

**STUDIES ON DYES AND PIGMENTS FOR DYEING AND
MASS COLOURATION OF PET AND NYLON 6**

By
B. V. RAO

*THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS OF
THE DEGREE OF
DOCTOR OF PHILOSOPHY*



**Centre for Materials Science & Technology
INDIAN INSTITUTE OF TECHNOLOGY, DELHI**

OCTOBER, 1989

DEDICATED

TO

MY BELOVED PARENTS

CERTIFICATE

This is to certify that the thesis entitled "STUDIES ON DYES AND PIGMENTS FOR DYEING AND MASS COLOURATION OF PET AND NYLON 6" being submitted by Mr B.V. Rao to the Indian Institute of Technology, Delhi, for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by him. Mr. B.V. Rao has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis which to our knowledge has reached the requisite standard.

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

I. K. Varma

Prof. (Mrs.) I.K. Varma

Veena

Dr. (Mrs.) Veena Choudhary

Centre for Materials Science and Technology
Indian Institute of Technology, Delhi
Hauz Khas, New Delhi-110016.

ACKNOWLEDGEMENT

It is with great pleasure, I express my sincere gratitude and indebtedness to my supervisors Prof. (Mrs.) I.K. Varma and Dr. (Mrs.) Veena Choudhary for their guidance and encouragement and taking keen interest throughout the duration of this work. I am also thankful to Dr. K.V. Datta, former Director, Sir Padampat Research Centre, (A Division of J.K. Synthetics Ltd.), for introducing me to this fascinating field and for his interest in this project.

I express my deep sense of gratitude to Dr.A.A. Vaidya, former principal Scientist & Head who is no more with us. His constant encouragement was a source of inspiration for me.

My sincere thanks are to Dr. N.D. Sharma, Principal Scientist and Head, Sir Padampat Research Centre, Prof. V. Raghavan and Dr. A.K. Gupta of Centre for Material Science and Technology, Prof. V.B. Gupta, Prof. P. Bajaj, Dr. R.B. Chavan, all of the Textile Technology Department for providing necessary facilities during this project work.

Ms. J.K. Synthetics Ltd., is acknowledged for giving permission and extending their facilities in completing this work.

I am extremely grateful to all staff and technical assistants at Sir Padampat Research Centre, Kota, and CMST, IIT Delhi for their continuous help throughout this work.

A very special thanks is due to my beloved friend Dr. S.K. Viswanadham, Asst. Professor, Chemistry Department, University of Pittsburgh, U.S.A., for the assistance provided in spectroscopic studies.

I am also grateful to my friends, Kasinath Bhaumick, Anand Kumar, Ashok Gupta, M.Patnaik, H.S. Varma, Rama Rao, Ratnam, Rakesh Koul, Radhakrishnan and all others for their help and encouragement.

I owe a great deal to my mother (late), father and brothers for their constant encouragement and affection through out the course of this work.

I owe a great deal to my wife Lakshmi who showed immense patience through out the course of my research work and to my daughters Yamini and Malini who had to sacrifice their enjoyable evenings and holidays.

B.V. Rao

ABSTRACT

Disperse dyes have been extensively used for colouration of PET and nylon 6 using conventional dyeing as well as mass colouration techniques. One of the basic requirements of such dyes is compatibility with the polymer. This helps in enhancing the dye uptake and better fastness properties. In mass colouration process thermal stability and volatility of the pigments are the limiting factors along with compatibility.

The main objective of the present work was to develop azo and anthraquinone dyes having better compatibility with PET and nylon 6 by introducing groups which ensure chemical and geometrical conformity. Several anthraquinone dyes having hydroxyethyl and carboxyalkyl groups were prepared by reacting 1-chloroanthraquinone, 1,5-dichloroanthraquinone or 1,8-dichloroanthraquinone with ethanolamine, aminocaproic acid, aminoundecanoic acid. The azo and anthraquinone dyes having β -hydroxyethyl groups were also modified by introducing acetyl, benzoyl, and terephthaloyl groups. The introduction of terephthaloylated and carboxyamylamino groups is expected to increase the dyestuff compatibility with PET and nylon 6 respectively due to their structural similarities.

A systematic study was also carried out to investigate the effect of structure on properties of perylene pigments. Pigments having methyl, hydroxyethyl and carboxyalkyl

groups were prepared by reacting perylene-3,4,9,10-tetracarboxylic acid dianhydride with methylamine, ethanolamine, aminoacetic acid, 4-aminobutanoic acid and 6-aminocaproic acid.

The modified dyes and pigments were characterised by elemental analysis, electronic, ir, $^1\text{H-NMR}$ and mass spectroscopic techniques. The structures of various dyes and pigments were confirmed by such analyses.

Electronic spectra of various dyes were recorded in different solvents. A hypsochromic shift was observed on acylation of hydroxy dyes. Higher solvochromic shift was also observed for all the dyes in DMF.

Modified azo and anthraquinone dyes were used for colouration of PET and nylon 6 using conventional dyeing and by mass colouration technique while perylene pigments were used for the mass colouration of PET and nylon 6.

Dyes substituted by only one benzoyl and terephthaloyl group showed better dye uptake as compared to the acetylated and hydroxy dyes. The trend was reversed when two such groups were present in the dye molecules which was attributed to the steric hindrance. These dyes also tended to have better light, wash and sublimation fastness properties in PET. Similarly, dyes containing carboxyamyl-amino groups showed an increase in dye uptake and better

wash and sublimation fastness properties in nylon 6 when compared to the other dyes of respective series.

Solubility parameters of dyestuffs were calculated theoretically using molar group contribution method. Increase in dye uptake of azo and anthraquinone dyes on PET was observed by decreasing the difference between the solubility parameter of the dye and fiber and increasing the difference between the solubility parameter of dye and water. However, in nylon 6, a better correlation was obtained with association solubility parameter and dye uptake. Highest dye uptake of terephthaloylated dyes on PET and carboxyamylamino acid substituted dyes on nylon 6 was explained on the basis of a bicomponent solubility parameter model.

In order to study the changes taking place in physical structure of PET during dyeing process, density, x-ray, birefringence, critical dissolution time (CDT) of dyed fibers and phase transition characteristics were evaluated. Such studies indicated a marginal increase in crystallinity in dyed fibers as compared to neat fiber treated under similar dyeing conditions. Lower crystallisation temperature and low heat of crystallization was observed in dyed fibers using acylated dyes as compared to the fibers dyed with hydroxy dyes.

The primary requirement for mass colouration is that the colourant should be stable at spinning temperatures of

polymer. Thermal stability of dyes and perylene pigments was evaluated by comparing onset temperature for weight loss and temperature of maximum rate of weight loss and char yields. Higher thermal stabilities for the acylated dyes were observed than the corresponding hydroxy compounds. All the perylene pigments were stable upto 350-400°C.

Thermal stability of dyes is also influenced by polymer substrate. Therefore, master batches of PET/nylon 6 having 10 % (w/w) azo/anthraquinone dyes were used for evaluating thermal behaviour. Increase in thermal stability of various dyes was observed in PET. Benzoylated and terephthaloylated dyes showed lower weight loss in PET as compared to the corresponding hydroxy and acetylated dyes. However, in nylon 6, azo dyes showed rapid weight loss.

Knowledge of melt viscosity is essential for optimising spinning parameters. For this purpose, melt flow index (MFI) of PET and nylon 6 containing 1 % dyestuff (coated chips) was investigated at temperatures of 260 and 270°C (nylon 6) and 270 and 280°C (PET). These studies indicated an increase in MFI of PET and nylon 6 with azo and anthraquinone dyes. However, acylated dyes showed lower MFI with PET as compared to the corresponding hydroxy dyes. In nylon 6, carboxyamylamino substituted dyes and perylene pigments having carboxyalkyl groups showed highest MFI as compared to the other dyes.

Mass coloured PET and nylon 6 fibers using perylene pigments were produced by melt spinning technique using coated chips and mass coloured chips. The surface characterisation of mass coloured filaments was carried out using a polarizing microscope. Surface characterisation clearly indicated greater uniformity in pigment dispersion when structurally similar groups were present in the pigment. The coloured filaments produced with perylene pigments showed fluorescence.

Mass coloured PET and nylon 6 fibers (1 % shade) were also produced using azo and anthraquinone dyes. Two sets of coloured filaments were prepared by using master batch chips or coated chips.

Mechanical and fastness properties of mass coloured fibers were also investigated. The fastness properties of mass coloured fibers with various azo and anthraquinone dyes were significantly superior as compared to the coloured fibers obtained by using same dyes by conventional dyeing process.

The thesis has been divided into six chapters. First chapter deals with a critical literature survey of azo, anthraquinone based disperse dyes and perylene based pigments. Colouration of PET and nylon 6 with these dyes using conventional dyeing method and mass colouration technique is also described. The results of these investigation are incorporated in the Chapters II-V.

Chapter II incorporates the details of experimental work regarding modification of some commercially available azo dyes, preparation of anthraquinone derivatives and their characterisation. Chapter III deals with the synthesis and characterisation of thermally stable pigments derived from 3,4,9,10-perylenetetracarboxylic acid dianhydride. The effect of dye structure on the dyeing and fastness characteristics on PET and nylon 6 is reported in Chapter IV. Chapter V deals with the mass colouration of PET and nylon 6 using some azo and anthraquinone dyes. General discussion and summary of work is given in Chapter VI of the thesis. Suggestions for future work are also given.

CONTENTS

	Page No.
CHAPTER I : INTRODUCTION AND LITERATURE SURVEY	1
1.1 Introduction	
1.2 Disperse dyes	
1.2.1 Azo dyes	
1.2.1.1 Modification of diazo component	
1.2.1.2 Modification of coupling component	
1.2.1.3 Modification of terminal amino group	
1.2.2 Anthraquinone dyes	
1.3 Dyeing theory	
1.3.1 Solubility parameter concept	
1.3.2 Structural changes on disperse dyeing	
1.4 Mass colouration	
1.4.1 Incorporation of colourants during polymerisation	
1.4.2 Incorporation of colourants during spinning	
1.4.3 Colourants for mass colouration	
1.4.3.1 Pigments for mass colouration	
1.4.3.2 Polymer soluble colourants	
1.5 Scope of the present work	
CHAPTER II : SYNTHESIS AND CHARACTERISATION OF AZO AND ANTHRAQUINONE DYES	31
2.1 Introduction	
2.2 Experimental	
2.2.1 Materials	
2.2.2 Modification of azo dyes	

- A. Hydrolysis of Foron Scarlet S-3G
 - B. Purification of hydroxy dyes
 - C. Acetylation of hydroxy dyes
 - D. Benzoylation of dyes
 - E. Monomethyl terephthaloylation of dyes
- 2.2.3 Synthesis of anthraquinone dyes
- 2.3 Characterisation
- 2.4 Results and discussion
- 2.4.1 Elemental analysis of dyes
 - 2.4.2 Melting point of dyes
 - 2.4.3 Electronic spectra of dyes
 - 2.4.4 Structural characterisation

CHAPTER III : SYNTHESIS AND CHARACTERISATION OF PERYLENE
BASED PIGMENTS

62

- 3.1 Introduction
- 3.2 Experimental
- 3.2.1 Materials
 - 3.2.2 Preparation Of various intermediates/
pigments
 - 3.2.3 Particle size reduction of pigments
 - 3.2.4 Preparation of pigment coated chips
 - 3.2.5 Preparation of mass coloured chips
 - 3.2.6 Melt spinning of nylon 6/PET
- 3.3 Characterisation
- 3.4 Results and discussion
- 3.4.1 Elemental analysis of pigments
 - 3.4.2 Density of pigments
 - 3.4.3 Structural characterisation

- 3.4.4 Electronic spectra of pigments
- 3.4.5 Thermogravimetric analysis of pigments
- 3.4.6 Characteristics of Mass coloured chips
- 3.4.7 Rheological properties
- 3.4.8 Fiber properties
- 3.4.9 Fastness properties

CHAPTER IV : DYEING OF PET AND NYLON 6 USING MODIFIED AZO AND ANTHRAQUINONE DYES

81

- 4.1 Introduction
- 4.2 Experimental
 - 4.2.1 Materials
 - 4.2.2 Preparation of dye dispersions
 - 4.2.3 Dyeing of polyester
 - 4.2.4 Dyeing of nylon 6
 - 4.2.5 Estimation of dye uptake
 - 4.2.6 Fastness properties
 - 4.2.7 Structure of dyed PET fibers
 - 4.2.7.1 Determination of density
 - 4.2.7.2 X-ray crystallinity
 - 4.2.7.3 Birefringence
 - 4.2.7.4 DSC Studies
 - 4.2.7.5 Critical dissolution time
- 4.3 Results and discussion
 - 4.3.1 Dyeing characteristics
 - 4.3.2 Solubility parameter of dyes and polyester/nylon 6
 - 4.3.3 Fastness properties

4.3.4 Structural characterisation of dyed fibers

4.3.4.1 Density of dyed PET fiber

4.3.4.2 X-ray crystallinity

4.3.4.3 Birefringence

4.3.4.4 DSC studies

4.3.4.5 CDT of dyed PET fibers

CHAPTER V : MASS COLOURATION OF PET AND NYLON 6 WITH MODIFIED AZO AND ANTHRAQUINONE DYES

108

5.1 Introduction

5.2 Experimental

5.2.1 Materials

5.2.2 Preparation of master batch of coloured PET and nylon 6

5.2.3 Thermal stability of dyes and master batch chips

5.2.4 Melt Behaviour of PET and nylon 6 in the presence of dyes

5.2.5 Melt spinning of PET/nylon 6

5.3 Characterisation

5.4 Results and Discussion

5.4.1 Thermal stability of dyes and master batch chips

5.4.2 Melt behaviour of PET and nylon 6 in the presence of dyes

5.4.3 Properties of mass coloured fibers

CHAPTER VI : GENERAL DISCUSSION AND COMCLUSIONS

122

6.1 Sources of Error

6.1.1 Dye uptake

- 6.1.2 Structural characterisation of dyed fibers
- 6.1.3 Mass colouration
- 6.1.4 Thermal studies
- 6.2 General Discussion
 - 6.2.1 Synthesis/modification of colourants
 - 6.2.1.1 Modification of azo dyes
 - 6.2.1.2 Synthesis of anthraquinone dyes
 - 6.2.1.3 Synthesis of perylene pigments
 - 6.2.2 Characterisation of dyes and pigments
 - 6.2.3 Effect of dye structure on dyeing properties
 - 6.2.3.1 Equilibrium dye uptake
 - 6.2.3.2 Solubility parameter of dyes and fibers
 - 6.2.3.3 Fastness properties
 - 6.2.3.4 Structural characterisation of dyed fibers
 - 6.2.4 Mass colouration of PET and Nylon 6
- 6.3 Suggestions for Future Work

APPENDIX I : SOLUBILITY PARAMETER OF DYES	132
1. Total Solubility Parameter	
2. Three Dimensional Solubility Parameter	
3. Calculation of Total Solubility Parameter	
4. Determination of Dispersion and Association Solubility Parameter	
REFERENCES	137
BIODATA	146
LIST OF PAPERS PUBLISHED/COMMUNICATED	147