SYNTHESIS OF ACRYLONITRILE / VINYL ACID/ METHYL ACRYLATE POLYMERS AND THEIR CONVERSION TO HIGH TENACITY FIBRES.

By

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crylic polymers
Synthetic fibres

by

Dedicated

To

My Parents

CERIFICATE

This is to certify that the thesis entitled **"SYNTHESIS OF ACRYLONITRILE/ VINYL ACIDS/ METHYL ACRYLATE POLYMERS AND THEIR CONVERSION TO HIGH TENACITY FIBRES"**, being submitted by Mr. Sreekumar Thaliyil Veedu, 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 him. Mr. Sreekumar Thaliyil Veedu has worked under our guidance and supervision and has fulfilled the requirements of the thesis.

The results presented in this thesis have not been submitted, in part or in full, to any other institute or university for the award of any degree or diploma.

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ABSTRACT

This dissertation deals with the synthesis, characterization and dry-jet-wet spinning of acrylonitrile (AN) polymers containing methacrylic acid (MAA), itaconic acid (IA) or methyl acrylate (MA) comonomers. Radical polymerization of acrylonitrile (AN) with methacrylic acid (MAA) and itaconic acid (IA) was carried out in a mixture of dimethyl formamide (DMF) and water at 70°C using α, α'- azobisisobutyronirile (AIBN) as initiator using DMF/H_2O suspension polymerization. Characterization of the polymers was carried out using FTIR, CHN analysis, ^{1}H- NMR, ^{13}C NMR, 2D- HETCOR NMR and viscometric techniques. The rate of polymerization (Rp) decreases with increase in DMF concentration in the reaction medium, viz., at 20% DMF level for AN/MAA system the Rp is 1.23 % min^{-1} in 1hr polymerization while at 80% DMF level Rp is reduced to 0.37% min^{-1}.

Terpolymers containing AN, MA, MAA [P(AN/MA/MAA)] and AN,MA,IA [P(AN/MA/IA)] have also been prepared for the production of high tenacity acrylic fibres. The intrinsic viscosity of the polymers ranges from 0.67 to 2.90 dLg^{-1} depending on the composition of the polymerization reaction medium. The IR absorbance ratio of the carbonyl peaks at 1734 cm^{-1} to that of the nitrile peak at 2243 cm^{-1} is used as a measure of the acid comonomer content in the copolymer. Using ^{13}C{H} and ^{1}H NMR, it could be followed that at low comonomer content, the AAA sequencing predominates, while, with increasing comonomer content (4-6-mole %) AAM or AAI sequencing increases. Sequence distribution of AN is found to be random ($n_m \sim n_r \cong 2.0$).

Thermal characterization of acrylonitrile homopolymer and copolymers has been carried out using DSC, high pressure DSC and TGA. Influence of methacrylic acid (MAA 3-6 mole %) and itaconic acid (IA 2-3 mole %) on the glass transition temperature, T_g, thermo-oxidative stabilization and hydration melting of acrylonitrile copolymers has been discussed in detail. While, two Tgs are observed, near 70 and 140°C, for PAN homopolymer, copolymers with 2-3 mole % of comonomers showed another base line shift below 70°C. The copolymers showed two distinct melting peaks in the first heating cycle through high pressure DSC, but on cooling the melt exhibits a single exotherm. The melting point (T_m) of IA copolymer (158.4°C) is found to be lower than that of MAA copolymer (164°C) and PAN homopolymer (186°C). The enthalpy of fusion, ΔH_f decreases with the incorporation of comonomers, e.g.; it is the highest for PAN homopolymer (57.8 Jg^{-1}) and the lowest for P(AN/IA) copolymer (26.1 Jg^{-1}). Similarly, the entropy of fusion is also

lower for copolymers. The lower entropy of fusion (ΔS_f) of copolymers indicates that they are less mobile in the molten state.

Dry-jet-wet spinning studies of three copolymers P(AN/MAA), P(AN/MA) and P(AN/IA) having comonomer content 1.3, 1.4 and 0.7 mole % reveals that the cross-sectional shape of gel fibres undergoes a transition from kidney to oval shape and macrovoids begin to appear at higher coagulation bath temperature. However, F(AN/IA) gel fibres change from kidney shape to irregular shoe type with a gel network of interconnected polymer fibrils. F(AN/MA) fibres show higher strength (3.1 g/den) and elongation (14.6%) at 40^0C coagulation bath temperature. Crystallinity does not change significantly (χ_c = 61-63%) with draw ratio, but crystal size increases from 22.9 to 43.4 A^0, and orientation factor 0.41 to 0.78.

Two terpolymers P(AN/MA/MAA), acid content 1.1 mol%, and P(AN/MA/IA),acid content 0.6 mole ratio, with intrinsic viscosity value [η] ranging between 2.6-2.7 dl g^{-1} after dry-jet-wet spinning and multi-stage drawing in boiling water and glycerol (total draw ratio 11.2) resulted in high tenacity fibres. F(AN/MA/MAA) fibres obtained after plasticized stretching in glycerol and subsequent collapsing on heater plates showed higher strength (6.44g/d), elongation-at-break (11%) and high modulus (251.9 g/d).

The main findings and general conclusions of the present work are summarized in the last chapter.

CONTENTS

CHAPTER 1 INTRODUCTION AND LITERATURE SURVEY.

CHAPTER 2 SYNTHESIS AND CHARACTERIZATION OF ACRYLONITRILE/ VINYL ACIDS/ METHYL ACRYLATE POLYMERS.

CHAPTER 3 THERMAL CHARACTERIZATION OF ACRYLONITRILE/ VINYL ACID COPOLYMERS

CHAPTER 4 DRY-JET-WET SPINNING OF ACRYLONITRILE/ VINYL ACID COPOLYMERS

CHAPTER 5 PRODUCTION OF HIGH TENACITY ACRYLIC FIBRES AND CHARACTERIZATION THEREOF

sulfur containing end groups, derived mainly because of transfer of free radicals to bisulfite ion during polymerization, were observed using FTIR and 13CNMR spectroscopic techniques.

Japan Exlan Co. [24-25] prepared an acrylonitrile copolymer with methyl acrylate having a molecular weight of 3-4 x 10^5. They used 900g AN, 100g MA and 10g AIBN which were added to 3000g of H_2O containing 15g of polyvinyl alcohol (PVA) at 60^0C. The reaction was continued for 2h to obtain a conversion of 57.5%. The presence of PVA has been suggested to have increased the solution viscosity which decreased the radical mobility and thus resulted in higher molecular weight.

1.2.2.3Solvent-Water suspension polymerization

In this method, approximately equivolume mixture of solvent (DMF, DMSO etc.,) and water (non-solvent) is used as the reaction medium, and more water is added on the onset of precipitation. The reaction is initiated by AIBN. The presence of solvent narrows the molecular weight distribution and water reduces the overall chain transfer leading to the formation of higher molecular weight polymer. The advantages of this method are:

- High percentage conversion.
- Shorter polymerization time (1-4 hrs).
- Higher molecular weight and
- Better degree of whiteness.

Although, published literature on this method is scarce, some information is available in some patents.

A patent assigned to Mitsubishi Rayon [11] discloses the production of acrylonitrile copolymer with methacrylic acid using DMF/water suspension polymerization. Here 6 Kg of AN was copolymerized with 82g of MAA in the

CHAPTER 6 SUMMARY AND CONCLUSIONS.