

SYNTHESIS OF METHACRYLIC ACID-ETHYL ACRYLATE BASED THICKENERS AND THEIR APPLICATION IN PIGMENT PRINTING

By
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*Thesis submitted
in fulfilment of the requirement of
the degree of*
DOCTOR OF PHILOSOPHY



to the
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
July, 1993

• • • *dedicated to my parents*

CERTIFICATE

This is to certify that the thesis entitled "**SYNTHESIS OF METHACRYLIC ACID-ETHYL ACRYLATE BASED THICKENERS AND THEIR APPLICATION IN PIGMENT PRINTING**" being submitted by **Miss Meenakshi Goyal**, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy, in the Department of Textile Technology, is a record of bonafide research work carried out by her. Miss Meenakshi Goyal has worked under our guidance and supervision and fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.



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ACKNOWLEDGEMENTS

I wish to place on record my sincere thanks to Prof. (Miss) P.Bajaj and Prof. R.B.Chavan for their valuable guidance, constant encouragement and unflinching help throughout the course of this research work. I am extremely thankful to them for their personal attention and painstaking efforts to complete this thesis.

My sincere thanks are due to Prof. P.K.Hari, Head, Department of Textile Technology for providing the necessary facilities.

I am thankful to Dr. A.S.Brar, Associate Prof. Department of Chemistry for his₃ conscientious and interested efforts in discussions of ¹³C NMR. My thanks are also due to Dr. C.R.Jagga of Industrial Tribology Machine Dynamics and Maintenance Engineering Centre for his help.

Credit goes to faculty members and technical staff of Textile Technology Department for creating an atmosphere conducive to the success of this work.

I owe a lot to Mr. J.Radhakrishnan for his constant encouragement and help during the entire period of my Ph.D work.

Mr. Rakesh Koul, S.J.Mahajan and Dr. S.K.Rana deserve my special gratitude. It is a pleasure to record my appreciation for several of my past and present colleagues: Dr. Anand Kumar, Dr. Kashinath Bhowmik, Mr. G.Nalankilli, D.K. Paliwal, M. Patnaik, A. K. Roopanawal, H. Bahrami, Sanjay Mehta, Praveen Arora, Y. C.Bhuvanesh, and K.R.Srinivasan. I am extremely thankful to Ms. Sunita and Jasmedh Kaur for the help provided during this work.

My friends, Shova Patrabansh, Somna Saha, Litty James, Latika Singh, Smita Manepatil, Sova Bhattacharya, Navneeta Mitra, Gargi Vishnoi, B.K.Ratnam and Nimmi R Nair deserve my special gratitude for their kind concern and warm affection.

I am grateful to the University Grants Commission for providing me the financial support.

I am thankful to Mr. B.B. Arora and Mr. C. Saraswat for the figure tracings.

Mention must be made of my brothers and sisters who have always been a source of encouragement to me.

Finally, I express my gratitude towards my parents who always stood by me in my venture and to them I solemnly dedicate this thesis.

A handwritten signature in black ink, appearing to read 'Goyal' with a stylized flourish extending from the end.

(Meenakshi Goyal)

ABSTRACT

The origin of this study lies in the development of a substitute of kerosene emulsion thickener used in pigment printing which has the disadvantages like, inadequate availability, risk of fire and air pollution. Generally, the copolymers of acrylic/methacrylic acid and alkyl acrylate and their crosslinked products are used as synthetic thickeners.

Methacrylic acid-ethyl acrylate copolymers of varying compositions (MAA 50.1-82.3 mol%) were synthesized using emulsion polymerization technique. Mechanism of polymerization which is not expected to be a true emulsion polymerization, because of the presence of higher amount of water soluble carboxylic acid monomer, was studied. From the partition behaviour of methacrylic acid in aqueous and ethyl acrylate phases, and reactivity ratios of methacrylic acid-ethyl acrylate pair, it was inferred that the system follows a two loci polymerization mechanism. Alongwith the emulsion polymerization, some water soluble polymer is also produced. IR and NMR techniques were employed to characterize the copolymers.

Thermal studies revealed a good correlation between the chemical structure and thermal behaviour of copolymers. An endothermic transition in DSC curves of methacrylic acid ethyl acrylate copolymers relates to the dehydration reaction of methacrylic acid units. Interestingly it has

been established that ethyl acrylate comonomer also participates in the dehydration reaction of methacrylic acid in methacrylic acid-ethyl acrylate copolymers. A decrease in the activation energy with increase in ethyl acrylate content of the copolymers was also observed. An increase in weight loss in the temperature range of 140-280°C with the increase in the ethyl acrylate content of the copolymer, further confirms the participation of ethyl acrylate in dehydration reaction. On the basis of detailed analysis of the degradation products of methacrylic acid-ethyl acrylate copolymers through mass spectroscopy, a comprehensive thermal degradation scheme has been proposed.

Brookfield viscosity of methacrylic acid-ethyl acrylate copolymers (at 5 rpm and pH 7.5 after adjusting with ammonia) was found to be very low, i.e., in the range of 5000-16000 cp at 10% solid contents. In order to accomplish the higher viscosity at lower solid content, the crosslinked polymers were synthesized by incorporating small amounts of crosslinking agent like, ethylene glycol dimethacrylate or N,N'-methylene bisacrylamide in conjunction with methacrylic acid and ethyl acrylate. A significant increase in the Brookfield viscosity was observed and the crosslinked polymers had a viscosity of 26000-70400 cp at a solid content of 4% only. Viscosity of these polymers was found to be dependent on pH and maxima was obtained in the pH range of 7.5-8. This behaviour has been related with the ionization of the carboxylic acid groups. Pseudoplastic

behaviour of these polymers confirmed their suitability for textile printing applications.

As the viscosity was very low in the linear copolymers, printing trials were confined to the crosslinked polymers only. The performance of these products in pigment printing of cotton was evaluated in terms of colour value, wash, rub and scrub fastness and handle, using four pigments. Though all other characteristics were quite comparable with the conventional and commercial (Alcoprint PTF) thickener, the feel of the fabric was stiffer which was improved by using a mixture of synthetic and kerosene emulsion thickener in the ratio of 80:20 and 60:40 (w/w).

CONTENTS

	page no.
CHAPTER 1 GENERAL INTRODUCTION AND LITERATURE SURVEY	
1.1 INTRODUCTION	1
1.2 SYNTHETIC THICKENERS	3
1.2.1 Chemical Composition	3
1.2.1.1 Selection of Monomers	7
1.2.1.2 Need for a Crosslinking Agent	10
1.2.2 Polymerization Techniques	10
1.2.2.1 Emulsion Polymerization	10
1.2.2.2 Inverse Emulsion Polymerization	16
1.2.2.3 Solution Polymerization	17
1.2.2.4 Radiation Induced Polymerization	18
1.2.3 Rheological Behaviour of Aqueous Based Synthetic Thickeners	18
1.2.3.1 Mechanism of Viscosity Development	18
1.2.3.2 Effect of Shear Rate on Viscosity	21
1.2.3.3 Effect of pH	21
1.2.3.4 Effect of Electrolyte	21
1.2.4 Performance of Synthetic Thickeners in Textile Printing	22
1.2.4.1 Acrylic Thickeners	22
1.2.4.2 Ethylene-maleic Anhydride Thickeners.	27
1.3 OBJECTIVE OF THE PRESENT WORK	31

CHAPTER 2 SYNTHESIS AND CHARACTERIZATION OF METHACRYLIC ACID-ETHYL ACRYLATE COPOLYMERS

2.1	INTRODUCTION	32
2.1.1	Emulsion Polymerization	32
2.1.2	Structural Investigations of Acrylic Polymers by IR and NMR spectroscopy	34
2.1.3	Reactivity Ratio Determination	37
2.2	EXPERIMENTAL	39
2.2.1	Materials	39
2.2.2	Polymer Synthesis	40
2.2.3	Reactivity Ratio Determination	41
2.2.4	Concentration of the Monomers in the Aqueous Phase	42
2.2.5	Polymer Characterization	42
2.2.5.1	Elemental Analysis	42
2.2.5.2	Acidimetric Titrations	43
2.2.5.3	Infra Red Spectral Studies	43
2.2.5.4	^1H NMR Studies	43
2.2.5.5	Proton Decoupled ^{13}C NMR Studies	43
2.2.5.6	Intrinsic Viscosity	44
2.3	RESULTS AND DISCUSSION	
2.3.1	Polymer Characterization	46
2.3.1.1	Elemental Analysis	46
2.3.1.2	Acidimetric Titrations	46
2.3.1.3	Intrinsic Viscosity	48
2.3.1.4	IR Studies	48
2.3.1.5	^1H NMR Studies	50
2.3.1.6	^{13}C $\{^1\text{H}\}$ NMR Studies	54

2.3.2	Mechanism of Polymerization	58
2.3.2.1	Reactivity Ratios	59
2.3.2.2	Concentration of the Monomers in the Aqueous Phase	61
2.3.2.3	Composition of the Initial Oligomeric Radicals Formed in the Aqueous Phase	63
2.3.2.4	Sequence Distribution of the Initial Oligomeric Radicals Formed in the Aqueous Phase	64
 CHAPTER 3 THERMAL BEHAVIOUR OF METHACRYLIC ACID-ETHYL ACRYLATE COPOLYMERS		
3.1	INTRODUCTION	69
3.2	EXPERIMENTAL	76
3.2.1	Thermal Analysis	76
3.2.2	DSC-FTIR	77
3.2.3	Mass Spectroscopy	77
3.3	RESULTS AND DISCUSSION	78
3.3.1	Differential Scanning Calorimetry	78
3.3.2	Thermogravimetric Analysis	82
3.3.3	DSC-FTIR	87
3.3.4	Mass Spectroscopy	88
 CHAPTER 4 RHEOLOGICAL BEHAVIOUR OF METHACRYLIC ACID-ETHYL ACRYLATE COPOLYMERS AND CROSSLINKED POLYMERS		
4.1	INTRODUCTION	94
4.1.1	Rheology of Thickeners	94
4.1.2	Influence of Chemical Structure of Thickeners on their Rheology	98
4.1.2.1	Influence of Cations and pH on the Viscosity	99

4.1.2.2	Electrolyte Sensitivity	102
4.1.2.3	Influence of Crosslinking Agents	102
4.2	EXPERIMENTAL	103
4.2.1	Materials	103
4.2.2	Synthesis of Crosslinked Polymers	103
4.2.3	Gel Content Determination	104
4.2.4	Brookfield Viscosity Measurement	104
4.3	RESULTS AND DISCUSSION	105
4.3.1	Brookfield Viscosity of Methacrylic acid -Ethyl acrylate (MAA-EA) copolymers	105
4.3.2	Gel Content of the Crosslinked Polymers	108
4.3.3	Brookfield Viscosity of the Crosslinked Polymers	112
4.3.4	Effect of Solid Content on the Brookfield Viscosity	114
4.3.5	Effect of Shear Rate on the Brookfield Viscosity	115
4.3.6	Effect of pH on the Brookfield Viscosity	117
4.3.7	Electrolyte Sensitivity	117
4.3.8	Storage Stability	119
CHAPTER 5 PERFORMANCE OF METHACRYLIC ACID- ETHYL ACRYLATE- ETHYLENE GLYCOL DIMETHACRYLATE / N, N'-METHYLENE- BISACRYLAMIDE TERPOLYMERS IN PIGMENT PRINTING		
5.1	INTRODUCTION	121
5.2	EXPERIMENTAL	125
5.2.1	Materials	125
5.2.1.1	Fabric	125
5.2.1.2	Printing Auxiliaries	125
5.2.2	Print Paste and Stock Paste Formulation	125

5.2.2.1	Stock Paste	125
5.2.2.2	Printing Paste	126
5.2.3	Printing	127
5.2.4	Partial Substitution of Kerosene Emulsion	127
5.2.5	Evaluation of Printed Samples	127
5.2.6	Viscosity Measurement	130
5.3	RESULTS AND DISCUSSION	130
5.3.1	Viscosity of Stock and Print Pastes	130
5.3.2	Printing Performance of Synthetic Thickeners	131
5.3.2.1	Colour Value (K/S)	131
5.3.2.2	Fastness Properties	132
5.3.2.3	Bending Length	137
5.3.3	Partial Substitution of Kerosene Emulsion	139
5.3.3.1	Colour Value	139
5.3.3.2	Fastness Properties	141
5.3.3.3	Bending Length	146
CHAPTER 6	SUMMARY AND CONCLUSIONS	149
REFERENCES		157
LIST OF PUBLICATIONS		