STUDIES ON THE POLYMERIZABILITY OF SOME ACRYLIC ACID DERIVATIVES

A THESIS

PRESENTED

BY

WAGDY YOUHANNA BOUTROS

EGYPTIAN ANTIQUITIES ORGANIZATION

IN PARTIAL FULFILLMENT FOR THE REQUIREMENT OF

M.SC. DEGREE

TO

FACULTY OF SCIENCE

AIN SHAMS UNIVERSITY

EGYPT

1993

STUDIES ON THE POLYMERIZABILITY OF SOME ACRYLIC ACID DERIVATIVES

Thesis Advisors	Aproval
Prof. Maher A. El-Hashash	(M A. EL-Hashash)
Assoc. Prof. Abdel-Azim A. Abdel-Azim	( )
Dr. Shawky M. Nakhla	(Shawky M. Nakhla)

Prof;A .M.F. Fahmy (A.F.M. Fahmy)

Chairman of the Chemistry Department
Faculty Of Science
Ain Shams University

بسم الله الرحمن الرحيم

STATEMENT

The work included in this thesis has been carried out by the author in the Egyptian Antiquities Organization, under the supervision of Assoc.. Prof. Abdel-Azim A. Abdel-Azim. The thesis has not been submitted and is not concurrently being submitted for any other degree.

Candidate	Wagdy Youhanna Boutros	( )
Supervisor	Assoc. Prof. Abdel-Azim A. A.	( )

DEDICATION

To my family

ACKNOWLEDGMENT

To acknowledge my sincere gratitudes to all those who taught me Chemistry and still do, words will be undeniably unjust

The author wishes to express his deepest gratitude to Assoc. Prof. Abdel-Azim A. Abdel-Azim, Assoc. Prof. of Polymer Chemistry, Egyptian Petroleum Research Institute, for suggesting the problem and for his close and continuous supervision, during all phases of this work, giving him the motivation to conduct this thesis.

The author is deeply indebted to Prof. Maher A. El-Hashash Professor. of Organic Chemistry, Faculty of Science, Ain Shams University, and Prof. Said El-Nagdy without their encouragement and support this thesis would have never been written.

Thanks are undoubtedly due to Dr. S. Nakhla General Director of Restoration and Conservation of antiquities, Egyptian Antiquities Organization for his support and encouragement. The author is also greatly indebted to Col. Dr. E. S. Nasr, Armed, Forces Technical Research Center, for helping and facilitating the measurement of the mechanical properties.

My thanks go also to the Department of Petroleum Applications, Egyptian Petroleum Research Institute, from which tremendous help was offered. Finally I would like to extend my gratitude to all my friends and colleagues in this department.

CURRICULUM VITAE

Wagdy Youhanna Boutros was born on March 7, 1962, in Cairo, Egypt. He attended Rod-Elfarag Secondary School. After graduating in 1980, he was enrolled at the Faculty of Science, Ain Shams University and got the B.Sc. Degree with grade "Good" in May 1984, and now he is working in the research laboratory for the restoration and conservation of antiquities, Egyptian Antiquities Organization, as a chemist.

He registered this thesis in April 1991 under the direct supervision of Asso. Prof. Abdel-Azim A. Abdel-Azim, Assoc. Prof. Of Polymer Chemistry, Egyptian Petroleum Research Institute and under attention of Prof. Maher A. El-Hashash and Dr. S. Nakhla.

NOTES

This thesis is submitted in partial fulfillment of the requirements of the M.Sc. degree, Faculty of Science, Ain Shams University. In addition to the work carried out in this thesis, the candidate: Wagdy Youhanna Boutros, has attended and passed successfully, during the academic year 1989-1990, post graduate studies in the following topics (delivered to the organic chemistry section):

1: Polymer chemistry
2: Pericyclic reaction chemistry
3: Spectroscopy
4: Photochemistry
5: Heterocyclic chemistry
6: Natural products
7: Organic reactions
8: Organic reagents
9: Organometallic compounds
10: Reaction mechanisms
11: Instrumental organic analysis
12: Aromaticity
13: English

Prof. Abdel-Gawad M. Rabie (   )

Chairman of the Chemistry Department
Faculty Of Science
Ain Shams University

List of abbreviations

Word	Abbreviation
Methyl ethyl ketone peroxide	MEKP
Cyclo hexanone peroxide	HCH
Cobalt octoate (10% soln. in styrene)	CO
Styrene	Sty
Acrylonitrile	AN
Ethylene glycol	EG
Diethylene glycol	DG
Triethylene glycol	TG
Propylene glycol	PG
Equivalent polymerizable double bonds	EPDB
Maleic anhydride	MA
Phthalic anhydride	PHA
Succinic acid	SU
Adipic acid	AD
Sebacic acid	SE
Unsaturated polyester	UP

LIST OF FIGURES

Fig.(2.1) Apparatus used for initial stage of polycondensation.
Fig.(2.2) Apparatus used for final stage of polycondensation.
Fig.(2.3) Stress-strain curve for a rigid resin.
Fig (2.4) Stress - strain curve for a cured flexible resin.
Fig.(3.1) Curing exotherms of formula No.1 in different styrene/AN solvents as function of time.
Fig.(3.2) Curing exotherms of formula No.2 in different styrene / AN solvents as function of time.
Fig.(3.3) Curing exotherms of formula No.3 in different styrene / AN solvents as function of time.
Fig.(3.4) Curing exotherms of formula No.4 in different styrene / AN solvents as function of time.
Fig.(3.5) Curing exotherms of formula No.5 in different styrene / AN solvents as function of time.
Fig.(3.6) Curing exotherms of formula No.6 in different styrene / AN solvents as function of time.
Fig.(3.7) Curing exotherms of formula No.7 in different styrene / AN solvents as function of time.
Fig.(3.8) Curing exotherms of formula No.8 in different styrene / AN solvents as function of time.
Fig.(3.9) Curing exotherms of formula No.9 in different styrene / AN solvents as function of time.
Fig.(3.10) Curing exotherms of formula No.10 in different styrene / AN solvents as function of time.
Fig.(3.11) Curing exotherms of formula No.11 in different styrene / AN solvents as function of time.
Fig.(3.12) Curing exotherms of formula No.12 in different styrene / AN solvents as function of time.
Fig.(3.13) Curing exotherms of formula No.13 in different styrene / AN solvents as function of time.
Fig.(3.14) Curing exotherms of formula No.14 in different styrene / AN solvents as function of time.
Fig.(3.15) Curing exotherms of formula No.15 in different styrene / AN solvents as function of time.
Fig.(3.16) Maximum curing time and temperature of formula No.1 as a factor of AN ratio.
Fig.(3.17) Maximum curing time and temperature of formula No.2 as a factor of AN ratio.
Fig.(3.18) Maximum curing time and temperature of formula No.3 as a factor of AN ratio.

Fig.(3.19) Maximum curing time and temperature of formula No.4 as a factor of AN ratio.
Fig.(3.20) Maximum curing time and temperature of formula No.5 as a factor of AN ratio.
Fig.(3.21) Maximum curing time and temperature of formula No.6 as a factor of AN ratio.
Fig.(3.22) Maximum curing time and temperature of formula No.7 as a factor of AN ratio.
Fig.(3.23) Maximum curing time and temperature of formula No.8 as a factor of AN ratio.
Fig.(3.24) Maximum curing time and temperature of formula No.9 as a factor of AN ratio.
Fig.(3.25) Maximum curing time and temperature of formula No.10 as a factor of AN ratio.
Fig.(3.26) Maximum curing time and temperature of formula No.11 as a factor of AN ratio.
Fig.(3.27) Maximum curing time and temperature of formula No.12 as a factor of AN ratio.
Fig.(3.28) Maximum curing time and temperature of formula No.13 as a factor of AN ratio.
Fig.(3.29) Maximum curing time and temperature of formula No.14 as a factor of AN ratio.
Fig.(3.30) Maximum curing time and temperature of formula No.15 as a factor of AN ratio.
Fig.(3.31) Effect of acid on curing behaviour of different resins contain EG.
Fig.(3.32) Effect of acid on curing behaviour of different resins contain EG+PG.
Fig.(3.33) Variation of maximum curing time with EPDB.
Fig.(3.34) Variation of maximum curing temperature with EPDB.
Fig.(3.35) Effect of glycol on curing behaviour of different resins based on SU in styrene monomer.
Fig.(3.36) Effect of glycol on curing behaviour of different resins based on AD in styrene monomer.
Fig.(3.37) Effect of glycol on curing behaviour of different resins based on SE in styrene monomer.
Fig.(3.38) Maximum curing time and temperature of copolymers.containing different glycol systems
Fig.(3.39) Mechanical properties of formula No.1 as a factor of AN ratio.
Fig.(3.40) Mechanical properties of formula No.2 as a factor of AN ratio.
Fig.(3.41) Mechanical properties of formula No.4 as a factor of AN ratio.
Fig.(3.42) Mechanical properties of formula No.6 as a factor of AN ratio.
Fig.(3.43) Mechanical properties of formula No.9 as a factor of AN ratio.
Fig.(3.44) Mechanical properties of formula No.14 as a factor of AN ratio.
Fig.(3.45) Mechanical properties of formula No.3 as a factor of AN ratio.

Fig.(3.46) Mechanical properties of formula No.7 as a factor of AN ratio.
Fig.(3.47) Mechanical properties of formula No.8 as a factor of AN ratio.
Fig.(3.48) Mechanical properties of formula No.11 as a factor of AN ratio.
Fig.(3.49) Mechanical properties of formulae No.5, 10, 12, 13 and 15 as a factor of AN ratio.

CONTENTS

		Page
	CHAPTER I	
I.	**INTRODUCTION & AIM OF WORK**	
1.1	Principles of Polymerization	1
1.1.1	Functionality	3
1.1.2	Radical polymerization	6
	Reactions of radicals	7
	Methods of initiation	8
1.1.3	Polymerizability of monomers	9
1.1.4	Polycondensation (step polymerization)	11
1.1.4.1	Different reactant systems	12
1.1.4.2	Basic regularities of polycondensation	13
1.1.4.3	Hydrolysis and acidolysis	14
1.2	Radical Copolymerization	15
1.3	Polyester	17
1.3.1	Cross-Linked Structure	19
1.3.2	Unsaturated polyester	20
1.3.3	Esterification catalysts	24
1.3.4	Curing systems	24
1.3.5	Catalysts	26
1.3.5.1	Types of initiators	26
1.3.5.2	Effect of metals as accelerators	31
1.4	Room Temperature Curing System	34
	AIM OF WORK	35

CHAPTER II

MATERIALS, APPARATUS AND TECHNIQUES

2.1	Raw Materials	38
2.2	Preparation of Polyester Resins	38
2.3	Preparation of an Unsaturated Polyester Resin Based on Poly(ethylene/maleate/succinate) (formula No.1)	40
2.3.1	Apparatus	40
2.3.2	Procedure	45
2.4	Determination of Molecular Weight and Acid Number	47
2.5	Curing	48
2.5.1	Measurement of curing exotherm	49
2.6	Mechanical Properties	50

CHAPTER III

RESULTS & DISCUSSION

3.1	Introduction	55
3.2	Unsaturated Polyester Resins	56
3.2.1	Formulae copolymerized with styrene and acrylonitrile monomers	57
3.3	Determination of Molecular Weight	57
3.4	Copolymerization of Styrene and Acrylonitrile Monomers with Unsaturated Polyester Resins	61
3.4.1	Effect of cross-linking vinyl monomers on the curing behaviour of unsaturated polyester resins	61
3.4.2	Effect of acid type on the curing behaviour	96
3.4.3	Equivalent of polymerizable double bonds	100
3.4.4	Effect of glycols on the copolymerizability of vinyl and acrylic monomers with unsaturated polyester resins	104

3.4.5 Structure / mechanical properties relationship 110

SUMMARY AND CONCLUSION 142
REFERENCES 146