

**THE MOLECULAR ORIGIN OF UNUSUAL PHYSICAL AND
MECHANICAL PROPERTIES IN NOVEL PHENOLIC
MATERIALS BASED ON BENZOXAZINE CHEMISTRY**

Ms. Supa Wirasate

A Thesis Submitted in Partial Fulfilment of the requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College
Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma
and Case Western Reserve University
1996
ISBN 974-633-598-7

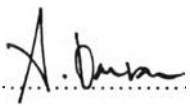
Thesis Title : The Molecular Origin of Unusual Physical and Mechanical Properties in Novel Phenolic Materials Based on Benzoxazine Chemistry

By : Ms. Supa Wirasate

Program : Polymer Science

Thesis Advisors : 1. Prof. Hatsuo Ishida
2. Asst. Prof. Sujitra Dhumrongvaraporn

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in Partial Fulfillment of the Requirements for the Degree of Master of Science.


..... Director of the College
(Prof. Somchai Osuwan)

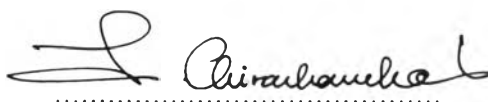
Thesis Committee



(Prof. Hatsuo Ishida)



(Asst. Prof. Sujitra Dhumrongvaraporn)



(Dr. Suwabun Chirachanchai)

ABSTRACT

##942013 : MAJOR POLYMER SCIENCE

KEYWORDS : POLYBENZOXAZINE/ PHENOLIC RESIN/ HYDROGEN
BONDING/ INFRARED SPECTROSCOPY

SUPA WIRASATE : THE MOLECULAR ORIGIN OF UNUSUAL
PHYSICAL AND MECHANICAL PROPERTIES IN NOVEL
PHENOLIC MATERIALS BASED ON BENZOXAZINE CHEMISTRY.

THESIS ADVISORS : PROF. HATSUO ISHIDA, Ph. D AND ASST.

PROF. SUJITRA DHUMRONGVARAPORN, Ph. D. 32 pp.

ISBN 974-633-598-7

The effect of temperature on hydrogen bonding was investigated by measuring the integrated absorbance of various hydrogen bonding modes as a function of temperature. It was found that intramolecular hydrogen bonding remains constant in intensity over the wide temperature range studied for both polybenzoxazines and a novolac-type phenolic resin. In particular, the chelation intramolecular hydrogen bond showed strong bonding that did not change over the temperature range. On the other hand, intermolecular hydrogen bonding showed the effect of temperature. Hydrogen bonding was influenced by the γ -transition of polybenzoxazines. The unusual physical and mechanical properties of polybenzoxazines, such as low water up-take, volumetric expansion upon polymerization, high thermal stability, and high glass transition temperature of polybenzoxazines, could be explained based on strong hydrogen bonding.

บทคัดย่อ

สุภา วิเศษรัฐ : แหล่งกำเนิดของโมเลกุลที่มีผลต่อคุณสมบัติทางกายภาพและทางเชิงกลของสารจำพวกเบนซอกซาซีน [The Molecular Origin of Unusual Physical and Mechanical Properties in Novel Phenolic Materials Based on Benzoxazine Chemistry], อาจารย์ที่ปรึกษา : Prof. Hatsu Ishida และ ผศ. ดร. สัจจitra อารังวารภรณ์, 32 หน้า ISBN 974-633-598-7

การศึกษาผลกระทบของอุณหภูมิที่มีต่อพันธะไฮโดรเจนกระทำได้ โดยการเปรียบเทียบการดูดกลืนแสง ของพันธะไฮโดรเจนประเภทต่างๆ ที่อุณหภูมิต่างๆ กัน จากการศึกษาพบว่า พันธะไฮโดรเจนภายในโมเลกุลของทั้งเบนซอกซาซีนโพลีเมอร์และ โนโวแลกเรซินค่อนข้างคงที่ในช่วงอุณหภูมิที่กว้างตลอดการทดลอง โดยเฉพาะพันธะไฮโดรเจนชนิดคีเลชัน อย่างไรก็ตามพันธะไฮโดรเจนระหว่างโมเลกุลได้รับผลกระทบจากอุณหภูมิ นั่นคือพันธะที่ได้กราฟลดลงเมื่ออุณหภูมิเพิ่มขึ้น นอกจากนี้ยังพบว่า เบตา-ทรานสิชันมีอิทธิพลต่อพันธะไฮโดรเจนเมื่ออุณหภูมิเพิ่มขึ้นด้วย คุณสมบัติทางกายภาพและทางเชิงกลของเบนซอกซาซีนโพลีเมอร์ สามารถอธิบายได้โดยอาศัยหลักการของพันธะไฮโดรเจนมาช่วยตัวอย่างเช่น ปริมาณน้ำในโมเลกุลมีน้อย, การขยายตัวทางปริมาตร หลังจากการโพลีเมอไรซ์, โมดูลัสและกลาสทรานสิชันมีค่าสูง

ACKNOWLEDGEMENTS

The author would like to thank the Petroleum and Petrochemical College, Chulalongkorn University, for providing her the opportunity to study in Polymer Science Program. She is indebted to the professors who taught her at this college. She also gratefully acknowledges the Petroleum Authority of Thailand and United State AID Program for their continuing financial support.

She specially thanks Prof. Hatsuo Ishida who not only gave her an inspirational guidance and encouragement, but also constructive criticism and intensive recommendation and training. She really would like to express her appreciation to Asst. Prof. Sujitra Dhumrongvaraporn for her good advices and vital help throughout this research work.

She would like to give a sincere thank to the graduate students under Prof. Ishida's advisorship at Case Western Reserve University who transferred their experiences to her and gave her helpful ideas for doing research.

Lastly, she would like to thank her family for their love, understanding, and encouragement as well as financial support throughout her study.

TABLE OF CONTENTS

| CHAPTER | | PAGE |
|----------------|---|-------------|
| | Title Page | i |
| | Abstract | iii |
| | Acknowledgements | v |
| | Table of Contents | vi |
| | List of Figures | viii |
| I | INTRODUCTION | |
| | 1.1 Background | 1 |
| | 1.2 Objective | 3 |
| II | EXPERIMENTAL SECTION | |
| | 2.1 Materials | 4 |
| | 2.2 Instrument | 4 |
| | 2.3 Benzoxazine Synthesis and Sample Preparation | 4 |
| | 2.4 Hydrogen Bonding as a Function of Temperature | 5 |
| III | RESULTS AND DISCUSSION | |
| | 3.1 Curve Analysis | 8 |
| | 3.2 Thermal Stability of Materials | 10 |
| | 3.3 Hydrogen Bonding Study as a Function of Temperature of Polybenzoxazine | 11 |
| | 3.4 Recovery of Hydrogen Bonding | 19 |

| CHAPTER | PAGE |
|--|-------------|
| 3.5 Hydrogen Bonding Study as a Function of Temperature of Phenolic Resin | 22 |
| IV CONCLUSIONS | 29 |
| REFERENCES | 30 |

LIST OF FIGURES

| FIGURE | PAGE |
|--------|---|
| 3.1 | Width at half intensity as a function of frequency shift of phenolic resin (⊙), 44O-a (◆) and B-a (□).....9 |
| 3.2 | Thermal stability of phenolic resin (⊙), 44O-a (◆), B-a (□) and B-m (●).....11 |
| 3.3 | Infrared spectra of cured 44O-a (A) , B-a (C) and B-m (B).....12 |
| 3.4 | Integrated absorbance of chelation hydrogen bonding as a function of temperature of 44O-a (◆) and B-a (□).....14 |
| 3.5 | Integrated absorbance of intermolecular hydrogen bonding as a function of temperature of 44O-a (◆) and B-a (□).....15 |
| 3.6 | Integrated absorbance of intramolecular hydrogen bonding between OH groups as a function of temperature of 44O-a (◆) and B-a (□).....16 |
| 3.7 | Integrated absorbance of nearly free OH as a function of temperature of 44O-a (◆) and B-a (□).....18 |
| 3.8 | Infrared spectra of hydrogen bond recovery study of B-a; at room temperature (A), at 190° C (B), at room temperature after cooling from 190 °C (C).....19 |

| FIGURE | | PAGE |
|---------------|---|-------------|
| 3.9 | Infrared spectra of hydrogen bond recovery study of B-m; at room temperature (A), at 190° C (B), at room temperature after cooling from 190 °C (C)..... | 20 |
| 3.10 | Infrared spectra of hydrogen bond recovery study of 44O-a; at room temperature (A), at 50° C (B), at 350° C (C), at room temperature after cooling from 350 °C (D) and allowing at room temperature for 11 h (E)..... | 21 |
| 3.11 | Infrared spectra of hydrogen bond recovery study of phenolic resin; at room temperature (A), at 210° C (B), at room temperature after cooling from 210 °C (C), and allowing at room temperature for 12 h (D)..... | 22 |
| 3.12 | Infrared spectrum of cured novolac-type phenolic resin..... | 23 |
| 3.13 | Integrated absorbance of nearly free OH (⊙), inter- (◆) and intramolecular hydrogen bonding (□), of phenolic resin..... | 24 |