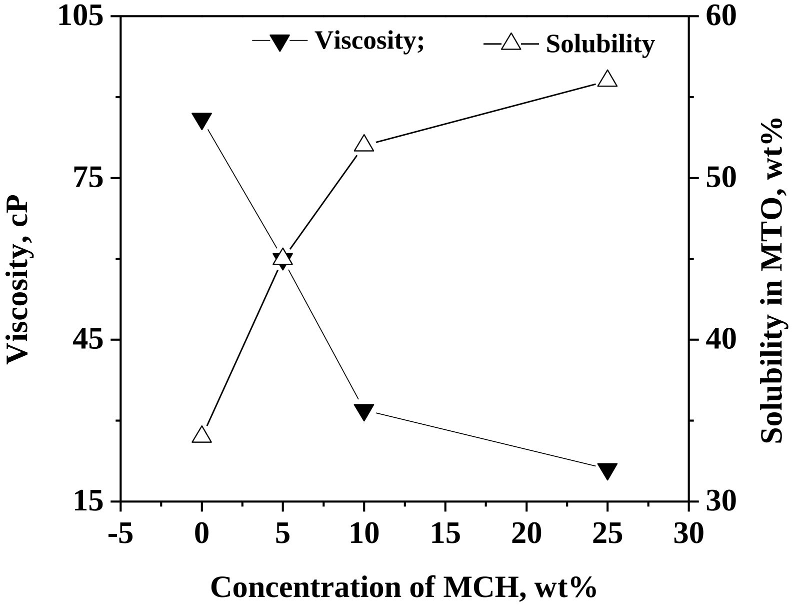


Figure 7.3. Effect of MCH concentration on Viscosity and Solubility of the resin products

7.2.3. Effect of cyclopentanone on physico–chemical properties of the resin

To study the effect of cyclopentanone on resin properties, the polymerization reactions were carried out at 145 °C for a time duration of 16 hrs with an A/K ratio of 0.18. The effect of cyclopentanone concentration on physico–chemical properties of the resin is shown in Table 7.3, Figure 7.4 and 7.5. The result shows that as the cyclopentanone concentration increased in the reaction mixture, the product color changed from white to yellow and then to brown. The physical state of the resin product also changed from solid to semi solid with the increase of cyclopentanone concentration.

Table 7.3. The effect of CP concentration on physico–chemical properties of the resins

Product ID	CS–75	CS–99	CS–100	CS–101
Resin type	CHR	CH–CPR	CH–CPR	CH–CPR
Concentration of CP	0	5	10	25
Concentration of CH	100	95	90	75
Product color	White	Yellow	Yellow	Brown
Physical state	Solid	Solid	Soft–solid	Semi–solid

The variation of hydroxyl value and iodine value with cyclopentanone concentration is shown in Figure 7.4. The figure shows that the hydroxyl value of the products drastically decreased with the increase of cyclopentanone concentration. However, an increasing trend in iodine value was observed with the increase of cyclopentanone concentration. Figure 7.5 shows that viscosity of the resins decreased with the increase in cyclopentanone concentration in reaction mixture. But the product solubility in MTO increased with the increase of cyclopentanone concentration.

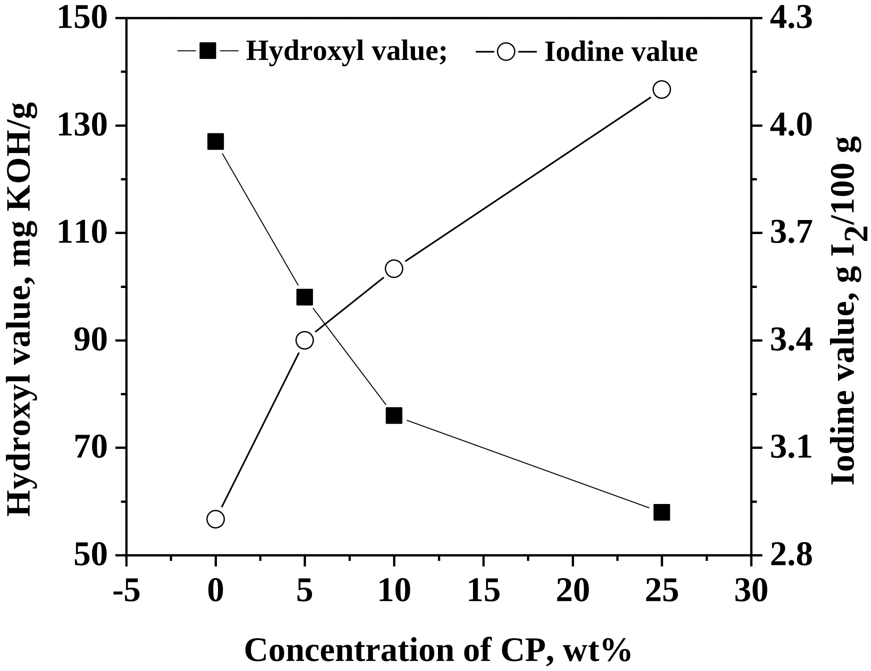


Figure 7.4. Effect of CP concentration on Hydroxyl value and Iodine value of the resin

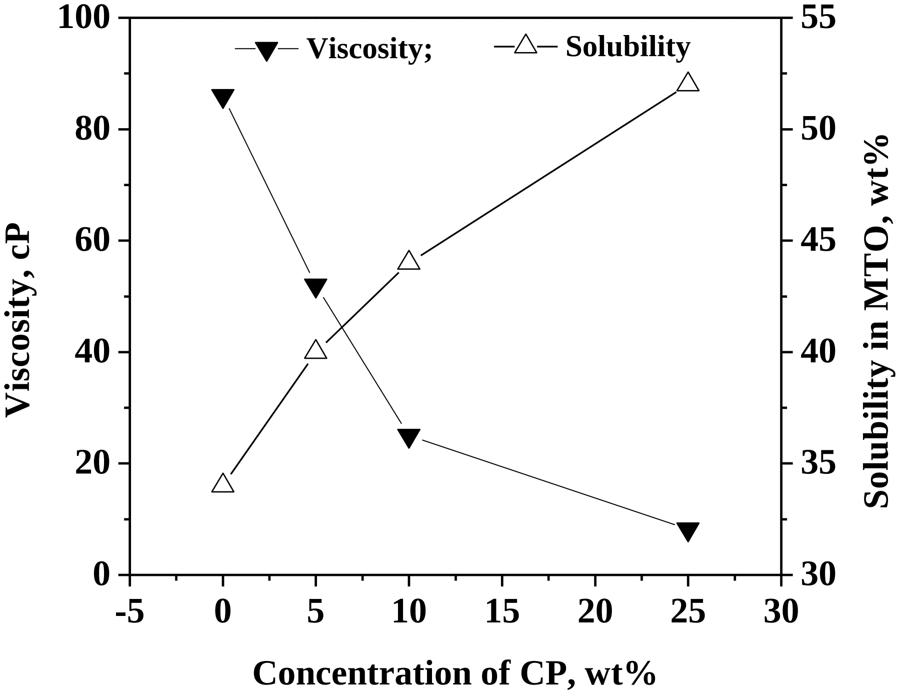


Figure 7.5. Effect of CP concentration on Viscosity and Solubility of the resin

7.2.4. Effect of reaction conditions on physico–chemical properties of resin products

The effect of methylcyclohexanone (MCH) and cyclopentanone (CP) concentrations on physico–chemical properties of the products under identical reaction conditions was examined. It was observed that hydroxyl value of the products decreased with MCH and CP concentration and solubility of the products increased with MCH and CP concentration. Therefore, the study further extended to prepare the resin by varying the reaction conditions to enhance the hydroxyl value of the products. The reaction conditions and obtained physico–chemical properties of the products prepared from CH–MCH and CH–CP are given in Table 7.4 and 7.5 respectively.

Table 7.4. Effect of reaction conditions on CH–MCH resin properties

Product ID	CS–69	CS–85	CS–96	CS–103
Resin type	CHR	CH–MCHR	MCHR	CH–MCHR
Reaction time, hr	20	18	20	20
Reaction temp., ºC	150	148	150	150
A/K ratio	0.18	0.18	0.18	0.18
Concentration of MCH, wt%	0	5	100	10
Concentration of CH, wt%	100	95	0	90
Product color	White	White	White	White
Physical state	Solid	Solid	Viscous–liquid	Solid
Hydroxyl value, mg KOH/g	134	123	67	118
Viscosity at 30 ºC, cP	580	188	9.8	140
Solubility in MTO, wt%	10	38	58	42
Iodine value, g I_2/100 g resin	3.8	3.6	4.3	4.0

The data (Table 7.4) shows that the product (CS–96) obtained from MCH monomer was a liquid state even though the reaction carried out at higher temperature and for longer duration. On the other hand, a solid product (CS–69) with better hydroxyl value was obtained from CH monomer under similar reaction conditions. The data further revealed that lower concentration of MCH (10 wt%) in reaction mixture offered a solid resin (CS−103) with improved hydroxyl value. Another good quality of resin (CS−85) was also obtained when the MCH concentration was further reduced to 5 wt%. Based on the present investigation, it can be said that the concentration of MCH in reaction mixture can be varied between 5−10 wt% to obtain a solid resin with desirable hydroxyl value and solubility for paint and coating applications. The other advantage of MCH in reaction mixture is that it offered light color resins.

Table 7.5. Effect of reaction conditions on physico−chemical properties of CH−CP resins

Product ID	CS−69	CS−97	CS−102	CS−104
Resin type	CHR	CPR	CH−CPR	CH−CPR
Reaction time, hr	20	20	20	18
Reaction temp., ºC	150	150	150	148
A/K ratio	0.18	0.18	0.18	0.18
Concentration of CP, wt%	0	100	10	5
Concentration of CH, wt%	100	0	90	95
Product color	White	Brown	Yellow	Yellow
Physical state	Solid	Viscous−liquid	Solid	Solid
Hydroxyl value, mg KOH/g	134	51	112	116
Viscosity at 30 ºC, cP	580	4.9	119	131
Solubility in MTO, wt%	10	55	31	28
Iodine value, g I_2/100 g resin	3.8	5.2	4.4	4.0

The data (Table 7.5) shows that with 10 wt% of CP concentration in the reaction mixture offered a yellow color solid resin (CS−102) with a hydroxyl value of 112 mg KOH/g of resin. When the CP concentration was further decreased to 5 wt%, the hydroxyl value of the product (CS−104) increased by 4 units and around 3 units solubility reduction was observed. The yellow color of CP−CH resins may be an issue for some specific applications.

7.2.5. Functional group analysis of the ketonic monomers and resin products

To identify the functional groups present in the resin products, FTIR analysis was performed for the in–house developed ketonic resins. The obtained FTIR spectrums of various monomers and resin products are shown in Figure 7.6. The spectrum shows that there is no characteristic band corresponding to the O–H group at around 3400 cm^{-1} for any of the three monomers (CH, CP and MCH). However, a broad band at around 3400 cm^{-1} and a band at 1650 cm^{-1} in the resin products indicates the presence of O–H group and C=C bond respectively. The other characteristic bands at 2900 cm^{-1} and 1700 cm^{-1} corresponds to C–H stretching and C=O stretching respectively.

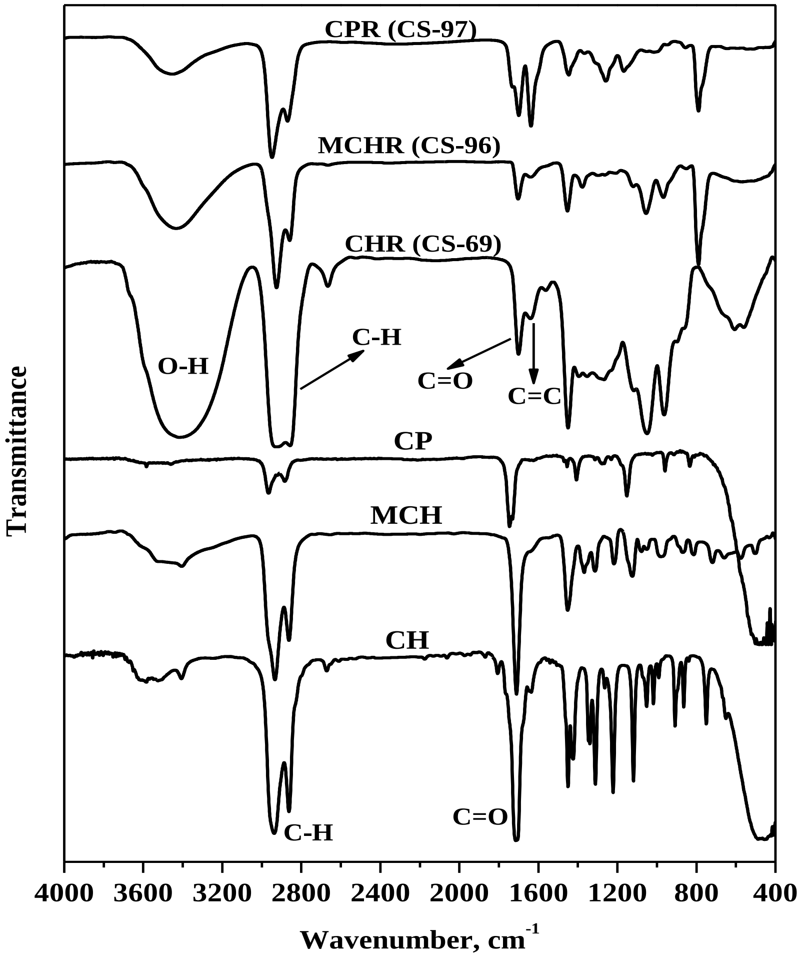


Figure 7.6. FTIR spectrums of ketonic monomers and resin products

7.2.6. Thermogravimetric analysis of the different ketonic resin products

The thermal stability of the in–house developed ketonic resins developed under similar reaction conditions was studied by using a thermogravimetric analyser (TGA). The resin sample was taken in the sample pan and heated from 30 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The TGA–thermograms of different resins are shown in Figure 7.7. From the TGA analysis, it was observed that around 2% weight loss was observed for cyclohexanone resin (CHR), methylcyclohexanone resin (MCHR) and cyclopentanone resin (CPR) products when the resins were heated up to 120 °C. This weight loss of the resin products was mainly due to the evaporation of moisture from the products. The obtained weight loss of the CH resin was around 4%, whereas around 8% loss was obtained for MCH and CP resins up to a temperature of 200 °C. This loss was mostly because of the evaporation of unconverted monomer and low molecular weight compounds. The actual degradation of polymeric material was started at a temperature of around 200 °C and almost completed at a temperature of around 500 °C.

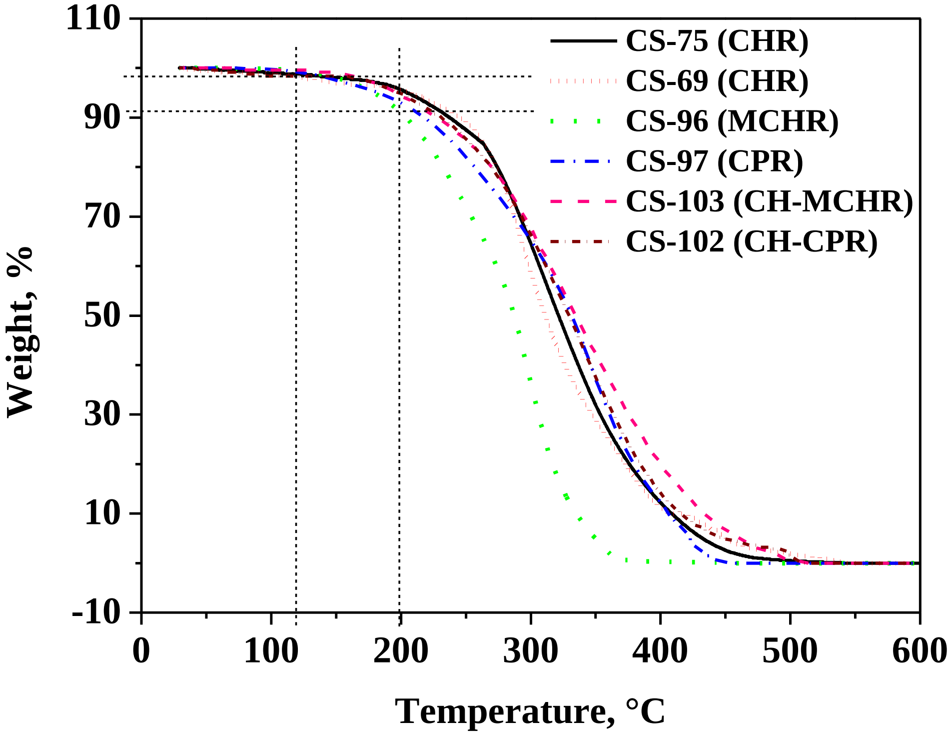


Figure 7.7. TGA thermograms of different ketonic resin products

From the thermograms, it can be said that CHR offered better thermal stability over MCHR and CPR. The order of the thermal stability of the resin products are CHR > CPR > MCHR. The thermograms also shows that CH−MCH and CH−CP mixture resins offered better thermal stability over pure MCH and CP resins. Therefore, based on the thermogravimetric analysis, it can be said that the in−house developed CHR products are thermally stable up to a temperature of around 200 °C. However, MCHR and CPR products are thermally stable up to a temperature of around 180 °C with a mass loss of around 5%.

7.3. Conclusions

In the present study, ketonic resins were prepared by self−polymerization of methylcyclohexanone and cyclopentanone. The cross−polymerization reactions of CH−MCH and CH−CP were also examined in the work. The effects of monomer concentration and reaction parameters on product properties have been studied. From the results, it was observed that the polymerization reactions with methylcyclohexanone or cyclopentanone monomers alone may not be suitable raw materials to obtain a solid resin with desired properties. However, addition of small proportion (5 to 10 wt%) of methylcyclohexanone or cyclopentanone along with cyclohexanone can play a significant role in obtaining a better quality product. It was observed that CH and MCH monomers offered white color resins whereas CP monomer offered brown color resins. Addition of MCH with CH may be an alternative choice to improve the solubility of resin products. The presence of hydroxyl group in the resin products has been re−established from the FTIR spectrum. The in−house developed resins are thermally stable up to a temperature of around 180 ºC. From the overall investigation, it can be concluded that the in−house developed ketonic resins (MCH−CH and CP−CH) can be a suitable substitute of alkyd or phenolic resins for paint and coating applications.

Table 7A. Synthesis details of the resin products

Product ID	Reaction time, hr	Reaction temp., °C	A/K ratio, wt/wt
CS–70	16	145	0.18
CS–71	16	145	0.18
CS–72	16	145	0.18
CS–74	16	145	0.18
CS–85	18	148	0.18
CS–96	20	150	0.18
CS–97	20	150	0.18
CS–98	16	145	0.18
CS–99	16	145	0.18
CS–100	16	145	0.18
CS–101	16	145	0.18
CS–102	20	150	0.18
CS–103	20	150	0.18
CS–104	18	148	0.18

<u>Chapter 8</u>

Kinetics of Self–Polymerization and Thermal Decomposition of Ketonic Resin

8.1. Kinetics of Self–Polymerization of Cyclohexanone

8.1.1. Introduction

Based on the literature review on the kinetics of self–polymerization of cyclo–ketones, it has been observed that very few literatures are available on the kinetics of dimerization reaction of cyclohexanone. Literature pertaining to the kinetics of oligomerization/ polymerization reaction of cyclohexanone is not reported in the literature. Therefore, the objective of the present investigation is to find the kinetics of self–polymerization reaction of cyclohexanone.

8.1.2. Results and Discussions

In the previous studies (Chapter 4), the ketonic resin was prepared from cyclohexanone monomer under atmospheric pressure conditions. In the present study, the kinetic and thermodynamic parameters such as, order of reaction (n), reaction rate constant (k), activation energy (E), activation entropy (ΔS^*), activation enthalpy (ΔH^*) and activation free energy (ΔG^*) change were estimated for the self–polymerization reaction of cyclohexanone. Monomer conversion data obtained from GC analysis was used to estimate the kinetic parameters.

8.1.2.1. Effect of reaction time, catalyst loading and temperature on monomer conversion

The effect of reaction parameters such as, reaction time, catalyst concentration, and reaction temperature on cyclohexanone monomer conversion and degree of polymerization was examined. To study the kinetics of self–polymerization reaction of cyclohexanone, the catalyst loading was varied in the range of 10–20 wt% based on initial monomer weight and temperature was varied in the range of 90–110 °C. During the reaction, the samples from the reactor were collected at a regular time interval for GC analysis. The conversion of cyclohexanone was calculated from the GC results, and the corresponding values are shown in Figure 8.1 and 8.2. The result shows that the monomer conversion increased with the increase of reaction time at a fixed catalyst loading and reaction temperature.

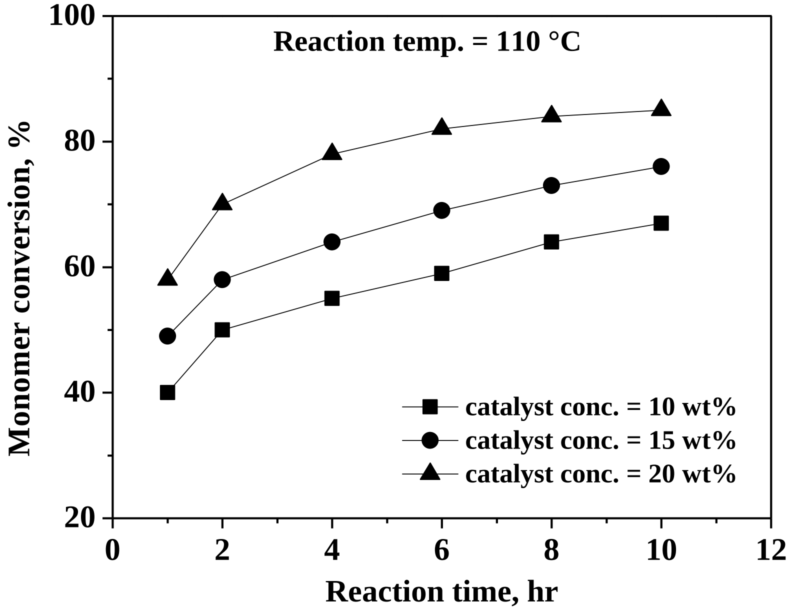


Figure 8.1. Effect of catalyst concentration on monomer conversion (Product ID: OS−6, OS−7, OS−8)

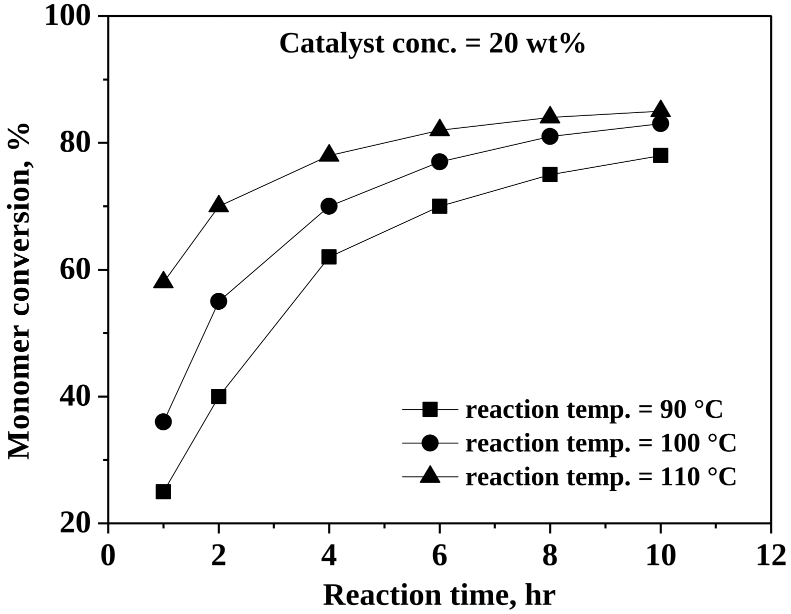


Figure 8.2. Effect of reaction temperature on monomer conversion (Product ID: OS−4, OS−18, OS−8)

Figure 8.1 shows that the monomer conversion gradually increased with the increase of catalyst concentration for a fixed value of reaction temperature. It was also observed that the conversion of cyclohexanone increased with the increase of reaction temperature for a fixed value of catalyst concentration (Figure 8.2). The increase in monomer conversion with the increase of reaction time, temperature and catalyst loading was due to the availability of longer contact time, higher thermal energy and more active sites respectively to enhance the reaction rates. The figure also shows that the rate of monomer conversion was relatively higher in the beginning stage (<4 hrs.) of reaction, and after 6 hrs, the increasing rate of conversion slowed down. The estimated value of monomer conversion was around 85% at 110 °C for a reaction time of 10 hrs and with a catalyst concentration of 20 wt%.

8.1.2.2. Kinetic and thermodynamic parameters of self–polymerization of cyclohexanone

In the self–polymerization of cyclohexanone, one monomer unit reacts with another monomer unit to yield a dimer product. The trimer product can be obtained either by reaction between a monomer and a dimer unit or by reaction between three monomer units. The number of possibility of reaction scheme increase with the increase of degree of polymerization. The experimentally obtained monomer conversion data has been used to find the kinetics of the reaction, and it is assumed that (i) the system is homogenous; (ii) the concentration of the catalyst does not change with time, and (iii) the process is isothermal and irreversible.

The following expressions were used to investigate the reaction order and rate constant for the present polymerization reaction:

$$\frac{1}{(1-x)^{n-1}} = (n-1).C_{CH_0}^{n-1}.k^1.t+1 \qquad \text{for } n \neq 1 \qquad (8.1)$$

$$-\ln(1-x) = k^1.t \qquad \text{for } n = 1 \qquad (8.2)$$

where, n = order of reaction, x = (C_{CH0} – C_{CH}) / C_{CH0} = fractional conversion, C_{CH} = concentration of cyclohexanone at any time 't', C_{CH0} = initial concentration of cyclohexanone, k^1=k.C_{cat}, k = reaction rate constant, and C_{cat} = catalyst concentration.

The kinetic plots were drawn based on experimentally obtained conversion data and using Equation (8.1) and (8.2) to find the probable reaction order. A typical kinetic plot is shown in Figure 8.3 for two different reaction temperatures. Based on the kinetic plots and R^2 (correlation coefficient) value, it has been found that the reaction followed a second–order kinetics at 90 °C and third–order kinetics at 110 °C for a fixed catalyst concentration of 20 wt%.

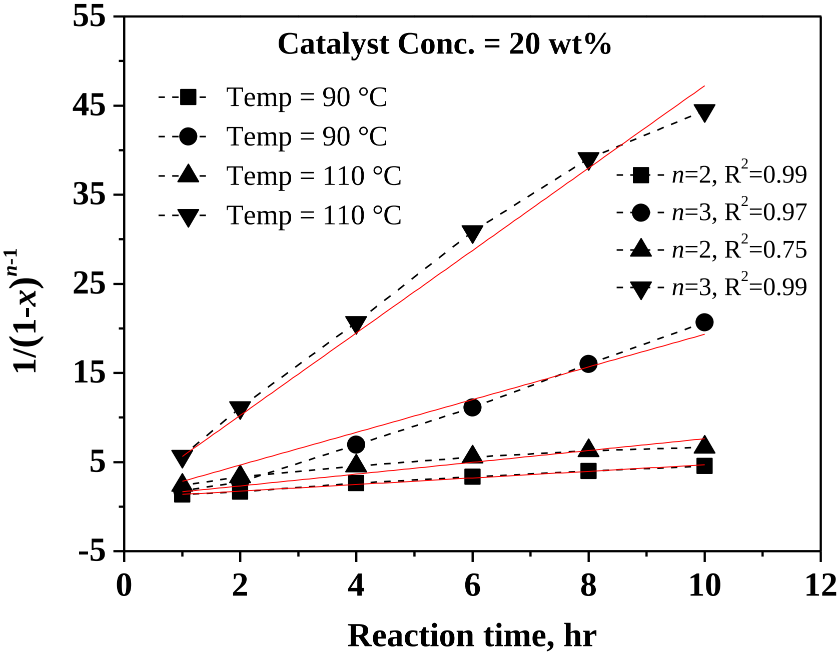


Figure 8.3. $1/(1–x)^{n-1}$ versus reaction time plots for different orders

Table 8.1. Reaction order and R^2 values at different reaction conditions

Temperature, °C	Catalyst conc., wt%	R^2 value			
		n = 1	*n* = 2	*n* = 2.5	*n* = 3
110	10	–	0.48	0.75	<u>0.90</u>
110	15	–	0.67	0.89	<u>0.97</u>
110	20	–	0.74	0.93	<u>0.99</u>
100	20	–	0.98	<u>0.99</u>	0.97
90	20	0.94	<u>0.99</u>	0.98	0.97

The value of reaction order and the corresponding R^2 value (for linear fitting) at different reaction conditions are shown in Table 8.1. The analysis shows that the reaction order varied mostly between 2 and 3 depending upon the reaction conditions. From the study, it can be said that the order of the reaction depends on the reaction severity. The value of reaction rate constant was estimated from the slope of the best fit kinetic plots and are shown in Figure 8.4 and 8.5.

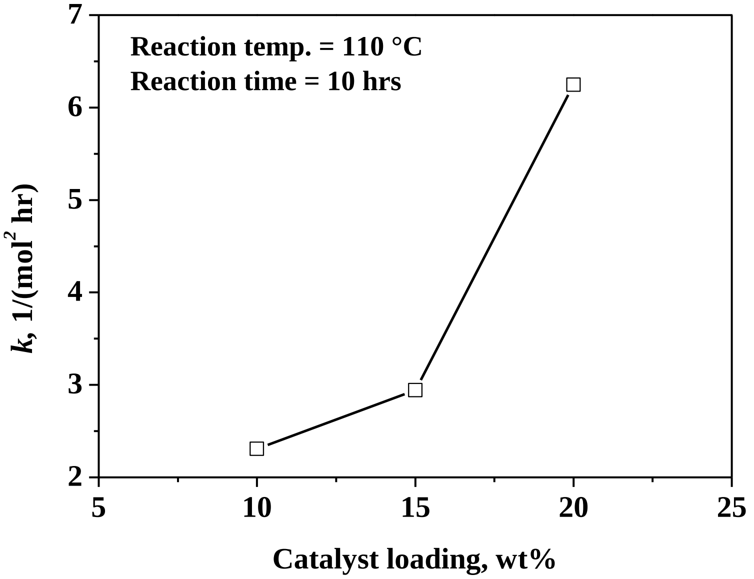


Figure 8.4. Effect of catalyst loading on reaction rate constant

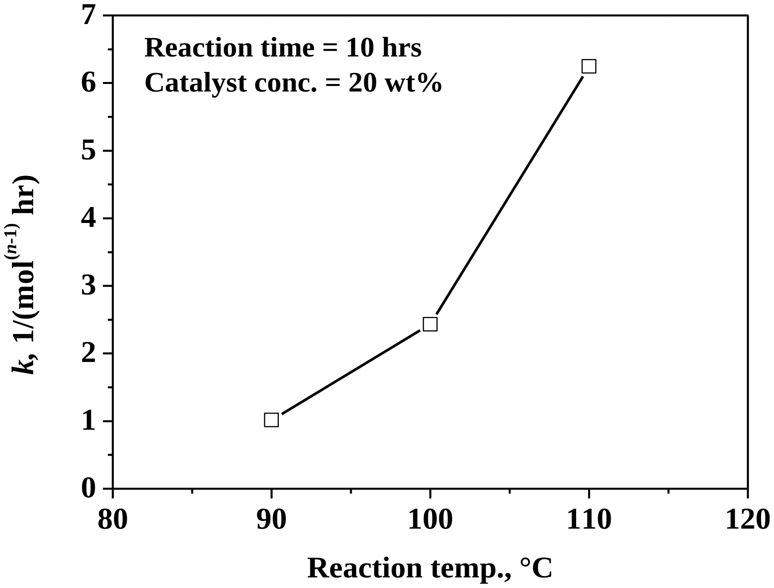


Figure 8.5. Effect of reaction temperature on reaction rate constant

Figure 8.4 shows that the rate constant value increased with the increase of catalyst loading. The data shows that the value of *'k'* increased by around 1.3 and 2.1 times when the catalyst concentration was increased from 10 to 15 wt% and from 15 to 20 wt% respectively for a fixed reaction temperature. The increase of rate constant with catalyst loading may be due to the availability of more number of active sites to progress the polymerization reaction. Figure 8.5 shows that the value of '*k*' increased with the increase of reaction temperature, and for every 10 °C increase in reaction temperature, the average value of '*k*' increased around 2.5 times.

The estimated rate constant value was used to calculate the activation energy (E) using the Arrhenius equation (Equation (8.3)) and the corresponding plot is shown in Figure 8.6.

$$k = k_0 . e^{-E/RT} \tag{8.3}$$

where, T = temperature (K); k_0 = pre–exponential factor; R = gas constant (8.314 J/(mol K).

The estimated value of apparent activation energy of the self–polymerization reaction of cyclohexanone is around 105 kJ/mol at a catalyst loading of 20 wt%, and the value is comparable with the literature reported value for similar kinds of study (Yeqiang et al., 2011; Lorenzo et al., 2013; Lorenzo et al., 2014).

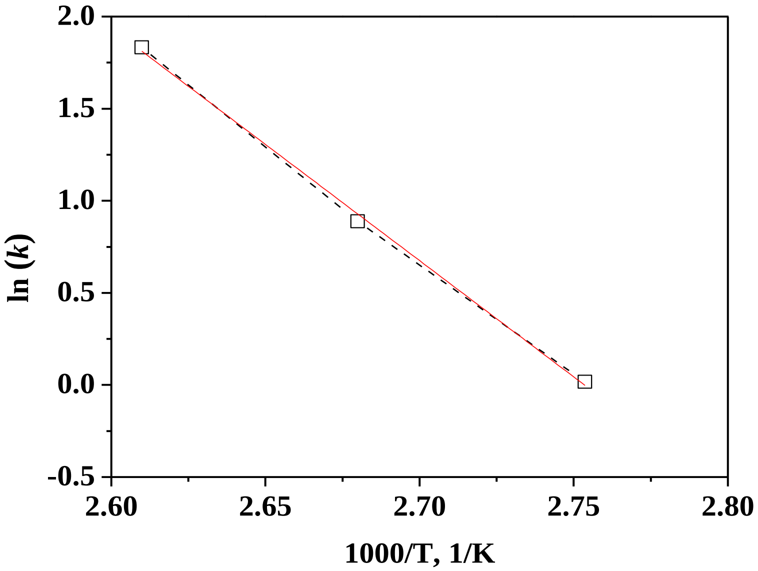


Figure 8.6. Arrhenius plot

A comparison of activation energy of self–condensation reaction of cyclohexanone between literature values and the value obtained in the present study is shown in Table 8.2.

Table 8.2. Comparison of activation energy of self–condensation reaction of cyclohexanone

Author's name and Year	System studied	Reaction conditions	Reported activation energy (E), kJ/mol
Yeqiang et al. (2011)	dimerization reaction of cyclohexanone	Temp. = 110–130 °C, Cat. = γ–alumina	177
Lorenzo et al. (2013)	dimerization reaction of cyclohexanone	Temp. = 127–149 °C, Cat. = NaOH	132.6
Lorenzo et al. (2014)	dimerization reaction of cyclohexanone	Temp. = 70–110 °C, Cat. = Amberlyst–15	68.5
In the present study	Self–polymerization of cyclohexanone	Temp. = 90–110 °C, Cat. = KOH	105

The values of thermodynamic parameters such as, entropy (ΔS^*), enthalpy (ΔH^*) and Gibbs free energy (ΔG^*) of activation were calculated using Equations (8.4), (8.5) and (8.6) respectively.

$$k = \frac{k_b.T}{h}.e^{-E/RT}.e^{\Delta S^*/R} \tag{8.4}$$

where, k_b = Boltzmann's constant (1.3807×10^{-23} J/K); h = Planck's constant (6.63×10^{-34} J s).

$$\Delta H^* = E - RT \tag{8.5}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{8.6}$$

The estimated values of thermodynamic parameters at mean reaction temperature (100 °C) and with 20 wt% catalyst loading are shown in Table 8.3. Similar kind of observation was also examined by few authors in literature (Priti and Deepak, 2014).

Table 8.3. Kinetic and thermodynamic parameter values of CH polymerization reaction

k, 1/(mol$^{1.5}$ hr)	Temp., K	E, kJ/mol	ΔS^*, J/(mol K)	ΔH^*, kJ/mol	ΔG^*, kJ/mol
2.432	373	105	–26.28	101.82	111.62

8.1.3. Conclusions

The kinetics of self–polymerization reaction of cyclohexanone was investigated in the present study. The effect of reaction parameters such as reaction time, temperature and catalyst concentration on monomer conversion was studied. It has been found that the rate of reaction increased with the increase in catalyst loading and reaction temperature. An effort has been made to find the kinetic and thermodynamic parameters value. It is observed that the reaction order (n) varies mostly between 2 and 3 depending upon the reaction conditions. The estimated activation energy of the reaction is around 105 kJ/mol.

8.2 Kinetics of Thermal Decomposition of Ketonic Resins

8.2.1. Introduction

Synthetic resins, such as phenol–formaldehyde, epoxy, alkyd, ketone–aldehyde and ketonic resins, are used in paint and coatings applications, to improve the adhesiveness and glossiness, light and chemical resistance of paints (Goldschmidt and Streitberger, 2007). The thermal degradation of resins is a phenomenon where the polymeric resin at elevated temperature undergoes chemical changes. The study of thermal degradation of resin is important for developing an efficient technology for resin processing and in understanding the thermal decomposition mechanism. The study is also important in understanding their applicability at elevated temperature and storage (Krzysztof and James, 2005). Thermogravimetric analysis (TGA) method is a useful technique to investigate the thermal stability and decomposition kinetics of a polymer material.

From the literature survey, it has been observed that most of the thermal decomposition studies were carried out with phenolic resins, alkyd resins, aldehyde resins. Though a phenolic resin is an attractive choice for high temperature applications, but the disadvantage of this resin is the toxic fumes associated with the high temperature applications. In case of alkyd resins, the residual carbon–carbon double bonds provided by the unsaturated fatty acids raw material may lead to atmospheric oxidation under ambient conditions. To the best of our knowledge, the studies pertaining to the thermal decomposition kinetics of ketonic resins obtained from cyclic–ketones are not reported in the literature. Therefore, the objective of the present study is to develop a synthetic resin from ketonic monomers, and to evaluate the thermal decomposition kinetics of the in–situ developed ketonic resins. The solid resins obtained from the closed system were considered to study the decomposition kinetics.

8.2.2. Results and Discussions

The preparation and characterization details of a ketonic resin obtained from cyclohexanone, methylcyclohexanone and cyclopentanone has been discussed in in previous chapters (Chapter 5 and Chapter 6). In the present study, the focus was extended to study the thermal stability of the in–house developed ketonic resins. Thermogravimetric analysis (TGA) technique was adopted to investigate the thermal decomposition kinetics, and to estimate thermodynamic parameters like order of reaction (n), reaction rate constant (k), activation energy (E), activation entropy (ΔS^*), activation enthalpy (ΔH^*) and activation free energy (ΔG^*). The obtained results were also compared with the thermal stability of the commercially available phenol–formaldehyde resin and alkyd resin.

8.2.2.1. Comparison between in-house developed ketonic resins and commercially available resins

The polymerization reactions of cyclohexanone (CH), cyclohexanone–methylcyclohexanone (CH–MCH) mixture, and cyclohexanone–cyclopentanone (CH–CP) mixture were carried out in a high pressure reactor at different reaction conditions. The reaction conditions and physico–chemical properties of few selected resins (whose hydroxyl value >110) are shown in Table 8.4. The properties of in–house developed ketonic resins were also compared with a commercially available phenolic resin (PR) and alkyd resin (AR) used for similar application. A comparison has been made to check the compatibility of the ketonic resins with the phenolic resin and alkyd resin.

The data (Table 8.4) shows that the hydroxyl value of the ketonic resins are relatively higher than the phenolic resin and alkyd resin. The solubility of ketonic resins was slightly lower than the phenolic resin and alkyd resin. The number–average molecular weights of the ketonic resins are in the range of 800–1400 g/mol and corresponding values for the phenolic resin and alkyd resin are around 1410 and 1210 g/mol respectively. The iodine values of the ketonic resins are comparatively lesser than the phenolic and alkyd resins. Resin with low degree of unsaturation is better for coating application. Therefore, based on the results, it can be said that the in–house developed ketonic resins are comparable with the studied commercial resins.

Table 8.4. Reaction conditions and physico–chemical properties of the resins

Product ID	CS–39	CS–75	CS–69	CS–103	CS–102	–	–
Resin type	CHR	CHR	CHR	MCH–CHR	CP–CHR	PR	AR
Reaction temp., °C	140	145	150	150	150	–	–
Time duration, hr	15	16	20	20	20	–	–
A/K ratio, wt/wt	0.2	0.18	0.18	0.18	0.18	–	–
Conc. of CH, wt%	100	100	100	90	90	–	–
Conc. of MCH, wt%	0	0	0	10	0	–	–
Conc. of CP, wt%	0	0	0	0	10	–	–
HV, mg KOH/g	111	127	134	118	112	106	101
IV, g I_2/100 g	3.0	2.9	3.8	4.0	4.4	4.6	4.9
$M_{n\cdot avg}$, g/mol	820	1220	1371	1025	1090	1411	1213
PDI	1.41	1.37	1.32	1.38	1.34	1.41	1.99
Solubility, wt%	37	34	10	42	31	47	56

8.2.2.2. Thermogravimetric analysis of the resin products

To study the thermal stability and kinetics of thermal degradation of the resin products, thermogravimetric analysis was carried out using a TGA instrument. The TGA measurements were recorded in the temperature range from 30 to 600 °C at a heating rate of 10 °C/min in presence of nitrogen atmosphere. The analysis details are mentioned in Chapter 3. The obtained TGA thermograms of different resin products and a typical DTA curve of a particular resin product (CS–75) at a heating rate of 10 °C/min are shown in Figure 8.7 and 8.8 respectively.

The TGA thermograms show that around 2.5% weight loss was obtained for ketonic resins, when the products were heated up to a temperature of 120 °C. The weight loss was mainly due to the evaporation of moisture content and solvent molecules from the products. When the resins were heated from 120 to 200 °C, the estimated weight loss of the ketonic resins was around 4%, and which may be due to the evaporation of unconverted monomer molecules trapped inside the solid products. In case of CS−39 product, the obtained weight loss was around 7% between 120 and 200 °C due to its low molecular weight. However, for phenolic resin, the weight loss was negligible (< 2%) up to 200 °C. The actual decomposition started at around 200 °C and completed nearly at 500 °C for ketonic resins. From the thermograms, a single−step degradation was observed for ketonic resins, whereas, two−steps degradation was observed for the phenolic and alkyd resins. In case of phenolic resin, first−step of degradation was observed from 220 to 380 °C and second−step of degradation was observed from 380 to 600 °C. In case of alkyd resin, around 20% mass loss was observed up to 140 °C. This loss was mainly due to the loss of moisture, volatile solvents and low molecular weight compounds from the material. The second degradation started at around 300 °C and completed at a temperature of 480 °C. The percentage weight loss obtained from the TGA thermograms for the in−house developed ketonic resins and commercial resins are shown in Table 8.5. The data shows that the ketonic resins were thermally stable up to 200 °C, and beyond 200 °C a significant weight loss was observed.

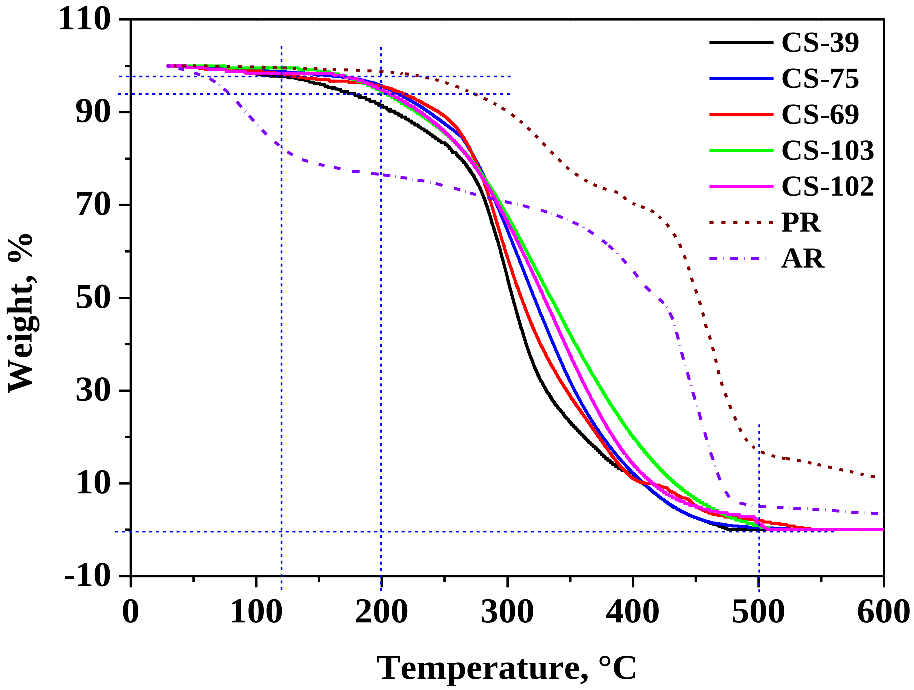


Figure 8.7. TGA thermograms of resin products at a heating rate of 10 °C/min

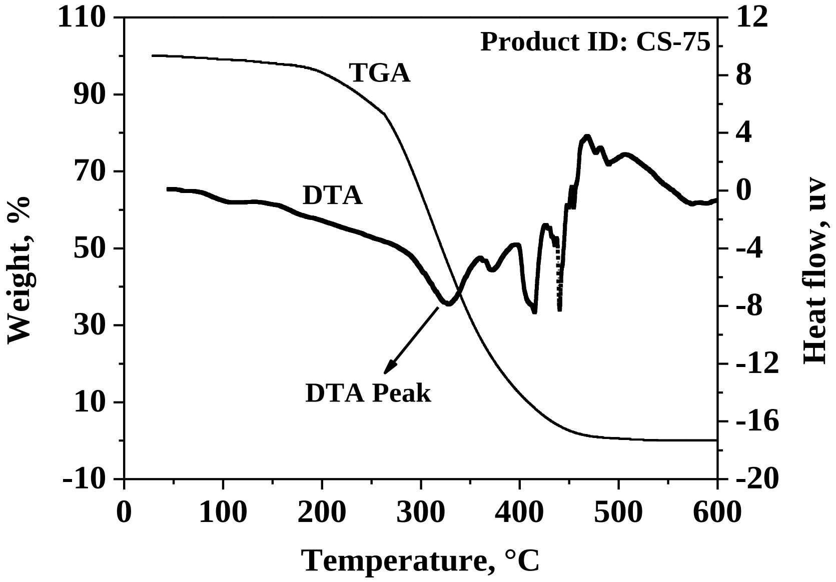


Figure 8.8. TGA and DTA curves of CS–75 resin product at a heating rate of 10 °C/min

Table 8.5. Percentage weight loss data of different resin products

Product ID	*$T_{5\%}$, °C	$T_{10\%}$, °C	$T_{50\%}$, °C	$T_{90\%}$, °C	$T_{95\%}$, °C
CS–39	164	208	304	407	430
CS–75	204	237	321	408	432
CS–69	208	245	311	412	451
CS–103	195	226	334	433	459
CS–102	197	230	329	416	447
PR	260	296	447	>600	>600
AR	74	91	418	470	504

* Temperature corresponds to percentage (5%, 10%, 50%, 90% and 95%) weight loss.

8.2.2.3. Decomposition kinetics of the resin products

Thermogravimetric techniques are used to study the thermal degradation kinetics of the polymer materials. Various methods, such as, Coats–Redfern (C–R) method, Madhusudhanan–Krishnan–

Ninan (M–K–N) method, and Van–Krevelen (V–K) method have been proposed by many authors to estimate the kinetic parameters for thermal degradation of polymer materials. Among the various methods, C–R and M–K–N methods are very popular to estimate the kinetic parameters from the weight loss data for a fixed heating rate. In the present study, decomposition kinetics of the ketonic resins was evaluated from the weight loss data obtained from the thermograms under non–isothermal condition. The TGA data was coupled with Arrhenius equation to find the decomposition kinetics. Coats–Redfern method has been used to evaluate the kinetics for the present system.

The Arrhenius equation was used to represent the dependency of reaction rate with temperature. The logarithmic form of Arrhenius equation can be written as:

$$\log k = \log A - \frac{E}{2.303RT} \tag{8.7}$$

where, k is decomposition rate constant, T is temperature (K), A is frequency factor, R is gas constant, and E is activation energy.

The rate of thermal decomposition, which is dependent on the temperature and the change in mass of the sample, can be expressed as:

$$\frac{dx}{dt} = k.f(x) = A.e^{-E/RT}.f(x) \tag{8.8}$$

where, x is the fractional conversion of a sample at time t.

The fractional conversion of a material at a particular temperature x_T was calculated using the following expression:

$$x_T = \left(\frac{W_i - W_T}{W_i - W_f} \right) \tag{8.9}$$

where W_i, W_f and W_T are initial weight, final weight and weight at a particular temperature respectively. Final weight was considered based on the plateau region of a thermogram.

If the sample temperature is changed at a constant heating rate, $a = dT/dt$; the change in the degree of conversion can be analyzed as a function of temperature, and this temperature being dependent on the time of heating. Therefore, the reaction rate can be written as:

$$\frac{dx}{dt} = \frac{dx}{dT}\frac{dT}{dt} = a\frac{dx}{dT} \tag{8.10}$$

The combination of Equation (8.8) and (8.10) yields the following expression:

$$\frac{dx}{dT} = \frac{A}{a}.e^{-E/RT}.f(x) \tag{8.11}$$

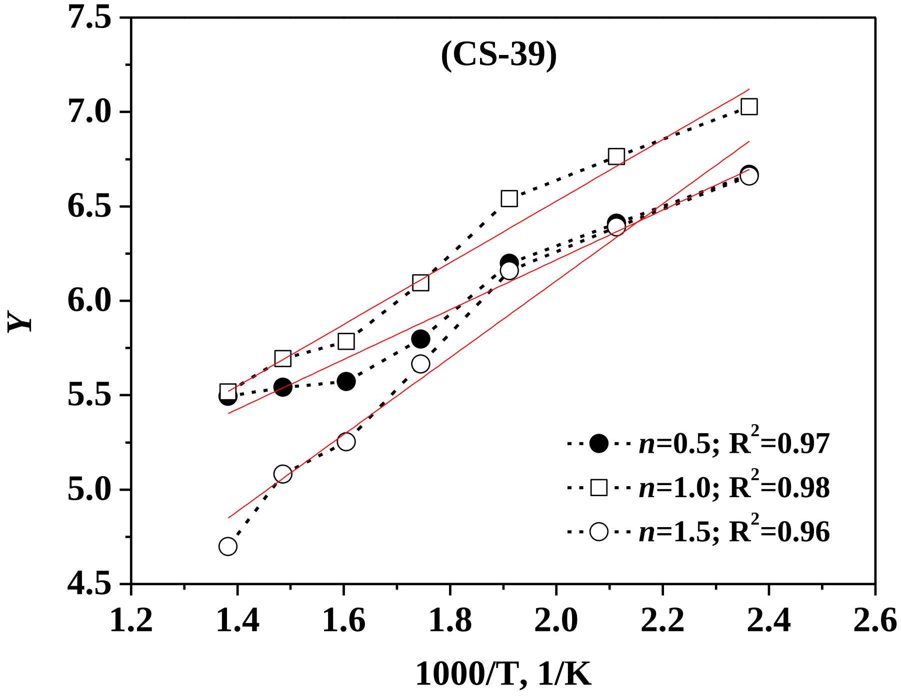
If $f(x) = (1–x)^n$ (where n is order of decomposition reaction) and constant heating rate, $a = dT/dt$, then according to the Coats–Redfern method, Equation (8.11) can be expressed by the following relations:

$$-\log\left(\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right) = (Y) = \frac{E}{2.303RT} - \log\left[\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)\right] \qquad (\text{for } n \neq 1) \tag{8.12}$$

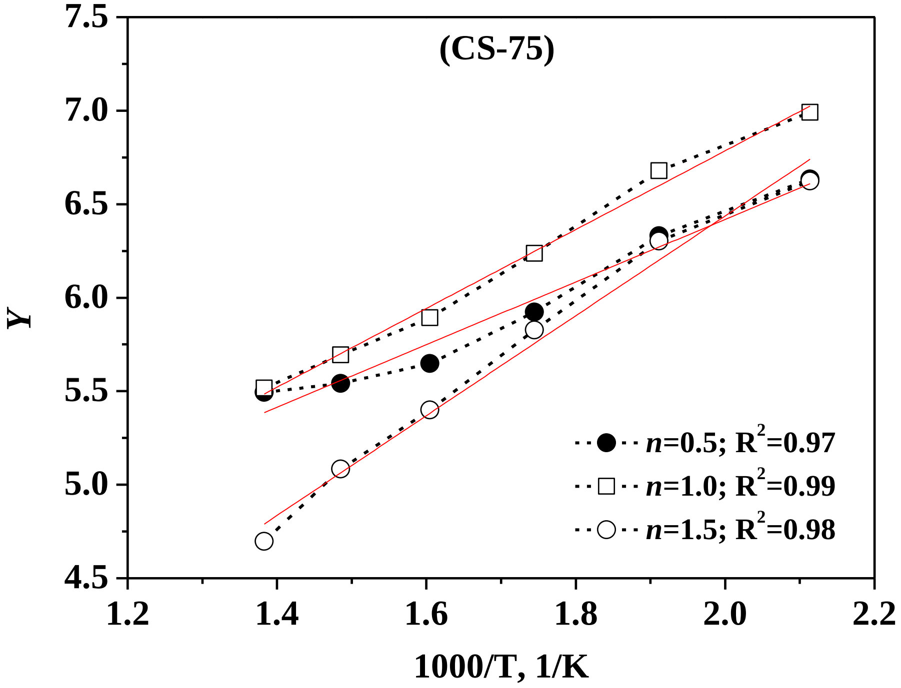
$$-\log\left(\frac{-\log(1-x)}{T^2}\right) = (Y) = \frac{E}{2.303RT} - \log\left[\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)\right] \qquad (\text{for } n=1) \tag{8.13}$$

The order of decomposition kinetics was estimated by setting different values of ‘n’ in Equation (8.12) or (8.13). The values of ‘Y’ were calculated from the TGA data and plotted against the reciprocal of decomposition temperature.

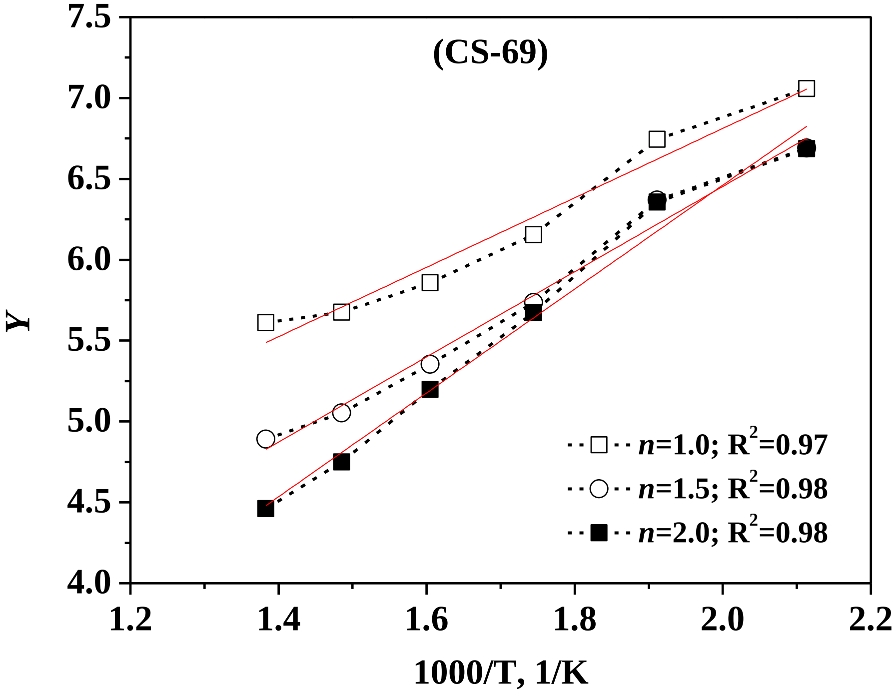
The Coats–Redfern plots of five ketonic resins (CS−39, CS−75, CS−69, CS−103, CS−102), the phenolic resin and alkyd resin for different values of ‘n’ are shown in Figure 8.9. The estimated values of apparent activation energy obtained from the Coats–Redfern plots along with the DTA peak temperature (T_p) obtained from DTA curves of the resin products are tabulated in Table 8.6.



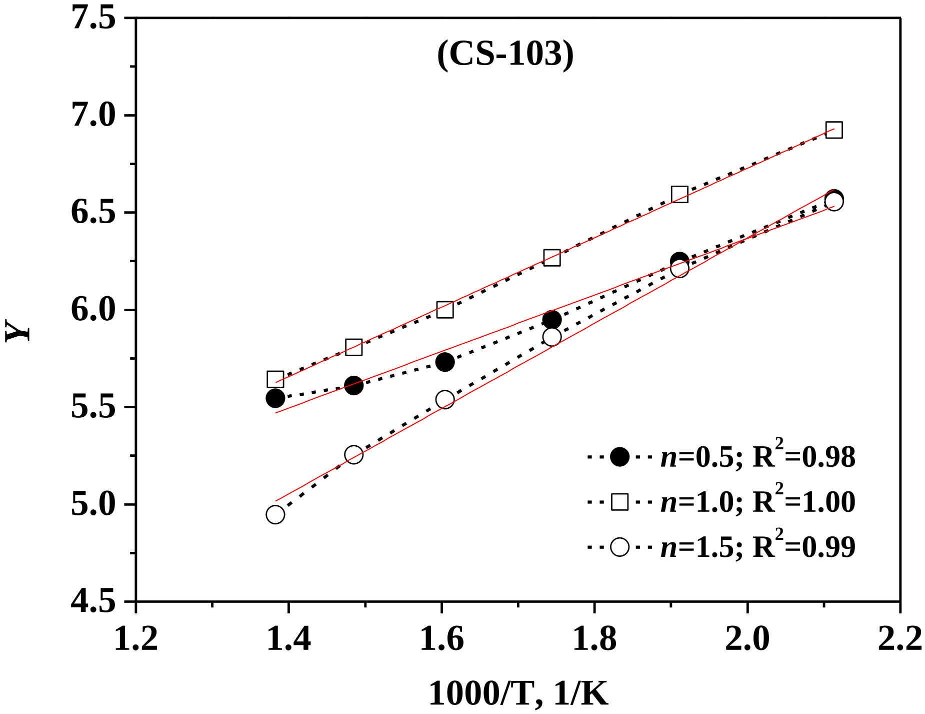
(CS-39)
Y
1000/T, 1/K
7.5
7.0
6.5
6.0
5.5
5.0
4.5
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
n=0.5; R²=0.97
n=1.0; R²=0.98
n=1.5; R²=0.96



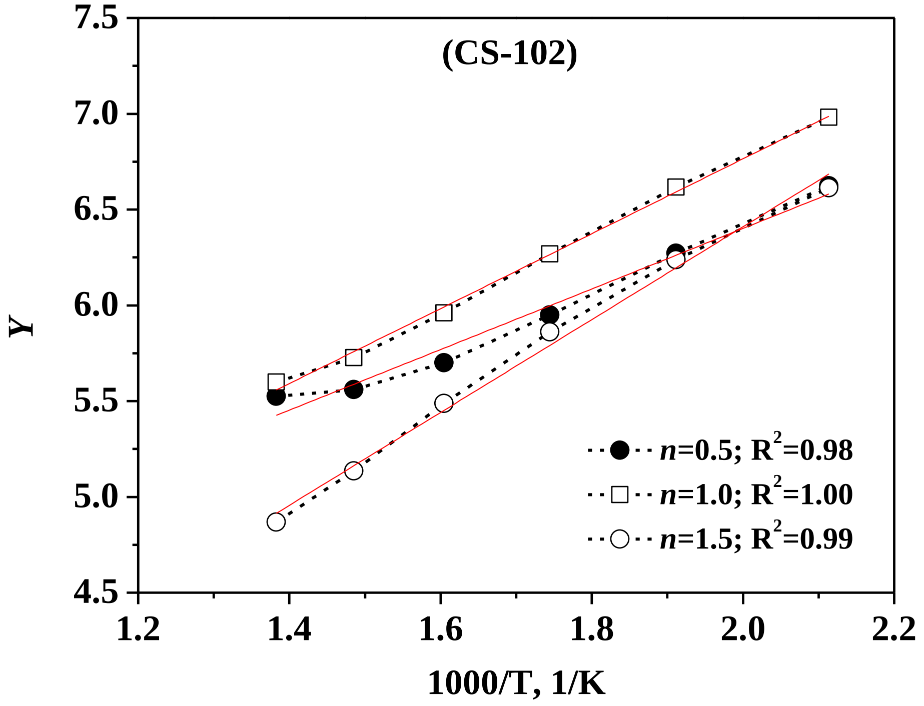
(CS-75)
Y
1000/T, 1/K
7.5
7.0
6.5
6.0
5.5
5.0
4.5
1.2
1.4
1.6
1.8
2.0
2.2
n=0.5; R²=0.97
n=1.0; R²=0.99
n=1.5; R²=0.98

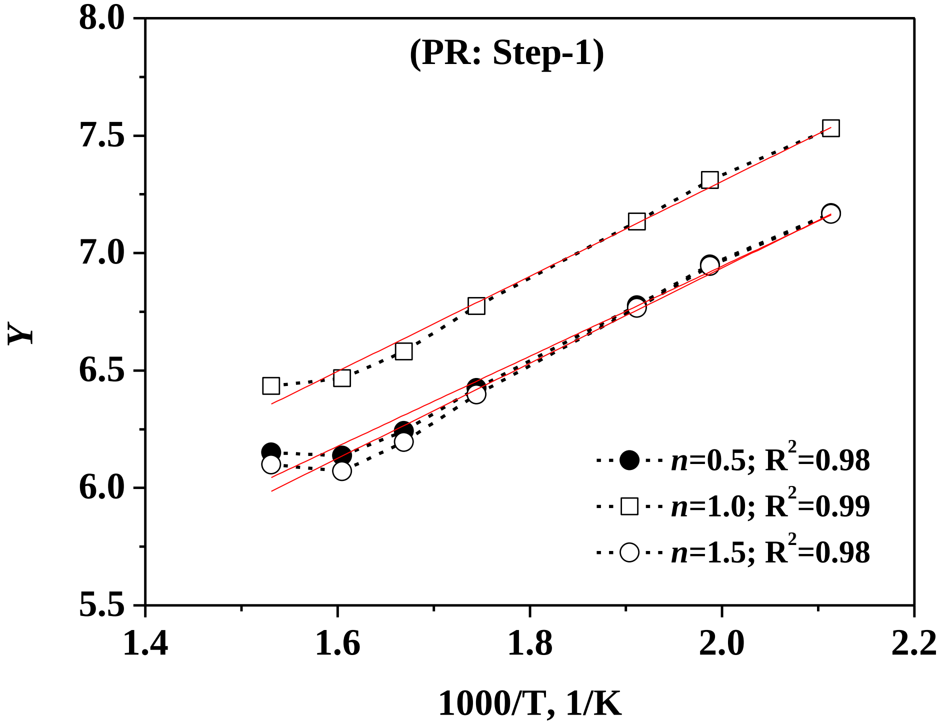


(CS-69)
Y
1000/T, 1/K
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
1.2
1.4
1.6
1.8
2.0
2.2
n=1.0; R²=0.97
n=1.5; R²=0.98
n=2.0; R²=0.98



(CS-103)
Y
1000/T, 1/K
7.5
7.0
6.5
6.0
5.5
5.0
4.5
1.2
1.4
1.6
1.8
2.0
2.2
n=0.5; R²=0.98
n=1.0; R²=1.00
n=1.5; R²=0.99


(CS-102)
Y
1000/T, 1/K
7.5
7.0
6.5
6.0
5.5
5.0
4.5
1.2
1.4
1.6
1.8
2.0
2.2
n=0.5; R2=0.98
n=1.0; R2=1.00
n=1.5; R2=0.99


(PR: Step-1)
Y
1000/T, 1/K
8.0
7.5
7.0
6.5
6.0
5.5
1.4
1.6
1.8
2.0
2.2
n=0.5; R2=0.98
n=1.0; R2=0.99
n=1.5; R2=0.98

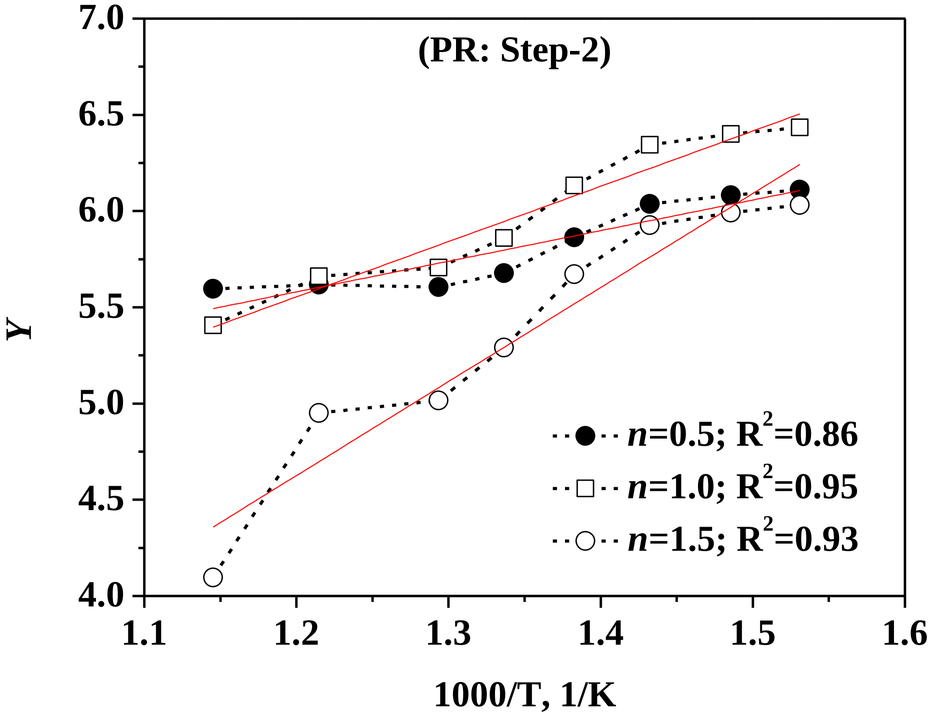


Figure 8.9. Coats–Redfern plots for different values of reaction order

The data (Table 8.6) shows that the apparent activation energy of the ketonic resins increased with the increase of resin average molecular weight. Apparent activation energy also increased with the increase of thermal stability (with respect to T_p) of the products. Based on the apparent activation energy data, it can be said that the studied phenolic resin is more stable (thermally) than the ketonic resins. It was found that the ketonic resins mostly followed first–order kinetics for decomposition reaction and in few cases the order lies between 1 and 1.5. The apparent activation energy of the ketonic resins is in the range of 31−41 kJ/mol for a first–order decomposition reaction. The average value of the apparent activation energy of the phenolic resin is around 47 kJ/mol and the value is comparable with the literature value (50−70 kJ/mol) reported by various authors for different kinds of phenol–formaldehyde resins (Alonso et. al., 2011; Lee et. al., 2003). For the alkyd resin, the average value of apparent activation energy is around 31 kJ/mol for a first–order decomposition reaction. The higher value of apparent activation energy for the second–step decomposition of the studied commercial resins is mainly due to the presence of higher molecular weight polymeric molecules, and which has been observed from the molecular weight distribution pattern. The similar type of observation was also reported by Zhao et al. for the phenol–formaldehyde resin (Zhao et. al., 2013).

Table 8.6 Values of kinetic parameters of different resin products

Product ID	$M_{n\cdot avg}$, g/mol	T_p, K	Order (n)	E, kJ/mol
CS−39	820	573	1	31.2
CS−75	1220	591	1	40.3
CS−69	1371	608	1	41.1
			1.5	50.4
CS−103	1025	593	1	34.2
CS−102	1090	588	1	37.4
PR: Step−1	1411	656	1	38.7
PR: Step−2			1	55.0
AR: Step−1	1213	523	1	25.7
AR: Step−2			1	35.9

8.2.2.4. Estimation and comparison of activation energy obtained from other methods

To find the deviation in estimated apparent activation energy values among various methods, the activation energy of the ketonic resins was also calculated by using other methods, namely, Madhusudhanan–Krishnan–Ninan (M–K–N) method and Van–Krevelen (V–K) method. Equation (8.14) and (8.15) were used to estimate the activation energy by M–K–N method and V–K method respectively, and the values are tabulated in Table 8.7. Based on the results, it can be concluded that the estimated activation energy obtained from the C–R method is comparable the with M–K–N method for the present system.

$$\ln\left(\frac{-\ln(1-x)}{T^{1.92}}\right)=\left(\ln\frac{AE}{aR}+3.77-1.92(\ln E)\right)-1.001\frac{E}{RT} \qquad \text{(for } n=1\text{)} \qquad (8.14)$$

$$\ln[-\ln(1-x)]=\ln\left[\frac{A}{a}\left(\frac{E}{RT_p}+1\right)^{-1}\left(\frac{0.368}{T_p}\right)^{\frac{E}{RT_p}}\right]+\left(\frac{E}{RT_p}+1\right)\ln T \qquad \text{(for } n=1\text{)} \qquad (8.15)$$

Table 8.7. Comparison of apparent activation energy among C−R, M−K−N and V−K methods

Product ID	n	E, kJ/mol		
		C−R method	M−K−N method	V−K method
CS−39	1	31.2	31.6	37.5
CS−75	1	40.3	40.7	45.9
CS−69	1	41.1	41.4	47.7
CS−103	1	34.2	34.5	39.7
CS−102	1	37.4	37.8	42.7

8.2.2.5. Thermodynamic parameters of decomposition kinetics of ketonic resins

In this study, thermodynamic parameters, such as, activation entropy change (ΔS^*), activation enthalpy change (ΔH^*) and activation free energy change (ΔG^*) were evaluated for the degradation kinetics of the resins. The following expressions were used to determine the parameters value.

$$\Delta S^* = 2.303 \times R \times \log\left(\frac{Ah}{k_b T_p}\right) \tag{8.16}$$

$$\Delta H^* = E - RT_p \tag{8.17}$$

$$\Delta G^* = \Delta H^* - T_p \Delta S^* \tag{8.18}$$

where, h and k_b are Planck's constant and Boltzmann constant respectively, T_p is peak temperature. The peak temperature was obtained from the differential thermal analysis (DTA) curve. The calculated values of thermodynamic parameters for thermal degradation of the resins are shown in Table 8.8. The first−order rate constants (k) value at the peak temperature was estimated in the range between 1.07 × 10^{-2} and 25.36 × 10^{-2} 1/s for the ketonic resins. The activation entropy change (ΔS^*) was found in the range between −131 and −145 J/(mol K).

Table 8.8. Values of thermodynamic parameters of different resin products

Product ID	n	T_p, K	$k \times 10^{-2}$, 1/s	ΔS^*, J/(mol K)	ΔH^*, kJ/mol	ΔG^*, kJ/mol
CS−39	1	573	25.36	−131.3	26.5	101.8
CS−75	1	591	1.09	−143.4	35.4	120.2
CS−69	1	608	1.07	−144.5	36.0	123.9
CS−103	1	593	13.56	−133.0	29.2	108.2
CS−102	1	588	3.43	−138.4	32.5	113.9
PR	1	656	4.07	−141.1	41.5	134.4
AR	1	523	16.9	−135.2	26.4	96.6

8.2.3. Conclusions

A systematic investigation of thermal stability and decomposition kinetics of the developed resins were performed using thermogravimetric analysis (TGA), and the results were compared with the commercially available phenolic resin and alkyd resin. The study shows that the ketonic resins are thermally stable up to around 200 °C. The apparent activation energy of the ketonic resin is in the range between 31 and 41 kJ/mol for a first−order reaction. For ketonic resins, the calculated rate constant (k) value was in between 1.07×10^{-2} and 25.36×10^{-2} 1/s at the peak temperature. The estimated values of entropy (ΔS^*) and free energy (ΔG^*) change of activation were in the range of −131 to −145 J/(mol K) and 101 to 125 kJ/mol respectively. The study showed that the thermal stability and apparent activation energy of the ketonic resins increased with the increase of product average molecular weights. Based on the above study, it can be concluded that the outcome of the present work will be very much useful to get an insight on processing and application of the developed resin products.

Chapter 9

Use of Additives to Improve Ketonic Resin Properties: A Feasibility Study

9.1. Introduction

It is known that additives / short stopping agents have been used to modify or to improve the properties of polymer materials. It is also reported that additives can be added to the reaction mixture during preparation time to control the polymerization reaction from run-away process to obtain a commercially value added product (Sharaby, 1988; Lawrence, 1958; Albert, 1971; Alan, 1970; Walter and Willie, 1947). From the literature survey, it has been found that, most of the studies pertinent to the application of additives / short stopping agents are on synthetic rubber, polystyrene, and polyvinyl chloride polymers. However, literature pertaining to the development of ketonic resins from cyclic ketones in presence additives has not been reported to the best of our knowledge. Therefore, an effort has been made to investigate some suitable additives which can be used to improve the physico-chemical characteristics (such as hydroxyl value, softening temperature, and solubility) of a ketonic resin.

9.2. Results and Discussions

After successful preparation of ketonic resin from cyclohexanone monomer, the focus was extended to find some suitable additives which can improve the properties of a ketonic resin. Initially an attempt has been taken to improve two important properties namely, hydroxyl value and solubility of a ketonic resin. For the present system, these two properties follow an opposite trend to each other. Few aromatic hydrocarbon compounds were chosen to study their suitability to improve the resin properties. To study the effect of additive on product properties, calculated amount of additive was added to the cyclohexanone monomer, and the reaction was allowed to continue for fixed time duration to obtain a solid resin.

9.2.1. Suitability of various additives to improve ketonic resin properties

In the present study, three different additives, namely, an alkyl aromatic (Add–1), an aromatic ketone (Add–2), and an aromatic alcohol (Add–3) compounds were tested to find their effects on the properties of ketonic resins. The polymerization reactions were carried out at 150 °C, for a duration of 20 hrs and with an A/K weight ratio of 0.18. In each case, additive concentration was maintained at a level of 2 wt%. The additive concentration was expressed as weight percentage with respect to monomeric material. The effect of additives on product properties obtained under similar reaction conditions are shown in Figure 9.1 and 9.2.

Figure 9.1 shows that hydroxyl value of the solid resin slightly decreased (around 4 to 6 units) in presence of additive Add–1 and Add–2 in comparison to the product obtained in absence of any additive (Add–0). However, the product solubility in MTO was slightly increased (around 3 to 5 units) in presence of Add–1 and Add–2. The result shows that, Add–3 offered better hydroxyl value product in comparison to the product obtained without additive. Product solubility increased marginally in presence of Add–3 compared to Add–0.

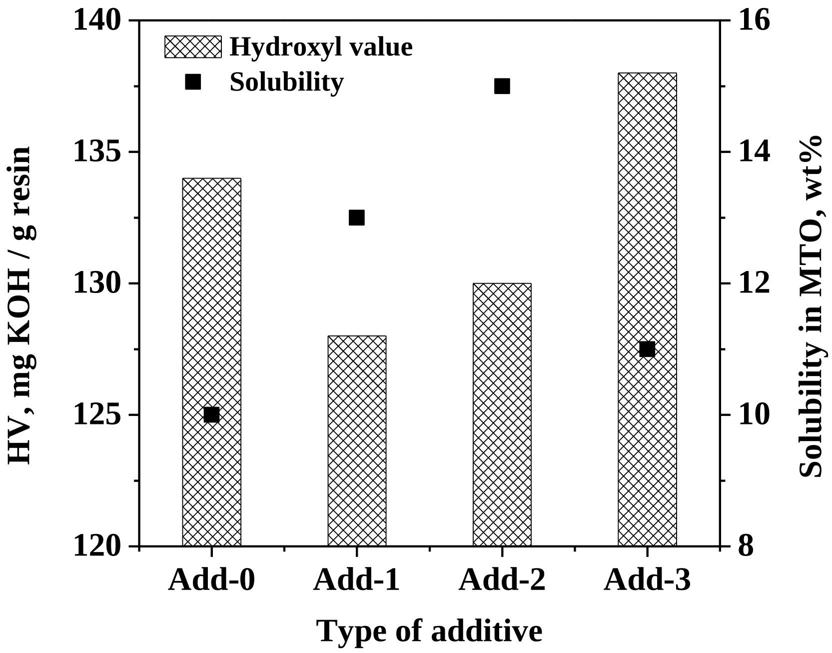


Figure 9.1. Effect of different additives on Hydroxyl value and Solubility value

(Product ID: CS–69, CS–77, CS–78, CS–81)

Figure 9.2 shows that in presence of Add–1, viscosity and softening temperature of the product decreased by around 25% and 4 units respectively. However, in presence of Add–3, the reduction of product viscosity and softening temperature was marginal. The results inferred that the degree of polymerization reduced in presence of additives and which can be confirmed from the viscosity and solubility data. It was also observed that the solubility of the products obtained in presence of additives are relatively higher compared to CS−69 product. Therefore, based on the present investigation, it can be said that the studied additives have a potential to improve the product solubility and Add−3 can be useful to obtained a product with better hydroxyl value.

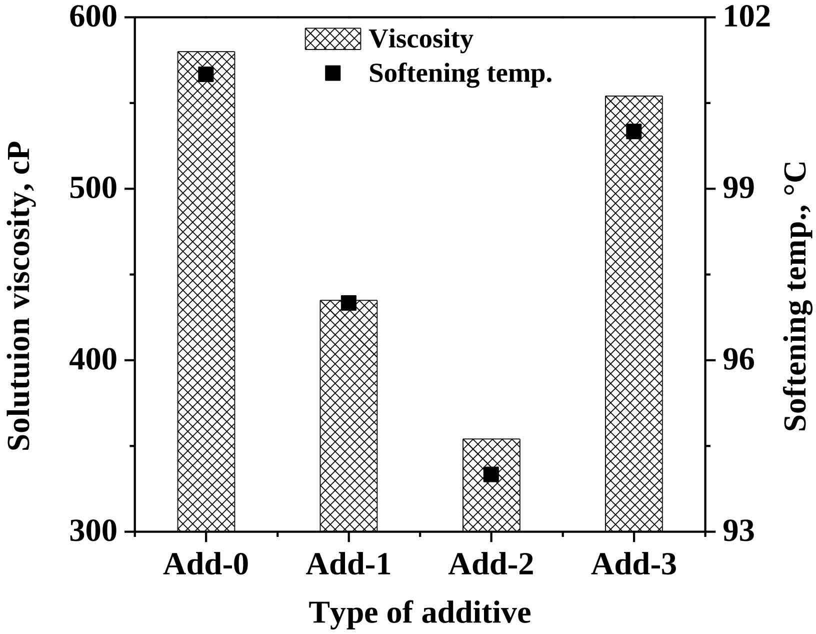


Figure 9.2. Effect of different additives on Viscosity and Softening temperature

(Product ID: CS−69, CS−77, CS−78, CS−81)

9.2.2. Effect of additive concentration on resin properties

Based on the preliminary understanding about the effects of three additives on the resin properties, Add−3 was considered for further in−depth study. Therefore, the focus was extended to investigate the effect of Add−3 concentration on resin properties. The reaction was carried out at a reaction temperature of 150 °C, reaction time of 20 hrs, and catalyst concentration of 0.18. The concentration of the additive was varied between 2 to 8 wt%. The effects of additive concentration on product properties are shown in Figure 9.3 and 9.4.

Figure 9.3 shows that both hydroxyl value and solubility of the products increased gradually with the increase of Add–3 concentration in the reaction medium. Around 17–units increment in hydroxyl value was observed when the additive concentration was increased to 8 wt%. The study shows that for every 2% increment in additive concentration, around 4–units increase in hydroxyl value was observed under present experimental conditions. Around 50% increment in product solubility was observed when the additive concentration was increased to 8 wt%. Figure 9.4 shows that around 30% decrease in product viscosity was obtained when Add–3 concentration was increased to 8 wt%. It is also observed that softening temperature of the product decreased with the increase of additive concentration. The obtained iodine values of the products were in the range of 3–4 g I_2/100 g. From the above results, it can be inferred that Add–3 could be an attractive choice to obtain a better quality (with improved hydroxyl value and solubility value) of ketonic resin.

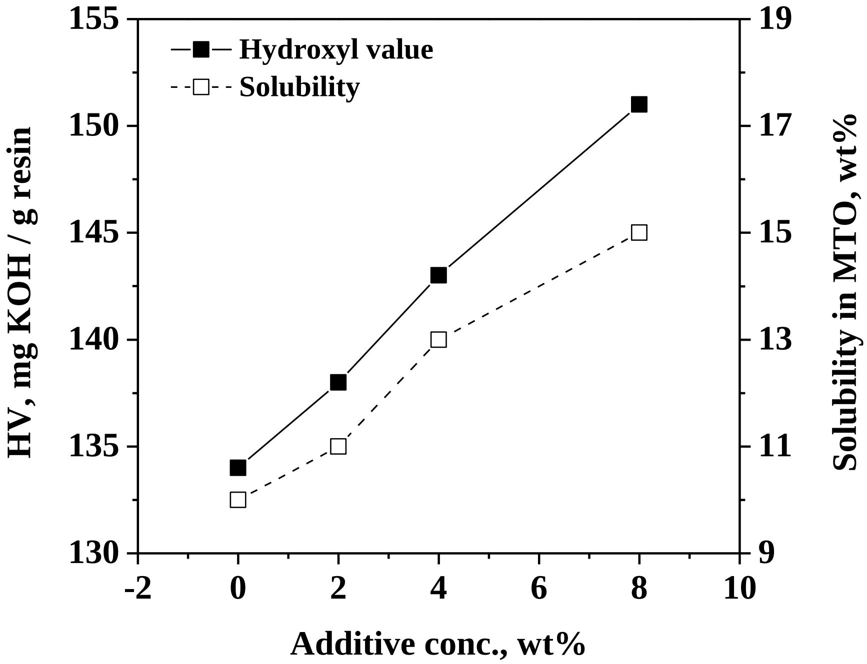


Figure 9.3. Effect of Add–3 concentration on Hydroxyl value and Solubility value

(Product ID: CS–69, CS–81, CS–86, CS–87)

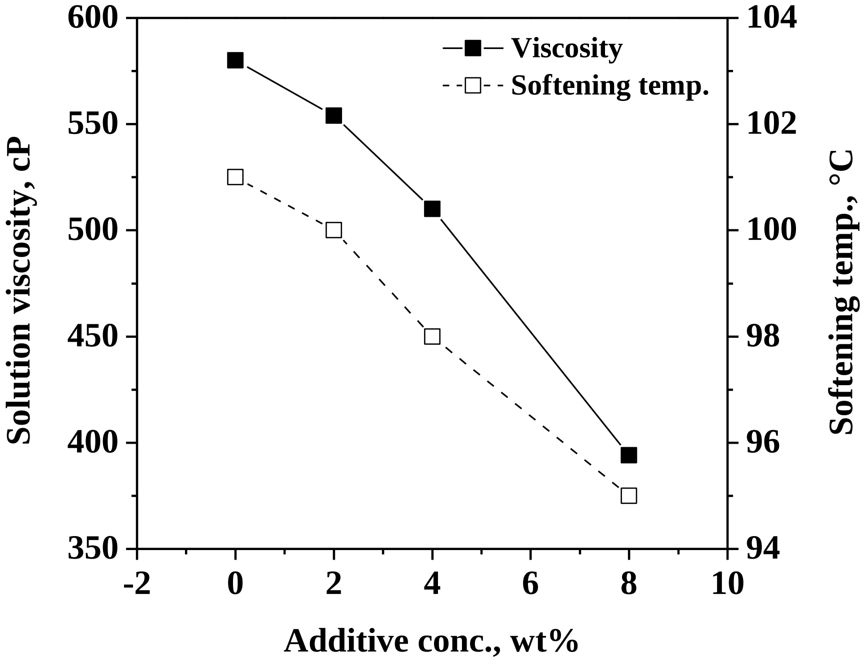


Figure 9.4. Effect of Add–3 concentration on Viscosity and Softening temperature

(Product ID: CS–69, CS–81, CS–86, CS–87)

9.2.3. Optimization of reaction conditions in presence of additive

From the previous study it was revealed that the Add–3 is useful to enhance the hydroxyl value and solubility of the resin products. In the present study, the focus was further extended to optimize the other operating parameters such as, reaction time and temperature on product properties for a fixed additive concentration. The effect of reaction temperature and time on product properties for a fixed concentration of Add–3 are shown in Table 9.1.

The data (Table 9.1) shows that the hydroxyl value of CS–91 product is around 4–units higher compared to CS–75 product obtained under similar reaction conditions. The MTO solubility of CS–91 product increased by around 20% in presence of additive. However, the softening temperature of the product decreased by around 6% in presence of additive. The data (CS–91 and CS–90) shows that, in presence of additive, when the reaction time was increased by one hour, a marginal increment in hydroxyl value and softening temperature was observed.

Table 9.1. Effect of reaction time and reaction temperature on resin properties

Product ID	CS−75	CS−91	CS−90	CS−93
Add−3 conc., wt%	0	5	5	5
Reaction temp., °C	145	145	145	148
Reaction time, hr	16	16	17	16
Physical state	Solid	Solid	Solid	Solid
Color of resin	White	White	White	White
HV, mg KOH/g resin	127	131	133	135
Solubility in MTO at 30 °C, wt%	34	41	37	35
Viscosity at 30 °C, cP	86	64	73	80
Softening temp., °C	75	71	73	75

The study also shows that, when the reaction temperature was increased by 3 °C in presence of additive, hydroxyl value of CS−93 product increased by 8 units (in comparison to CS−75 product) without deteriorating solubility value and softening temperature. Therefore, based on the present investigation, it can be concluded that it is possible to develop a good quality resin for paint and coating applications from cyclohexanone in presence of additive. Addition of small quantity of additive to reaction mixture can be useful to create an extra room for varying the reaction conditions to obtain a desired quality resin depending on specific applications.

9.2.4. Suitability of mixed additives on resin properties: a feasibility study

After gathering some information about the effects of individual additive on resin properties, the focus was extended to carry out the polymerization reactions in presence of both Add−1 and Add−3 in reaction mixture. For the study, the polymerization reactions were carried out at 150 °C for a duration of 16 hrs and with an A/K ratio of 0.18. The effects of mixed additives on product properties are shown in Table 9.2. The data shows that an increasing trend was observed in hydroxyl value with the decrease of Add−1 concentration in the reaction mixture under identical reaction conditions. It was also observed that viscosity and softening point of the product decreased with the increase of Add−1 concentration. However, an increasing trend in product solubility was observed with the increase of Add−1 concentration. A good quality resin (CS−95) was obtained in presence of 1.5 wt% Add−1 and 5 wt% Add−3 in the reaction mixture. The results shows that a resin (CS−95) with around 10% increase in hydroxyl value and more than 15% increase in product solubility was obtained in presence of mixed additive with reference to one of the best product (CS−75) obtained in absence of additive.

Table 9.2. Effect of mixed additive on physico−chemical properties of resin products

Product ID	CS−92	CS−94	CS−95
Add−1 conc., wt%	5	2.5	1.5
Add−3 conc., wt%	5	5	5
Physical state	Solid	Solid	Solid
Color of resin	White	White	White
HV, mg KOH/g resin	130	135	139
Solubility in MTO at 30 °C, wt%	46	43	40
Viscosity at 30 °C, cP	52	71	80
Softening temp., °C	69	72	74

9.3. Conclusions

In the present study, ketonic resins were prepared by self−polymerization of cyclohexanone in presence additives using a stirred batch reactor. The suitability of different additives and their individual or combined effects on product properties was investigated. The effects of various operating parameters were also examined in the study. The study shows that the hydroxyl value of the product significantly increased in presence of Add−3. A significant increment in product solubility in MTO was observed in presence of Add−1. A resin (CS−95) with around 10% higher in hydroxyl value and more than 15% greater in product solubility was obtained in presence of mixed additive. Therefore, based on the present investigation, it can be concluded that it is possible to develop a good quality resin in presence of additive at optimum conditions. The conditions include a temperature range of 145−150 °C, alkali−to−ketone weight ratio of around

0.18, and reaction time between 16–18 hrs. Addition of small quantity (5 to 10 wt%) of additive to the reaction mixture can be useful to create an extra room for varying the reaction conditions to obtain a desired quality resin.

Chapter 10

Conclusions

10.1. Conclusions on polymerization and kinetics study of ketonic resin

The polymerization/oligomerization reactions of ketonic monomers, viz. cyclohexanone, cyclopentanone and methylcyclohexanone were studied to develop a ketonic resin for paint and coating applications. Two types of batch systems; glass reactor (open system) and high pressure stainless steel reactor (closed system) were considered to perform the experiments under atmospheric and elevated pressure conditions respectively. Various characterization techniques were used to investigate the physico–chemical properties of the resin products. An attempt was made to find the thermal decomposition kinetics of resin products. Also, the effect of various additives on product properties was studied in the present work. The summary of the studies are as follows:

1. The self–polymerization reactions of cyclohexanone (CH) were carried out using open system (reactions under atmospheric pressure) in presence of KOH as a base catalyst. The reactions were carried out using a 250 mL capacity three–neck glass reactor. To investigate the effects of reaction parameters on cyclohexanone conversion and physico–chemical properties of the final products, reaction time was varied from 7 to 20 hrs, catalyst loading (expressed as ‘A/K ratio’) was varied between 0.05 to 0.2, and temperature was varied from 90 to 140 °C. It has been observed that the degree of polymerization of cyclohexanone depends on alkali concentration, reaction temperature, and reaction time. The degree of polymerization increased with the increase of catalyst loading and reaction time. Reaction temperature greater than 110 °C shows some detrimental effect on monomer conversion and product properties. Viscosity of the products increased substantially when the reaction time was increased from 7 to 20 hrs. A high viscous liquid resin with a hydroxyl value of around 85 mg KOH/g resin was able to prepare. The product solubility in MTO was in the range of 65–90 wt% and the iodine values were in the range of 3–6 g I_2/100 g. The average molecular weight of the products was in the range of 300– 500 g/mol. The study confirmed that KOH offers better quality product than NaOH as a base catalyst under identical reaction conditions. Moreover, the liquid product with lower hydroxyl value and higher unsaturation may not be suitable for paint and coating applications.

2. The ketonic resin was prepared by self–polymerization reaction of cyclohexanone using a mechanically agitated batch reactor (referred as 'closed system') in presence of KOH as a base catalyst. The effect of various process parameters, such as, stirring speed, catalyst concentration, reaction time, reaction temperature, and reactor pressure on product properties have been studied and quantified. The stirring speed range of 300−1200 revolutions per minute (rpm), reaction temperature range of 130−160 °C, reaction time from 10 to 20 hrs, catalyst concentration (expressed as 'A/K ratio') range of 0.1−0.4, and reactor pressure range of 1−12 kg/cm^2(g) were considered for the study. Efforts have been made to standardize the analysis protocol, and to characterize various physico–chemical properties like hydroxyl value, viscosity, solubility, softening temperature, average molecular weight etc. of the resin products. It was observed that, for every 10 °C increase in reaction temperature, hydroxyl value and softening point of the products increased around 18 units and 9 units respectively, and solubility in MTO decreased around 12 units. Good quality resins, with hydroxyl value greater than 120 mg KOH/g, MTO solubility more than 30 wt%, iodine value less than 3.5 g I_2/100 g, and softening temperature around 80 °C, was able to prepare. The number average molecular weight of the in–house developed resins is in the range of 450–1400 g/mol. The products are adequately soluble in n–butyl alcohol, n–butyl acetate, aromatic hydrocarbons, and ketonic solvents. TGA analysis revealed that the products are thermally stable up to a temperature of around 200 ºC. Adhesive property of the solid resin was confirmed from the lap shear strength test. The study shows that >97% yield can be obtained from self–polymerization reaction of cyclohexanone. Therefore, the outcome of the present study will be very much useful to develop a desired quality of resin product and its characterization depending on specific applications.

3. Mathematical regression models were developed with the help of statistical analysis tools, such as, MINITAB 17 and Microsoft Excel using experimentally obtained laboratory data to optimize the reaction parameters for obtaining a desired quality resin for coating applications. An effort has been made to develop empirical models to predict the product properties like average molecular weight, solubility and softening point of resin products. The developed models were good in agreement with the experimental results.

4. The ketonic resin was prepared from other ketonic compounds, such as, methylcyclohexanone (MCH) and cyclopentanone (CP). The polymerization reactions of methylcyclohexanone and cyclopentanone were carried out in a high pressure reactor to develop the ketonic resins. The cross–polymerization reactions of ketonic monomers were also considered in the study. The effect of reaction parameters on various physico–chemical properties of the resin products was investigated. In the study, reaction time was varied from 15 to 20 hrs and temperature was varied from 145 to 150 °C. It was observed that the polymerization reactions with methylcyclohexanone or cyclopentanone monomers alone may not be suitable to obtain a solid resin. However, small proportion of methylcyclohexanone or cyclopentanone along with cyclohexanone can play a significant role in obtaining a product with enhanced solubility. It was observed that viscosity and hydroxyl value of the resins decreased with the increase of MCH and CP concentrations in reaction mixture. The results revealed that MCH and CP amounts in the reaction mixture can be used up to 5 wt% to obtain a solid resin product with desired hydroxyl value and MTO solubility. From the FTIR spectrum, the presence of hydroxyl group was confirmed in all the resin products. The in–house developed cyclohexanone resins are thermally stable up to a temperature of around 200 ºC. However, pure MCH and CP resins were thermally stable up to a temperature of around 180 ºC. From the overall study, it can be concluded that the in–house developed ketonic resins can be used for paint and coating applications.

5. In the work, the kinetics of self–polymerization reaction of cyclohexanone has been studied. From the study, it is observed that reaction order of the self–polymerization reaction varied mostly between 2 and 3 depending upon the reaction conditions. The estimated activation energy of the polymerization reaction is around 105 kJ/mol. The estimated values of entropy (ΔS^*) and free energy (ΔG^*) change of activation are around –26 J/(mol K) and 112 kJ/mol respectively.

6. A systematic investigation of thermal stability and decomposition kinetics of the developed resins were performed using thermogravimetric analysis (TGA). The estimated thermal stability data of the in–house developed ketonic resins was also compared with commercially available phenolic resin and alkyd resin. The study shows that the developed

ketonic resins were thermally stable up to a temperature of around 200 °C. The apparent activation energy of the ketonic resins was in the range between 31 and 41 kJ/mol for a first–order decomposition reaction. The calculated rate constant (k) value was in between 1.07×10^{-2} and 25.36×10^{-2} 1/s at the peak temperature. The estimated values of ΔS^* and ΔG^* were in the range of −131 to −145 J/(mol K) and 101 to 125 kJ/mol respectively. The study showed that the thermal stability and apparent activation energy of the ketonic resins increased with the increase of product average molecular weights. Based on the above study, it can be concluded that the in–house developed ketonic resins were comparable with the studied phenolic resin. Therefore, the outcome of the present work will be very much useful to get an insight on processing and application of the developed resin products.

7. A feasibility study was performed on the development of ketonic resin from cyclohexanone in presence of different additives. In the study, the effects of various additives, their concentration, and reaction conditions on ketonic resin properties was investigated. The study shows that the hydroxyl value of the product significantly increased in presence of Add–3. A significant increment in product solubility in MTO was observed in presence of Add–1. A resin with around 10% higher in hydroxyl value and more than 15% greater in product solubility was obtained in presence of mixed additive. Therefore, based on the present investigation, it can be concluded that it is possible to develop a good quality resin in presence of additive at optimum conditions. The conditions include a temperature range of 145−150 °C, alkali–to–ketone weight ratio of around 0.18, time between 16–18 hrs. Addition of small quantity (5 to 10 wt%) of additive to the reaction mixture can be useful to create an extra room for varying the reaction conditions to obtain a desired quality resin.

From the overall study, it can be concluded that open system (under atmospheric pressure) will be an appropriate choice to obtain a viscous liquid resin with hydroxyl value of less than 90 mg KOH/g resin. Nevertheless, closed system (under elevated pressure) can offer a white color solid resin with a hydroxyl value of more than 120 mg KOH/g resin. These endogenous solid resins are adequately (more than 35 wt%) soluble in commercial MTO solvent. Concomitantly, in presence of mixed additive, a solid resin was obtained with around 10% higher hydroxyl value and 15% higher solubility in MTO solvent. Consequently, it was also contemplated that MCH and CP concentrations can be used up to 5 wt% to obtain a solid resin with the desired hydroxyl value and MTO solubility. Conclusively, the optimum conditions corroborated to obtain a desired product for paint and coating applications are: reaction time is in the range of 16–18 hrs, reaction temperature is in the range of 145–150 °C, A/K ratio is in the range of 0.17–0.2 and additive concentration is in the range of 5–10 wt%. The summary of the product properties obtained from open system, closed system and in presence of additives are given in Table 10.1, 10.2 and 10.3 respectively.

Table 10.1. Summary of the resin product properties obtained from open system study

Physical state of the product	Viscous liquid
Hydroxyl value, mg KOH/g resin	40 – 85
Iodine value, g I_2/100 g resin	3.0 – 6.0
Solubility in MTO at 30 °C, wt%	65 – 90
Number average mol. wt, g/mol	300 – 500

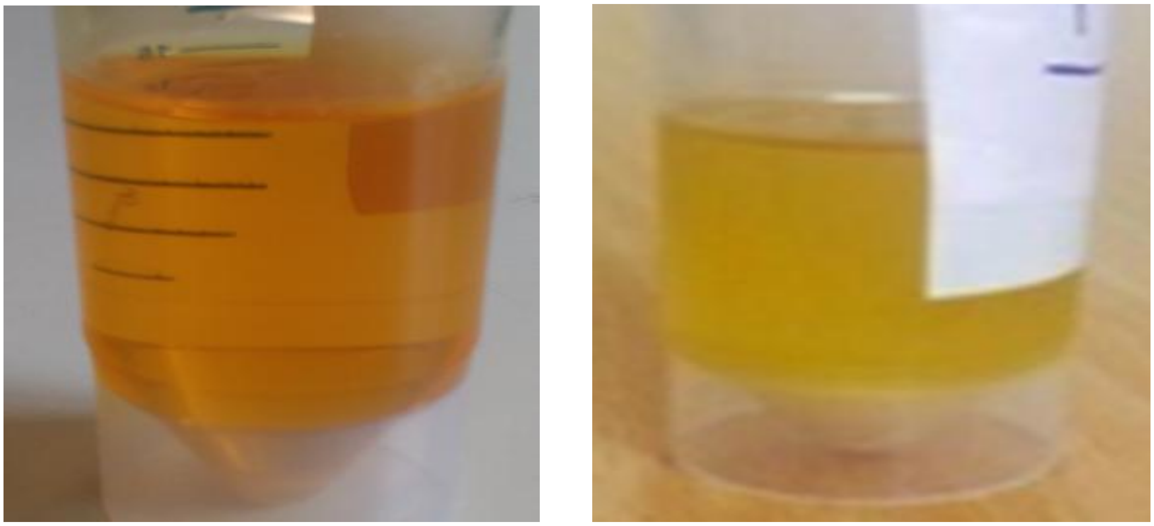
Table 10.2. Summary of the resin product properties obtained from closed system study

Physical state of the product	Solid
Hydroxyl value, mg KOH/g resin	80 – 165
Iodine value, g I_2/100 g resin	2.0 – 4.1
Solubility in MTO at 30 °C, wt%	10 – 40
Softening temp., °C	55 – 85
Number average mol. wt, g/mol	650 – 1400
Refractive index	1.52 – 1.53

Table 10.3. Summary of the resin product properties obtained in presence of additives

Physical state of the product	Solid
Hydroxyl value, mg KOH/g resin	127 – 140
Iodine value, g I_2/100 g resin	3.0 – 4.0
Solubility in MTO at 30 °C, wt%	30 – 46
Softening temp., °C	72 – 80
Number average mol. wt, g/mol	800 – 1300

The physical appearances of few resin products obtained from open and closed system are shown in Figure 10.1.



Product ID: OS–18 **Product ID: OS–28**

Viscous cyclohexanone resin

Cyclohexanone resin products before washing

Product ID: CS–5

Solid cyclohexanone resin

Product ID: CS–75

Solid cyclohexanone resin

Product ID: CS–69

Solid cyclohexanone resin

Product ID: CS–104

Solid cyclohexanone–cyclopentanone resin

Figure 10.1. The physical appearance of different resin products

<u>Chapter 11</u>

Scope for Further Study

11.1. Scope for Further Study

The thesis presents detailed studies on the polymerization of cyclic ketones such as, cyclohexanone, methylcyclohexanone and cyclopentanone in presence of base catalyst to obtain a ketonic resin. The characterization and thermo–kinetic details of the ketonic resins are mentioned explicitly in the thesis. The thesis also presents the development of ketonic resin in presence of different additives. The thesis further explains the development of mathematical regression models to optimize the process parameters and also to predict the product properties. Further investigation, however, could be conducted in the following direction:

- In–depth optimization of reaction parameters, such as, reaction time, temperature, and catalyst loading to obtain a desired quality of the resin depending upon the application.

- Polymerization reactions of cyclohexanone could also be studied with some more additives to improve the product property further.

- Kinetics study needs to be explored for the closed system reactions to estimate kinetic and thermodynamic parameters.

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List of Publications based on present research

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1. **Appala Naidu U**., Srikanta Dinda. Hydroxyl–Functionalized Resin: Preparation, Characterization, Parameter Optimization and Property Prediction. *Pigment & Resin Technology*, **2018**, 47:236–245.
2. Poornima K., **Appala Naidu U.**, Srikanta Dinda. Development of Resin Material from Cyclic–Ketones for Coating Applications. *Material Today: Proceedings*, **2018** (in press)
3. **Appala Naidu U**., Srikanta Dinda. Kinetics of thermal decomposition of ketonic resins. *Materials Today Communications*, **2017**, 12:88–94.
4. **Appala Naidu U**., Srikanta Dinda. Development of Poly–cyclohexanone resin material for coating applications. *Material Today: Proceedings*, **2016**, 3:3838–3843.
5. **Appala Naidu U**, Srikanta Dinda, Pravallika K, Karthik Chethan V. Preparation and Characterization of Ketonic Polymer for Coating Applications. *Progress in Organic Coatings,* **2016,** 99:251–262.
6. **Appala Naidu U**, Srikanta Dinda. Development of Ketonic Resin by Polymerization Reaction: A critical review. *Polymer*, **2015**, 61:204–212.
7. **Appala Naidu U.**, Srikanta Dinda. Synthesis of Ketonic Resin in Presence of Various Additives. (manuscript under preparation)

Papers Presented in National / International Conferences:

1. **Appala Naidu U**., Srikanata Dinda. Synthesis of Eco-Friendly Resin Material for Paint and Coating Applications. **Emerging Environmental Challenges: An Engineering Approach (EEC – 2018),** Hyderabad, Telangana, India, 16th February, **2018.**
2. **Appala Naidu U**., Srikanata Dinda. Self–Polymerization Kinetics of Cyclo–ketone. **CHEMCON 2017, PCM00169,** Haldia, West Bengal, India, 27−30 December, **2017.**

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5. **Appala Naidu Uttaravalli**, Srikanta Dinda. Development of Mathematical Model to Predict Polymer Properties. International conference of polymer processing and characterization **(ICPPC–2016),** Kerala, India, 9–11 December, **2016**.

6. **Appala Naidu U**., Srikanta Dinda. Characterization of Ketonic Resin. **SCHEMCON−2016**, pp. 1242, Medak, Telangana, India, 10−11 September, **2016.**

7. Srikanta Dinda, **Appala Naidu U**. Functional polymer for Coating Applications. Energy, material and nano–science (**EMN Dubai meeting 2016**), Dubai, UAE, 1–4 April **2016**.

8. **Appala Naidu Uttaravalli**, Srikanta Dinda. Synthesis of Resin from Cyclohexanone for Adhesive Applications. **IISF–2015**, IIT–Delhi, India, 4–8 December **2015**.

9. **Appala Naidu U**., Srikanta Dinda, Pravallika K. Studies on Synthesis of Ketonic Resin from Cyclohexanone for Paint Applications. **APA–2015**, pp. 116, Rajkot, India, 29–31 October **2015**.

10. **Appala Naidu U**., Karthik Chethan V., Srikanta Dinda. Polymerization Studies of Ketonic Resin. **CHEMCON–2014,** Chandigarh India; 27–30 December **2014**.

Biography of Supervisor

Prof. Srikanta Dinda is working as associate professor in chemical engineering department in BITS Pilani Hyderabad Campus since February 2015. He joined in the department as an assistant professor in July 2011. Prior to join with BITS Pilani, he worked in Reliance Jamnagar Refinery from September 2007 to July 2011. He has completed his Doctor of Philosophy (Ph.D.) degree in chemical engineering discipline from Indian Institute of Technology, Kharagpur (IIT-Kharagpur) in 2008. He completed his B.Tech. and M.Tech. degree in chemical engineering discipline from University of Calcutta, in 2001 and 2003 respectively. Prof. Dinda also finished his Bachelor of Science (B.Sc.) degree in chemistry honors from Vidyasagar University in 1998.

Dr. Dinda is actively involved in teaching and research activities. His research activities include studies on heterogeneous kinetics, development of refining catalyst, synthetic resins, biomaterials from non-edible plant oils, and CO_2 capture, which resulted in more than 21 publications in international journals and 35 presentations/proceedings in national and international conferences. Moreover, Dr. Dinda has contributed three book chapters published by Springer, B.S., and CRC publications. He also had invented few refining catalysts that can be used for catalytic cracking to improve olefins yields, and received four international patents in this area. He has completed three research grants from DST, M/s Suparna chemicals, and BITS Pilani and currently working on a CSIR funded project. He had guided four M.E dissertation and supervising three Ph.D. students.

Biography of Student

Mr. Appala Naidu Uttaravalli has completed Diploma in Chemical Engineering from Jawaharlal Nehru Government Polytechnic, Hyderabad, India in 2005. After his diploma, he has completed his Bachelor of Technology (B.Tech) and Master of Technology (M.Tech) in Chemical Engineering from Jawaharlal Nehru Technological University, Hyderabad, in 2009 and 2012 respectively. After his master's degree, he worked as a teaching faculty in Department of Chemical Engineering at DVR College of Engineering and Technology, Hyderabad, for one year. Then, he has joined in Doctor of Philosophy (Ph.D.) degree in chemical engineering department in Birla Institute of Technology and Science (BITS) Pilani, Hyderabad Campus, in August–2013 and submitted his thesis in February–2018.