SYNTHESIS, CHARACTERIZATION AND PRODUCTION OF ACRYLONITRILE-CARBOXYLIC ACID COPOLYMERS AND FIBRES

by

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Dedicated to
My Parents

CERTIFICATE

This is to certify that the thesis entitled " **SYNTHESIS, CHARACTERIZATION AND PRODUCTION OF ACRYLONITRILE - CARBOXYLIC ACID COPOLYMERS AND FIBERS** ", being submitted by **Mr. Seyed Hajir Bahrami**, 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. Seyed Hajir Bahrami has worked under our guidance and supervision and has fulfilled the requirements for the submission 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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ABBREVIATIONS

AA	-	Acrylic Acid
AIBN	-	2,2'-Azobis-isobutyronitrile
AN	-	Acrylonitrile
DMAc	-	N:N-dimethyl acetamide
DMSO	-	Dimethyl sulphoxide
E	-	Activation Energy
EA	-	Ethyl acrylate
IA	-	Itaconic acid
MA	-	Methylacrylate
MAS	-	Sodium methallyl sulphonate
PAN	-	Poly acrylonitrile
P(AN-AA)	-	Acrylonitrile-acrylic acid copolymer
P(AN-IA)	-	Acrylonitrile-itaconic acid copolymer
P(AN-MAA)	-	Acrylonitrile-methacrylic acid Copolymer
Ts	-	Tensile Strength
VA	-	Vinyl acetate
DSC	-	Differential Scanning Calorimetry
DSC-FTIR	-	DSC interfaced with FTIR
FTIR	-	Fourier Transform Infra-red Spectroscopy
IM	-	Initial Modulus
IV	-	Intrinsic Viscosity
MWD	-	Molecular weight distribution
NMR	-	Nuclear Magnetic Resonance Spectroscopy
SAF	-	Special Acrylic Fibres
SEM	-	Scanning Electron Microscopy
T_g	-	Glass transition temperature
TGA-FTIR	-	TG interfaced with FTIR
TMA	-	Thermo-mechanical analysis
WAXD	-	Wide angle X-ray diffraction

CODING OF THE POLYMERS AND FIBRES USED IN THIS DISSERTATION

P_0	-	Polyacrylonitrile
PA	-	Acrylonitrile-acrylic acid copolymer (acrylic acid =3.1 mol%)
PA_1	-	Acryonitrile-acrylic acid copolymer (acrylic acid=5.51 mol%)
PA_2	-	Acrylonitrile-acrylic acid copolymer (acrylic acid=7.12%)
PA_3	-	Acrylonitrile-acrylic acid copolymer (acrylic acid=8.52 mol%)
PA_4	-	Acrylonitrile-acrylic acid copolymer (acrylic acid=17.51%)
PM	-	Acrylonitrile-Methacrylic acid copolymer (Methacrylic acid= 2.6 mol %)
PM_1	-	Acrylonitrile-methacrylic acid copolymer (Methacrylic acid=3.08 mol%)
PM_2	-	Acrylonitrile-methacrylic acid copolymer (Methacrylic acid=4.57%)
PM_3	-	Acrylonitrile-methacrylic acid copolymer (Methacrylic acid=8.22 mol%)
PM_4	-	Acrylonitrile-methacrylic acid copolymer (Methacrylic acid=10.15%)
PM_5	-	Acrylonitrile-methacrylic acid copolymer (Methacrylic acid=14.61%)
PI	-	Acrylonitrile-Itaconic acid Copolymer (Itaconic acid = 2.2 mol%)
PI_1	-	Acrylonitrile-Itaconic acid Copolymer (Itaconic acid = 3.58 mol%)
PI_2	-	Acrylonitrile-Itaconic acid Copolymer (Itaconic acid = 4.35 mol%)
PI_3	-	Acrylonitrile-Itaconic acid Copolymer (Itaconic acid = 5.87 mol%)
PI_4	-	Acrylonitrile-Itaconic acid Copolymer (Itaconic acid = 6.07 mol%)
PI_5	-	Acrylonitrile-Itaconic acid Copolymer (Itaconic acid = 8.81 mol%)
FA	-	Fibres spun from copolymer PA
FA5	-	Fibre spun from Copolymer PA at 5^oC coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone)
FA15	-	Fibre spun from Copolymer PA at 15^oC coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).

FA25	-	Fibre spun from Copolymer PA at 25°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FA35	-	Fibre spun from Copolymer PA at 35°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FA 5D	-	Fibre spun from Copolymer PA at 5°C coagulation bath temperature and drawn up to draw ratio = 8.5) (II nd drawing zone.
FA 15D	-	Fibre spun from Copolymer PA at 15°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone.
FA 25D	-	Fibre spun from Copolymer PA at 25°C ccagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone.
FA 35D	-	Fibre spun from Copolymer PA at 35°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone.
FM	-	Fibres spun from Copolymer PM
FM5	-	Fibre spun from Copolymer PM at 5°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FM15	-	Fibre spun from Copolymer PM at 15°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FM25	-	Fibre spun from Copolymer PM at 25°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FM35	-	Fibre spun from Copolymer PM at 35°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FM 5D	-	Fibre spun from Copolymer PM at 5°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone)
FM 15D	-	Fibre spun from Copolymer PM at 15°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone).
FM 25D	-	Fibre spun from Copolymer PM at 25°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone)

FM 35D	-	Fibre spun from Copolymer PM at 35°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone)
FI	-	Fibre spun from Copolymer of PI
FI5	-	Fibre spun from Copolymer PI at 5°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FI15	-	Fibre spun from Copolymer PI at 15°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FI25	-	Fibre spun from Copolymer PI at 25°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FI35	-	Fibre spun from Copolymer PI at 35°C coagulation bath temperature and drawn up to draw ratio = 6.5 (I st drawing zone).
FI 5D	-	Fibre spun from Copolymer PI at 5°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone)
FI 15D	-	Fibre spun from Copolymer PI at 15°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone)
FI 25D	-	Fibre spun from Copolymer PI at 25°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone)
FI 35D	-	Fibre spun from Copolymer PI at 35°C coagulation bath temperature and drawn up to draw ratio = 8.5 (II nd drawing zone)
PA/Fe	-	Metal complex of PA Copolymer with $FeSo_4$
PA/Al	-	Metal complex of PA Copolymer with $Al_2(So_4)_3$
PA/Zn	-	Metal complex of PA Copolymer with $ZnSo_4$
PA/Cu	-	Metal complex of PA Copolymer with $CuSo_4$

ABSTRACT

Acrylonitrile was copolymerized with carboxylic acid comonomers, viz. acrylic (AA), methacrylic acid (MAA) and itaconic acid (IA) using solution polymerization technique in DMF as a solvent and AIBN initiator. The reactivity ratios of these comonomers were calculated using Kelen Tüdös and Fineman-Ross method. These copolymers were characterized using CHN analysis, FTIR and NMR techniques. Sequence length distribution and Tacticity of these copolymers were calculated using ^{13}C NMR spectroscopy.

Thermal behaviour of acrylonitrile-carboxylic acid in air and nitrogen was investigated using DSC (Dynamic & Isothermal), TGA and DSC-FTIR. Influence of these carboxylic acids on thermal behaviour of acrylonitrile copolymers has been investigated. Quantitative analysis of infrared absorption bands at 2243 cm^{-1} due to ν C≡N, and 2940 cm^{-1} due to ν CH_2 absorption has confirmed superiority of itaconic acid over AA or MAA in initiating the dehydrogenation and cyclization reaction at a much lower temperature but the propagation is slow.

Metallation of acrylonitrile-acrylic acid copolymer with $Al_2(SO_4)_3$, $CuSO_4$, $ZnSO_4$ and $FeSO_4$ was carried out by the addition of these metal salts to the polymer dope. Thermal and rheological behaviour of these metal complexes was investigated by Brookfield viscosity measurements, and DSC, DSC-FTIR structural changes. The sequence of

exothermic reactions leading to nitrile oligomerization has been monitored through DSC-FTIR and deconvulation of absorbance bands in 1500-1800 cm^{-1} region.

Acrylonitrile-carboxylic acid copolymers, i.e., acrylic, methacrylic and itaconic acid were spun into fibres using dry jet wet spinning technique. Spinning has been carried out on a laboratory spinning unit using dimethylformamide (DMF) and water (60:40 v/v) as a coagulation mixture. The coagulation bath temperature was varied from 5 to 35°C. Gel fibres collected after the first coagulation bath were examined for their cross-sectional shape and mechanical properties.

Drawing of the acrylic copolymer fibres was carried out in two steps. First on a heater plate upto a draw ratio of 6.5 at 140°C and in the second drawing zone upto a total draw ratio 8.5 at 160°C. Effect of spinning parameters on structure-properties of acrylonitrile-carboxylic fibres has been established through WAXD, density, boiling water shrinkage and mechanical properties. SEM has been used to study the fracture morphology of these fibres.

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