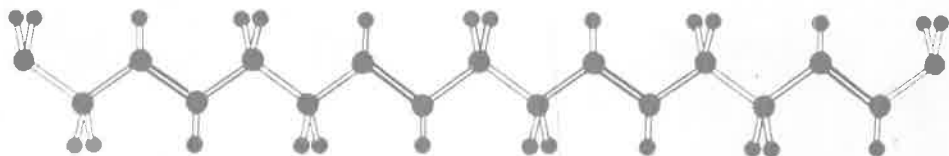
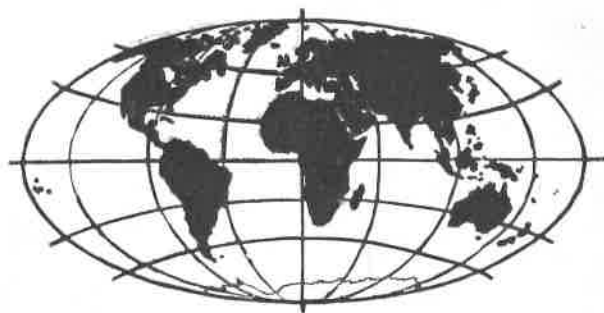
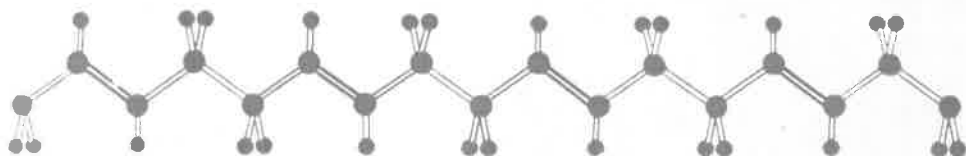


INTERNATIONAL SYMPOSIUM ON
NEW FRONTIERS IN
POLYMER SCIENCE AND
POLYMER APPLICATIONS
ABSTRACTS



7-11. JANUARY 1980



Central Leather Research Institute, Adyar, Madras-600 020, India.

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INTERNATIONAL SYMPOSIUM ON

NEW FRONTIERS IN POLYMER SCIENCE AND POLYMER APPLICATIONS

7—11, *January* 1980

PROGRAMME AND COLLECTED ABSTRACTS

Central Leather Research Institute,

Adyar, Madras - 600 020, INDIA.

A Warm Welcome

The organizers of the International Conference on "New Frontiers in Polymer Science and Polymer Applications" wish all the delegates a hearty welcome and a happy New Year and hope that your trip to Madras will be useful and interesting.

Be most welcome, and enjoy yourselves!

CONTENTS

| | Page |
|---|-------------|
| Programme | ... ii—xxxv |
| 1. Electrochemical polymerization and deposition on carbon fibers | ... 1 |
| 2. The chemical bonding between c-fibers and polymer matrix in composites | ... 2 |
| 3. Microfractographical investigations of plastics short fiber RP, GRP and CRP composites | ... 3 |
| 4. Studies on the various pan precursors and its bearing on the ultimate mechanical properties of carbon fibers | ... 4 |
| 5. The effect of molecular orientation on the tensile properties of butadiene rubber modified styrene acrylonitrile copolymers (ABS) | ... 5 |
| 6. Redox polymerisation kinetics and mechanism of reactions initiated by systems based on Mn(III) complexes in aqueous and nonaqueous media | ... 6 |
| 7. A kinetic study of the Lewis acid assisted decomposition of benzoyl peroxide and its implication to the mechanism of complex copolymerizations | ... 7 |
| 8. Two component hydrogel 5. Theoretical considerations and experiments | ... 7 |
| 9. Methylene blue as chain terminator in free radical polymerisation 1. Polymerization of styrene, methyl methacrylate and acrylamide | ... 8 |
| 10. Grafting of acrylate monomers onto chlorinated rubber | ... 9 |
| 11. Ultra high-strength/high-modulus fibers from rigid and semi-rigid polymers | ... |
| 12. Studies on acrylic polymers with reference to fiber spinning | ... 10 |

| | Page |
|---|------|
| 13. The fracture of elastomer-modified epoxy polymers ... | 10 |
| 14. A comparative evaluation of glass/carbon/kevlar fibers as reinforcement in composite pressure bottles ... | 11 |
| 15. Structures and properties of rubber reinforced thermoplastics ... | 12 |
| 16. Compounding of glass fiber reinforced polypropylene and investigation of its mechanical properties under simple and complex loading ... | 12 |
| 17. Effect of aditives in the spinning dope on the mechanical properties of the pan fibers ... | 13 |
| 18. Semi-crystalline poly (arylene ether sulfone) copolymers ... | 14 |
| 19. Synthesis and characterization of certain para-azoaromatic polyamides ... | 14 |
| 20. Molecular significance of the c_2 -term ... | 15 |
| 21. Sythnesis of some new metal-containing polyurethanes ... | 15 |
| 22. Addition polyimides based on bis (m-Aminophenyl) methylphosphine oxide ... | 16 |
| 23. Effect of the rigid natu,e of the backbone on synthesis of poly-p-phenyleneterephthalamide ... | 17 |
| 24. Polyesteramide fibers ... | 17 |
| 25. Rational utilisation of polyacrylonitrile (PAN) for high performance carbon fiber: A systems approach ... | 18 |
| 26. Studies on aromatic-aliphatic fiber forming copolyesters ... | 18 |
| 27. Polymers in textile wet processing ... | 19 |
| 28. An analysis of non linear viscoelastic behaviour of polypropylene and glass reinforced polypropylene in creep ... | 19 |
| 29. New frontiers of acrylics in adhesives and coatings ... | 20 |
| 30. The application of spent sulfite liquor as an adhesive for Particle boards ... | 21 |

| | Page |
|---|------|
| 31. Studies towards structure of aromatic polyimides ... | 22 |
| 32. Adhesive materials used in medicine and dentistry ... | 22 |
| 33. Room-temperature-curing organotin polymers ... | 23 |
| 34. Preparation and biomedical applications of poly (hydroxy-ethyl methacrylate-methacrylic acid) hydrogel ... | 24 |
| 35. Newest experience on carbon fiber reinforced bone plates ... | 24 |
| 36. Biological testing of implantable materials for medical applications: A preliminary report ... | 26 |
| 37. Therapeutic systems from biodegradable polymers ... | 26 |
| 38. Microbial degradation of gelatin graft copolymers ... | 27 |
| 39. New results on the anionic polymerization of polar monomers ... | 28 |
| 40. Preliminary study of cationic polymerization of α -methyl-styrene using t-BuCl/Et ₃ AlCl/CH ₂ Cl ₂ system ... | 29 |
| 41. Anionic polymerisation of 2, 4-dinitrostyrene ... | 29 |
| 42. Synthesis, characterization and mechanism of graft copolymerization of methylmethacrylate onto cellulose nitrate ... | 30 |
| 43. γ -Ray induced grafting reactions onto polypropylene and its electrokinetic behaviour ... | 30 |
| 44. Synthesis and characterization of mica-vinyl graft copolymer ... | 31 |
| 45. Studies in graft copolymerization of vinyl monomers onto wool in presence of VO(acac) ₃ as initiator ... | 32 |
| 46. Surface and bulk parameters affecting contact electrification of polystyrene ... | 32 |
| 47. Glass transition temperature from dielectrics relaxation data: Glass transition temperature of polyacrylonitrile ... | 33 |

| | Page |
|--|------|
| 48. Theoretical treatment of the kinetic parameters of glass transitions ... | 34 |
| 49. Adiabatic compressibilities of drag reducing polymers ... | 34 |
| 50. Dielectric behaviour of foams from polystyrene-polymethyl methacrylate blends at X-band microwave frequency ... | 35 |
| 51. Thermal modification of poly (vinyl chloride) and formation of dehydrochlorinated poly (vinyl chloride) poly (methyl methacrylate) polymer blend in the process of foaming: Identification and application ... | 36 |
| 52. Mechanism and structure properties relationship for thermo-oxidative degradation of polyethylene during thermal ageing ... | 36 |
| 53. The origin of the variability in the properties of commercial poly (vinyl alcohol co-acetate) ... | 37 |
| 54. Hydrophobic interactions on the binding of poly-vinylpyrrolidone ... | 39 |
| 55. Kinetic studies on the formation of poly (chloro-cyclo phosphazenes) ... | 40 |
| 56. Gamma radiation induced bulk polymerization of some methyl phenoxymethacrylates ... | 40 |
| 57. Cu (DPM) initiate vinyl polymerization ... | 41 |
| 58. Studies on the chain-transfer property of thiourea in radical polymerization and its tautomeric equilibrium in acid aqueous medium by the application of dye-technique ... | 41 |
| 59. Substituent effects in polymerization reactions in terms of generalised substituent constants F & R and generalised weighting factors f & r devised by Swain & Lupton and Willims & Norrington ... | 42 |
| 60. New processing methods also suited to high temperature plastics ... | 42 |
| 61. Diffusion effects in initiator decomposition in highly viscous and macromolecular solutions ... | 43 |

| | Page |
|--|------|
| 62. Processing and rheology of glass fiber-filled polypropylene ... | 44 |
| 63. Recent advances in the understanding of the mechanisms of environmental stress cracking of polyethylene ... | 44 |
| 64. A non-destructive method for mechanical testing of cement-polymer composite ... | 45 |
| 65. On errors in pressure-hole measurements in the flow of polypropylene melts through circular dies ... | 46 |
| 66. Preparation of large monodisperse latex particles ... | 47 |
| 67. Water borne wire enamels ... | 48 |
| 68. Polymer impregnation of ferrocement ... | 49 |
| 69. Critical reliability parameters in silicones processing ... | 50 |
| 70. Phthalic anhydride based cation exchange resin from n-vinyl carbazole ... | 50 |
| 71. Copolymers of polystyrene glycol and glyceryl phthalate resins in surface coatings ... | 51 |
| 72. Radiation induced polymerization of vinylidene chloride in solution ... | 51 |
| 73. On the use of the Mayo equation in cationic polymerization ... | 52 |
| 74. Polymerizable ultraviolet stabilizers ... | 52 |
| 75. Photopolymerization of n, n'-methylene bisacrylamide in aqueous solution by potassium trisoxalato-ferrate (III) ... | 53 |
| 76. Application of various viscosity theories to the viscosity data of methyl methacrylate-acrylonitrile random copolymers ... | 53 |
| 77. Copolymerization of styrene and acrylonitrile in suspension system: Properties of the system and the polymer in relation to the degree of conversion ... | 54 |

| | Page |
|--|------|
| 78. Morphology and properties of polybutylene terephthalate . . . | 54 |
| 79. Polycyclotrimers-novel thermostable plastics . . . | 55 |
| 80. Recent experiments on rubber-like elasticity . . . | 56 |
| 81. Basalt fibers . . . | 56 |
| 82. Carbon fiber-reinforcing component for advanced materials . . . | 57 |
| 83. The potential of composites with hollow fibers in aerospace structure . . . | 58 |
| 84. The effect of heat-setting on the structure and properties of polyacrylonitrile fibers . . . | 58 |
| 85. Development of indigenous technology for production of fiber glass . . . | 59 |
| 86. Polymer systems for controlled release of organotin toxin . . . | 60 |
| 87. New techniques of polymer characterization using the ultracentrifuge . . . | 61 |
| 88. Raman spectroscopic study of polyacrylamide gels . . . | 62 |
| 89. Irreversible phase transition in macromolecules . . . | 62 |
| 90. Electrical conduction in thin films of polyvinyl acetate . . . | 63 |
| 91. Thermodynamic evidence for polymerization of alcohols . . . | 63 |
| 92. Ultrasonic relaxation studies in dicyclohexylamine . . . | 64 |

MONDAY

7 JANUARY

MORNING

ROOM NO. 1

OPENING SESSION

10.00 a.m.

Inauguration by
His Excellency Shri Prabhudass B. Patwari
Governor of Tamilnadu

10.30 a.m.

Keynote address by
S. Varadarajan
Chairman and Managing Director,
Indian Petrochemicals Corporation Limited,
Baroda

11.30 a.m.

TEA

SESSION I

PLENARY LECTURE

Chairman: Bernhard Wunderlich

LECTURE 1

11.45 a.m.

**NEW STUDIES ON THE MECHANISM OF
SOME TRANSFER AND PROPAGATION RE-
ACTIONS**

C.H. Bamford,
The University of Liverpool,
Liverpool L69 3BX, U.K.

AFTERNOON

**ROOM NO. 1
PARALLEL SESSIONS**

SESSION II

**PAPER SESSION
2.00 p.m. - 3.40 p.m.**

FIBERS AND COMPOSITES

Chairman: J. Preston

(01) 2.00 p.m. - 2.20 p.m.

**THE POTENTIAL OF COMPOSITES WITH HOLLOW FIBERS
IN AEROSPACE STRUCTURE**

H.W. BERGMANN,
Institute for Structural Mechanics,
DFVLR-Braunschweig,
WEST GERMANY.

(02) 2.20 p.m. - 2.40 p.m.

**THE CHEMICAL BONDING BETWEEN C-FIBERS
AND POLYMER MATRIX IN COMPOSITES**

E. FITZER, W. HUETTNER AND R. WEISS,
Institute fuer Chemische Technik,
Universitaet Karlsruhe,
7500 Karlsruhe 1,
WEST GERMANY.

(03) 2.40 p.m. - 3.00 p.m.

**MICROFRACTOGRAPHICAL INVESTIGATIONS OF PLASTICS,
SHORT FIBER RP, GRP AND CRP COMPOSITES**

HANS LEIS,
Central Laboratory of
Messerschmitt Bolkow Blohm GMBH,
8000 Muenchen 80,
Munich, WEST GERMANY.

(04) 3.00 p.m. - 3.20 p.m.

**STUDIES ON THE VARIOUS PAN PRECURSORS AND ITS
BEARING ON THE ULTIMATE MECHANICAL PROPERTIES OF
FIBERS**

EVENING

S.S. CHARI, O.P. BAHL AND R.B. MATHUR,
National Physical Laboratory,
NEW DELHI-110 012.

(05) 3.20 p.m. - 3.40 p.m.

**THE EFFECT OF MOLECULAR ORIENTATION ON THE
TENSILE PROPERTIES OF BUTADIENE RUBBER MODIFIED
STYRENE ACRYLONITRILE COPOLYMERS (ABS)**

G. GROENINCKX,
Laboratory of Macromolecular and Organic Chemistry,
University of Leuven,
Celestijnenlaan 200 F,
B-3030 Heverlee,
BELGIUM.

3.40 p.m. TEA

AFTERNOON

ROOM No. 2

SESSION III

PAPER SESSION

PARALLEL SESSIONS

2.00 p.m. - 3.40 p.m.

KINETICS OF POLYMERISATION

Chairman: C.H. Bamford

(06) 2.00 p.m. - 2.20 p.m.

**REDOX POLYMERISATION - KINETICS AND MECHANISM OF
REACTIONS INITIATED BY SYSTEMS BASED ON $Mn(III)$
COMPLEXES IN AQUEOUS AND NON-AQUEOUS MEDIA**

V. MAHADEVAN, M. HARAGOPAL AND A. JAYAKRISHNAN,
Indian Institute of Technology,
MADRAS 600 036.

AFTERNOON

(07) 2.20 p.m. - 2.40 p.m.

A KINETIC STUDY OF THE LEWIS ACID ASSISTED DECOMPOSITION OF BENZOYL PEROXIDE AND ITS IMPLICATION TO THE MECHANISM OF COMPLEX COPOLYMERIZATIONS

S. SIVARAM, R.K. SINGHAL AND I.S. BHARDWAJ,
Indian Petrochemicals Corporation Limited,
Vadodara,
BARODA 391 346.

(08) 2.40 p.m. - 3.00 p.m.

METHYLENE BLUE AS CHAIN TERMINATOR IN FREE RADICAL POLYMERIZATION. 1. POLYMERIZATION OF STYRENE, METHYL METHACRYLATE AND ACRYLAMIDE

NIRANJAN K. DAS AND BROJA M. MANDAL,
Indian Association for the Cultivation of Science,
CALCUTTA

(09) 3.00 p.m. - 3.20 p.m.

GAMMA RADIATION INDUCED BULK POLYMERIZATION OF SOME METHYL PHENOXYMETHACRYLATES

RAMASWAMY DEVARAJAN, THAIKKANNU BALAKRISHNAN
AND M. SANTAPPA,
University of Madras,
MADRAS 600 025.

(10) 3.20 p.m. - 3.40 p.m.

GRAFTING OF ACRYLATE MONOMERS ONTO CHLORINATED RUBBER

K. KALEEM, -C.R. REDDY AND S. RAJADURAI,
Central Leather Research Institute,
MADRAS 600 020.

3.40 p.m. TEA

EVENING

PLENARY LECTURES

ROOM No. I SESSION IV 4.00 p.m. - 5.30 p.m.

Chairman N. Ramanathan

LECTURE 2

4.00 p.m. - 4.45 p.m.

NEWEST EXPERIENCE IN CARBON FIBERS

B. FITZER,
Institute fuer Chemische Technik,
Universitaet Karlsruhe,
7500 Karlsruhe 1,
WEST GERMANY.

LECTURE 3

4.45 p.m. - 5.30 p.m.

**ORIENTED POLYMER MATERIALS WITH HIGH LEVEL
STRENGTH AND ELASTIC PROPERTIES**

A.S. CHEGOLYA,
All-Union Research Institute of Synthetic Fibers,
Kalinin, USSR.

MORNING

m. RAYMOND SEYMOUR,
University of Southern Mississippi,
Hattiesburg,
Mississippi, U.S.A.

(12) 11.00 a.m. - 11.20 a.m.

SEMI-CRYSTALLINE POLY (ARYLENE ETHER SULFONE)
COPOLYMERS

RAVI VISWANATHAN AND JAMES E. MCGRATH,
Virginia Polytechnic Institute and State University,
Blacksburg,
Virginia 24061, U.S.A.

(13) 11.20 a.m. - 11.40 a.m.

ION SYNTHESIS AND CHARACTERIZATION OF CERTAIN PARA
AZOAROMATIC POLYAMIDES

M. BALASUBRAMANIAN, M.J. NANJAN AND M. SANTAPPA,
University of Madras,
MADRAS 600 025.

(14) 11.40 a.m. - 12.00 noon

POLYCYCLORIMERS—NOVEL THERMOSTABLE PLASTICS

J.E. KRESTA,
University of Detroit,
Detroit, Michigan MI48221, U.S.A.

(15) 12.00 noon - 12.20 p.m.

ION SYNTHESIS OF SOME NEW METAL CONTAINING POLYURE-
THANES

p.m. B. DORAIRAJ AND K. VENKATA RAO,
University of Madras,
MADRAS 600 025.

(16) 12.20 p.m. - 12.40 p.m.

ADDITION POLYIMIDES BASED ON BIS (m-AMINOPHENYL)
METHYLPHOSPHINE OXIDE

AFTERNOON

I.K. VARMA, GEORGE M. FOHLEN AND J.A. PARKER,
Chemical Research Projects Office,
NASA, Ames Research Center,
Moffett Field, CA 94035, U.S.A.

(17) 12.40 p.m. - 1.00 p.m.

EFFECT ON THE RIGID NATURE OF THE BACKBONE ON
THE SYNTHESIS OF POLY-PHENYLENE TEREPHTHALAMIDE

M.K. SRIDHAR, P. KANAKALATHA AND N. BALASUBRAMA-
NIAN,
National Aeronautical Laboratory,
BANGALORE 560 017.

1.00 p.m. - 2.00 p.m. LUNCH

MORNING

ROOM NO. 1
PARALLEL SESSIONS

SESSION VII

PAPER SESSION
10.00 a.m. - 1.00 p.m.

FIBERS AND COMPOSITES

Chairman: Bela Van Falkai

(18) 10.40 a.m. - 11.00 a.m.

ULTRA HIGH STRENGTH/HIGH MODULUS FIBERS FROM
RIGID AND SEMI RIGID POLYMES

J. PRESTON,
Monsanto Triangle Park Development Center Inc.,
Research Triangle Park,
NC. 27709, U.S.A.

(19) 11.00 a.m. - 11.20 a.m.

STUDIES ON ACRYLIC POLYMERS WITH REFERENCE TO
FIBER SPINNING

MORNING

GANGA RADHAKRISHNAN, G. V. RAMANA REDDY, ANNE JOSEPH, T. NAGABHUSHANAM, K. THOMAS JOSEPH AND N. RAMANATHAN,
Central Leather Research Institute,
MADRAS 600 020.

(20) 11.20 a.m. - 11.40 a.m.

THE FRACTURE OF ELASTOMER-MODIFIED EPOXY POLYMERS

WILLARD D. BASCOM AND DONALD L. HUNSTON
Naval Research Laboratory, Washington, D.C., U.S.A. 23075

(21) 11.40 a.m. - 12.00 noon

A COMPARATIVE EVALUATION OF GLASS/CARBON/KEVLAR FIBERS AS REINFORCEMENT IN COMPOSITE PRESSURE BOTTLES

M. MURUGANANDAM AND P.K. BAGCHI
Vikram Sarabhai Space Centre,
TRIVANDRUM 695 022.

(22) 12.00 noon - 12.20 p.m.

STRUCTURES AND PROPERTIES OF RUBBER REINFORCED THERMOPLASTICS

FRANZ HAAF,
Kunststofflaboratorium of BASF AG,
Ludwigshafen,
GERMAN FEDERAL REPUBLIC.

(23) 12.20 p.m. - 12.40 p.m.

COMPOUNDING OF GLASS FIBER REINFORCED POLYPROPYLENE AND INVESTIGATION OF ITS MECHANICAL PROPERTIES UNDER SIMPLE AND COMPLEX LOADING

S.N. PANDIT, V.B. GUPTA AND K. SUBRAMANIAN,
Indian Institute of Technology,
NEW DELHI 110 029.

AFTERNOON

(24) 12.40 p.m. - 1.00 p.m.

**EFFECT OF ADDITIVES IN THE SPINNING DOPE ON THE
PROPERTIES OF THE PAN FIBERS**

N. JOSEPH, A.K. MURTHY,
K. THOMAS JOSEPH AND N. RAMANATHAN,
Central Leather Research Institute,
MADRAS 600 020.

1.00 p.m. - 2.00 p.m. LUNCH

ROOM NO. 2

SESSION VIII

PAPER SESSION

PARALLEL SESSIONS

2.00 p.m. - 3.40 p.m.

POLYMER PHYSICS AND ADHESIVES

Chairman: Raymond Seymour

(25) 2.00 p.m. - 2.20 p.m.

RECENT EXPERIMENTS ON RUBBERLIKE ELASTICITY

J.E. MARK,
The Polymer Research Center,
University of Cincinnati,
U.S.A.

(26) 2.20 p.m. - 2.40 p.m.

**TWO COMPONENT HYDROGELS 5: THEORETICAL CONSI-
DERATIONS AND EXPERIMENTS**

WILLIAM R. GOOD AND H.J. CANTOW,
Institut fuer Makromolekulare Chemie
der Universitaet, Freiburg,
WEST GERMANY.

AFTERNOON

(27) 2.40 p.m. - 3.00 p.m.

NEW FRONTIERS FOR ACRYLICS IN ADHESIVES AND COATINGS

MANILAL SAVLA,
Skeist Laboratories, Inc., 112 Naylor Avenue,
Livingston, New Jersey, U.S.A.

(28) 3.00 p.m. 3.20 p.m.

SURFACE AND BULK PARAMETERS AFFECTING CONTACT ELECTRIFICATION OF POLYSTYRENE

J. FUHRMANN,
Fachbereich Chemie,
Universitaet Kaiserslautern,
WEST GERMANY.

(29) 3.20 p.m. - 3.40 p.m.

THE APPLICATION OF SPENT SULFITE LIQUOR AS AN ADHESIVE FOR PARTICLE BOARDS

H.H. NIMZ AND G. HITZE,
University of Karlsruhe 21,
WEST GERMANY.

3.40 p.m. TEA

ROOM NO. 1

SESSION IX

PAPER SESSION

PARALLEL SESSION

2.00 p.m. - 3.40 p.m.

FIBERS AND COMPOSITES

Chairman: A.S. Chegolya,

(30) 2.00 p.m. - 2.20 p.m.

POLYESTERAMIDE FIBERS

AFTERNOON

L.C. ROHELA, A.K. MAHESWARI, VEENA AND D.S. VARMA,
Indian Institute of Technology,
NEW DELHI 110 029.

(31) 2.20 p.m. - 2.40 p.m.

RATIONAL UTILISATION OF POLYACRYLONITRILE (PAN)
FOR HIGH PERFORMANCE CARBON FIBER: A SYSTEMS
APPROACH

K. GOVINDARAJU, R. DORAIRAJ, P. VISHNU SHARMA AND
M.K. MUKHERJEE,
Vikram Sarabhai Space Centre,
TRIVANDRUM 695 022.

(32) 2.40 p.m. - 3.00 p.m.

STUDIES ON AROMATIC-ALIPHATIC FIBER FORMING
COPOLYESTERS

P. BAJAJ, A.K. SENGUPTA AND D.N. KHANNA,
Indian Institute of Technology,
NEW DELHI 110 029.

(33) 3.00 p.m. - 3.20 p.m.

AN ANALYSIS OF NON-LINEAR VISCOELASTIC BEHAVIOUR
OF POLYPROPYLENE AND GLASS REINFORCED POLY-
PROPYLENE IN CREEP

V.B. GUPTA AND J. LAHIRI,
Indian Institute of Technology,
NEW DELHI 110 029.

(34) 3.20 p.m. - 3.40 p.m.

DEVELOPMENT OF AN INDIGENOUS TECHNOLOGY FOR
PRODUCTION OF FIBER GLASS

S. KUMAR,
Central Glass & Ceramic Research Institute,
Jadavpur University, CALCUTTA 700 032.

3.40 p.m. TEA

EVENING

SESSION X

PLENARY LECTURES

4. 00 p.m. - 5.00 p.m.

Chairman: K.J. Ivin

LECTURE 6

4.00 p.m. - 4.45 p.m.

FACTORS DETERMINING CATALYTIC ACTIVITY AND STEREOCHEMISTRY IN MACROMOLECULAR SYSTEM

F. CIARDELLI,
Institut Di Chimica Organica
Industriale University Di Pisa,
ITALY.

LECTURE 7

4.45 p.m. - 5.30 p.m.

STRUCTURALLY COLOURED MATERIAL FOR TEXTILE FIBERS AND UV CURING

E. MARECHAL,
Laboratory Di Chemie Macromolekulare
University of Paris,
FRANCE.

MORNING

RES
m.
S. BANDYOPADHYAY AND D.R. BEECH,
Australian Dental Standards Laboratory,
Abbotsford, Victoria 3067.
AUSTRALIA.

(36) 11.00 a.m. - 11.20 a.m.

POLYMER SYSTEMS FOR CONTROLLED RELEASE OF
ORGANOTIN TOXIN

R.V. SUBRAMANIAN,
Washington State University,
Pullman, WA 99164, U.S.A.

(37) 11.20 a.m. - 11.40 a.m.

PREPARATION AND BIOMEDICAL APPLICATIONS OF POLY
(HYDROXYETHYL METHACRYLATE-METHACRYLIC ACID)
HYDROGEL

IEIR
HARPAL SINGH, PADMA VASUDEVAN, ALOK R. RAY AND
SUJOY K. GUHA,
All India Institute of Medical Sciences,
NEW DELHI 110 016.

(38) 11.40 a.m. - 12.00 noon

NEWEST EXPERIENCE ON CARBON FIBER REINFORCED
BONE PLATES

m.
E. FITZER, W. HUETTNER L. CLAES, AND L. KINZL,
Institut fuer Chemische Technik,
Universitaet Karlsruhe,
7500 Karlsruhe 1, WEST GERMANY.

(39) 12.00 noon - 12.20 p.m.

NTI-
BIOLOGICAL TESTING OF IMPLANTABLE MATERIALS FOR
MEDICAL APPLICATIONS: A PRELIMINARY REPORT

P.V. VEDANARAYANAN, K. RATHINAM AND A.C. FERNANDEZ,
Sree Chitra Tirunal Medical Centre,
TRIVANDRUM 695 011.

AFTERNOON

(40) 12.20 p.m. - 12.40 p.m.

**THERAPEUTIC SYSTEMS FROM BIODEGRADABLE POLY-
MERS**

MANINDER SINGH, PADMA VASUDEVAN, MAN MOHAN
MISRO, ALOK R. RAY AND SUJOY K. GUHA

Indian Institute of Techlology, (and) All India Institute of Medical
Sciences
NEW DELHI 110 029.

(41) 12.40 p.m. - 1.00 p.m.

**MICROBIAL DEGRADATION OF GELATIN GRAFT COPOLY-
MERS**

G. SUDESH KUMAR, V. KALPAGAM AND U.S. NANDI,
Indian Institute of Science,
BANGALORE 560 012.

1.00 p.m. - 2.00 p.m. LUNCH

MORNING

ROOM NO. 2

SESSION XIII

PAPER SESSION

10.40 a.m. - 1.00 p.m.

IONIC AND GRAFT COPOLYMERS

Chairman: J.P. Kennedy

(42) 10.40 a.m. - 11.00 a.m.

**NEW RESULTS ON THE ANIONIC POLYMERIZATION OF
POLAR MONOMERS**

H. HOECKER,
Universitaet Bayreuth,
D-8580 Bayreuth,
GERMANY.

MORNING

(43) 11.00 a.m. - 11.20 a.m.

PRELIMINARY STUDY OF CATIONIC POLYMERIZATION OF
ALPHA-METHYLSTYRENE USING $t\text{-BuCl}/\text{Et}_2\text{AlCl}/\text{CH}_2\text{Cl}_2$
SYSTEM

P.D. TRIVEDI, H.K. ACHARYA AND I.S. BHARDWAJ,
Indian Petrochemicals Corporation Limited,
BARODA 391 346.

(44) 11.20 a.m. - 11.40 a.m.

SYNTHESIS, CHARACTERIZATION AND MECHANISM OF
GRAFT CO-POLYMERISATION OF METHYLMETHACRYLATE
ONTO CELLULOSE NITRATE

D. SUDHAKAR, K.S.V. SRINIVASAN, K. THOMAS JOSEPH
AND M. SANTAPPA,
Central Leather Research Institute,
MADRAS 600 020.

(45) 11.40 a.m. - 12.00 noon

ANIONIC POLYMERISATION OF 2, 4-DINITROSTYRENE

R.K. SHUKLA,
Vikram Sarabhai Space Centre,
TRIVANDRUM 695 022.

(46) 12.00 noon - 12.20 p.m.

SYNTHESIS AND CHARACTERIZATION OF MICA-VINYL
GRAFT COPOLYMERS

E.P. KANNIAPPAN, K. PANDURANGA RAO, K. THOMAS
JOSEPH AND K.S. JAYARAMAN,
Central Leather Research Institute,
MADRAS 600 020.

AFTERNOON

(47) 12.20 p.m. - 12.40 p.m.

STUDIES IN GRAFT COPOLYMERIZATION OF VINYL MONOMERS ONTO WOOL IN PRESENCE OF VO (a.cac)₂ AS INITIATOR

B.N. MISRA, INDERJEETKAURMEHTA AND DEEPAK S. SOOD,
Himachal Pradesh University,
SIMLA 171 005.

(48) 12.40 p.m. - 1.00 p.m.

GAMMA RAY INDUCED GRAFTING REACTIONS ONTO POLY-PROPYLENE AND ITS ELECTROKINETIC BEHAVIOUR

H.T. LOKHANDE AND A.G. JOG, K.N. RAO AND M.H. RAO,
Bombay University,
BOMBAY 400 019.

1.00 p.m. - 2.00 p.m. LUNCH

ROOM NO. I

SESSION XIV

PAPER SESSION

2.00 p.m. - 3.40 p.m.

FIBERS AND COMPOSITES

Chairman: E. Fitzer

(49) 2.00 p.m. - 2.20 p.m.

THE EFFECT OF HEAT-SETTING ON THE STRUCTURE AND PROPERTIES OF POLY ACRYLONITRIL-FIBERS"

BELA VON FALKAI,
Bayerwerk,
4047, Dormagen,
WEST GERMANY.

(50) 2.20 p.m. - 2.40 p.m.

CARBON FIBERS - REINFORCING COMPONENT FOR ADVANCED MATERIALS

AFTERNOON

H. BOEDER,
SIGRI, Meitingen,
WEST GERMANY.

(51) 2.40 p.m. - 3.00 p.m.

BASALT FIBERS
R.V. SUBRAMANIAN,
Washington State University,
Pullman, WA 99164, U.S.A.

(52) 3.00 p.m. - 3.20 p.m.

SURFACE FINISHING OF CARBON FIBERS FOR ADHESION

R. WEISS,
Institut fuer Chemische Technik,
Universitaet Karlsruhe,
7500 Karlsruhe 1,
WEST GERMANY.

(53) 3.20 p.m. - 3.40 p.m.

Title of Lecture will be announced later
D. ADAMS,
Wyomig,
WEST GERMANY

3.40 p.m. - TEA

AFTERNOON

ROOM NO. 2

SESSION XV

PAPER SESSION

2.00 p.m. - 3.40 p.m.

POLYMER PHYSICS & DEGRADATION

Chairman:

(54) 2.00 p.m. - 2.20 p.m.

IRREVERSIBLE PHASE TRANSITION IN MACROMOLECULES

BERNHARD WUNDERLICH,
Rensselaer Polytechnic Institute,
Troy, New York 12181, U.S.A.

(55) 2.20 p.m. - 2.40 p.m.

**GLASS TRANSITION TEMPERATURE FROM DIELECTRIC
RELAXATION DATA: GLASS TRANSITION TEMPERATURE
OF POLYACRYLONITRILE**

A.K. GUPTA AND NAVIN CHAND,
Indian Institute of Technology,
NEW DELHI 110 029.

(56) 2.40 p.m. - 3.00 p.m.

**THEORETICAL TREATMENT OF THE KINETIC PARAMETERS
OF GLASS TRANSITIONS**

H. KOTHANDARAMAN AND C.T. VIJAYAKUMAR,
University of Madras,
MADRAS 600 025.

(57) 3.00 p.m. - 3.20 p.m.

**ADIABATIC COMPRESSIBILITIES OF DRAG REDUCING POLY-
MERS**

S. MAJUMDAR, S.H. HOLAY AND R.P. SINGH,
Indian Institute of Technology,
KHARAGPUR 721 302.

EVENING

(58) 3.20 p.m. - 3.40 p.m.

DIELECTRIC BEHAVIOUR OF FOAMS FROM POLYSTYRENE-POLYMETHYL METHACRYLATE BLENDS AT X-BAND MICROWAVE FREQUENCY

TAPAN K. CHAKI, SRINATH SRIVASTAVA AND PRANAB C. BANDYOPADHYAY,
Indian Institute of Technology,
KHARAGPUR 721 302.

3.40 p.m. - TEA

ROOM NO. 1

SESSION XVI

PLENARY LECTURES

4.00 p.m. - 5.30 p.m.

Chairman: J.E. Mark

LECTURE 10

4.00 p.m. - 4.45 p.m.

DYNAMIC THERMOMECHANOMETRY OF AROMATIC POLYMERS

HIRATORO KAMBE,
Institute of Space and Aeronautical Science,
University of Tokyo,
JAPAN.

LECTURE 11

4.45 p.m. - 5.30 p.m.

ELECTRICALLY CONDUCTING POLYMERS

F.E. KARASZ,
The University of Massachusetts,
Amherst, U.S.A.

MORNING

(60) 11.00 a.m. - 11.20 a.m.

DIFFUSION EFFECTS IN INITIATOR DECOMPOSITION IN
HIGHLY VISCOUS AND MACROMOLECULAR SOLUTIONS

M.G. KULKARNI AND R.A. MASHELKAR,
National Chemical Laboratory,
PUNE 411 008.

(61) 11.20 a.m. - 11.40 p.m.

MORPHOLOGY AND PROPERTIES OF POLYBUTYLENE TERE-
PHTHALATE

A. MISRA AND S.N. GARG,
Indian Institute of Technology,
NEW DELHI 110 029.

(62) 11.40 a.m. - 12.00 noon

PROCESSING AND RHEOLOGY OF GLASS FIBER FILLED
POLYPROPYLENE

DINESH C. GOEL,
National Chemical Laboratory,
PUNE 411 008.

(63) 12.00 noon - 12.20 p.m.

A NON-DESTRUCTIVE METHOD FOR MECHANICAL TESTING
OF CEMENT-POLYMER COMPOSITE

KUMUD R. KIRTANIA AND SUKUMAR MAITI,
Indian Institute of Technology,
KHARAGPUR 721 302.

(64) 12.20 p.m. - 12.40 p.m.

RECENT ADVANCES IN UNDERSTANDING OF THE MECHA-
NISMS OF ENVIRONMENTAL STRESS CRACKING OF POLY-
ETHYLENE

S. BANDYOPADHYAY,
Monash University,
Clayton, AUSTRALIA.

MORNING

(65) 12.40 p.m. - 1.00 p.m.

**ON ERRORS IN PRESSURE HOLE MEASUREMENTS IN THE
FLOW OF POLYPROPYLENE MELTS THROUGH CIRCULAR
DIES**

J.S. ANAND AND I.S. BHARDWAJ,
Indian Petrochemicals Corporation Limited,
BARODA 391 346.

1.00 p.m. - 2.00 p.m. LUNCH

ROOM NO. I

SESSION XIX

**PAPER SESSION
10.40 a.m. - 1.00 p.m.**

KINETICS OF POLYMERISATION

Chairman: J. Fuhrmann

(66) 10.40 a.m. - 11.00 a.m.

**THE ORIGIN OF THE VARIABILITY IN THE PROPERTIES OF
COMMERCIAL POLY (VINYL ACETATE-CO-ACETATE)**

S.R. NARAVANE AND A.S. DUNN,
University of Manchester
Institute of Science and Technology
Manchester, U.K.

(67) 11.00 a.m. - 11.20 a.m.

**KINETIC STUDIES ON THE FORMATION OF POLY (CHLORO-
CYCLO PHOSPHAZENES)**

E. DEVADOSS,
Vikram Sarabhai Space Centre,
TRIVANDRUM 695 022.

MORNING

(68) 11.20 a.m. - 11.40 a.m.

RADIATION INDUCED POLYMERISATION OF VINYLIDENE
CHLORIDE

M.S. PANAJKAR AND K.N. RAO,
Bhabha Atomic Research Center,
BOMBAY 400 085.

(69) 11.40 a.m. - 12.00 noon

Cu (DPM)₂ INITIATED VINYL POLYMERISATION

PRABHA CHATTERJI AND UMA S. NANDI,
Regional Research Laboratory,
HYDERABAD 500 009.

(70) 12.00 noon - 12.20 p.m.

STUDIES ON THE CHAIN TRANSFER PROPERTY OF THIO-
UREA IN RADICAL POLYMERISATION AND ITS TAUTOMERIC
EQUILIBRIUM IN ACID AQUEOUS MEDIUM BY THE
APPLICATION OF DYE TECHNIQUE.

D. PRAMANICK AND A.K. CHATTERJEE,
University of Kalyani,
Kalyani, Nadia,
WEST BENGAL.

(71) 12.20 p.m. - 12.40 p.m.

SUBSTITUENT EFFECTS IN POLYMERISATION REACTIONS
IN TERMS OF GENERALISED SUBSTITUENT CONSTANTS
F & R AND GENERALISED WEIGHTING FACTORS f AND r
DEvised BY SWAIN AND LUPTON AND WILLIAMS AND
NORRINGTON

LALIT N. PATNAIK, M.K. ROUT, SWOYAM P. ROUT AND
ANURADHA ROUT,
Ravenshaw College,
CUTTACK 753 003.

AFTERNOON

(72) 12.40 p.m. - 1.00 p.m.

PHOTOPOLYMERISATION OF N, N'-METHYLENE BISACRYLAMIDE IN AQUEOUS SOLUTION BY POTASSIUM TRISOXALATOFERRATE (III)

MOHAMMED IBRAHIM AND Q. ANWARUDIN,
NEW COLLEGE, MADRAS 600 014.

1.00 p.m. - 2.00 p.m. LUNCH

ROOM NO. 2

SESSION XX
MISCELLANEOUS

2.00 p.m. - 3.40 p.m.
PAPER SESSION

Chairman: H. Hoecker

(73) 2.00 p.m. - 2.20 p.m.

POLYMERIZABLE ULTRAVIOLET STABILIZERS

Y.N. SHARMA, PRABHA, GAWANDE AND I.S. BHARDWAJ,
Indian Petrochemicals Corporation Ltd.,
BARODA 391 346

(74) 2.20 p.m. - 2.40 p.m.

ON THE USE OF THE MAYO EQUATION IN CATIONIC POLYMERIZATION

BROJA M. MANDAL,
Indian Association for the Cultivation of Science,
Jadavpur,
CALCUTTA 700 032.

(75) 2.40 p.m. - 3.00 p.m.

POLYMER IMPREGNATION OF FERROCEMENT

V. VELPARI, N.M. RAGHAVENDRA AND N. BALASUBRAMANIAN,
National Aeronautical Laboratory,
BANGALORE 560 017.

RY-
KA-

AFTERNOON

(76) 3.00 p.m. - 3.20 p.m.

CRITICAL RELIABILITY PARAMETER IN SILICONE PROCESS-
ING

R. KUMAR, V. CHANDRASEKARAN AND M.K. MUKHERJEE,
Vikram Sarabhai Space Centre,
TRIVANDRUM 695 022.

(77) 3.20 p.m. - 3.40 p.m.

COPOLYMER OF POLYSTYRENE GLYCOL AND GLYCERYL
PHTHALATE RESINS IN SURFACE COATING

SUSHIL CHANDRA AND SUMAN PASARI,
Harcourt Butler Technological Institute,
KANPUR 208 002

3.40 p.m. - TEA

VAJ,
ROOM NO. 1

SESSION XXI

PAPER SESSION

2.00 p.m. - 3.40 p.m.

MISCELLANEOUS

Chairman: Marechal

(78) 2.00 p.m. - 2.20 p.m.

MOLECULAR SIGNIFICANCE OF THE C₂ - TERM

SEBASTIAN V. KANAKKANATT
University of Akron,
Akron, Ohio 44325, U.S.A.

(79) 2.20 p.m. - 2.40 p.m.

HYDROPHOBIC INTERACTIONS IN THE BINDING POLYVINYL-
PYRROLIDONE

MEENAKSHI MARUTHAMUTHU AND MEENASKHI SOBHANA,
University of Madras,
MADRAS 600 025.

EVENING

(80) 2.40 p.m. - 3.00 p.m.

WATER BORNE WIRE ENAMEL

S.N. NARKHEDE, S.P. POTNIS, AND P.F. PARIKH,
University of Bombay,
BOMBAY 400 019.

(81) 3.00 p.m. - 3.20 p.m.

PHTHALIC ANHYDRIDE BASED CATION EXCHANGE RESIN
FROM N-VINYL CARBAZOLE

MUKUL BISWAS AND S. PACKIRISAMY,
Indian Institute of Technology,
KHARAGPUR 721 302.

(82) 3.20 p.m. - 3.40 p.m.

STUDIES TOWARDS STRUCTURE OF AROMATIC POLY-
IMIDES

DEVENDRA KUMAR,
Vikram Sarabhai Space Centre,
TRIVANDRUM 695 022.

3.40 p.m. - TEA

EVENING

ROOM NO. 1 SESSION XXII PLENARY LECTURES
4.00 p.m. - 5.30 p.m.

Chairman: R.K. Eby

LECTURE 14

4.00 p.m. - 4.45 p.m.

**MECHANISM OF RING-OPENING POLYMERIZATION OF CYCLO-
ALKENES INITIATED BY METATHESIS CATALYSTS**

K.J. IVIN,
The Queen's University of Belfast,
Belfast BT9 5AG,
NORTHERN IRELAND, U.K.

LECTURE 15

4.45 p.m. 5.30 p.m.

RECENT ADVANCES IN EXTENSIONAL RHEOLOGY OF POLYMERS

R.A. MASHELKAR,
National Chemical Laboratory,
PUNE 411 008.

FRIDAY

11 JANUARY

MORNING

ROOM NO. I

SESSION XXIII

PAPER SESSION
9.00 a.m. - 12.00 noon

MISCELLANEOUS

Chairman:

(83) 9.00 a.m. - 9.20 a.m.

THERMAL MODIFICATION OF POLY (VINYL CHLORIDE)
AND FORMATION OF DEHYDROCHLORINATED POLY
(VINYL CHLORIDE) - POLY (METHYL METHACRYLATE)
POLYMER BLEND IN THE PROCESS OF FOAMING: IDENTI-
FICATION AND APPLICATION

M. JAYABALAN,
University of Madras,
MADRAS 600 025.

(84) 9.20 a.m. - 9.40 a.m.

MECHANISM AND STRUCTURE PROPERTIES RELATIONSHIP
FOR THERMO OXIDATIVE DEGRADATION OF POLYETHY-
LENE DURING THERMAL AGEING

A.B. MATHUR, VIJAY KUMAR AND G.N. MATHUR,
H.B. Technological Institute,
KANPUR 208 002.

(85) 9.40 a.m. - 10.00 a.m.

APPLICATION OF VARIOUS VISCOSITY THEORIES TO THE
VISCOSITY DATA OF METHYL METHACRYLATE - ACRYLO-
NITRILE RANDOM COPOLYMERS

A.K. KASHYAP AND V. KALPAGAM,
Indian Institute of Science,
BANGALORE 560 012.

MORNING

(86) 10.00 a.m. - 10.20 a.m.

COPOLYMERISATION OF STYRENE AND ACRYLONITRILE
IN SUSPENSION SYSTEM: PROPERTIES OF THE SYSTEM AND
THE POLYMER IN RELATION TO THE DEGREE OF CONVER-
SION

G.S. BHARGAVA, V.K. GUPTA, H.U. KHAN, R.K. CHAWLA,
P.K. GOEL AND K.K. BHATTACHARYYA,
Indian Institute of Petroleum,
DEHRADUN 248 005.

(87) 10.20 a.m. - 10.40 a.m.

POLYMERS IN TEXTILE WET PROCESSING

H.C. SRIVASTAVA AND T.K. DAS
Ahmedabad Textile Industry's Research Association,
Polytechnic P.O.
AHMEDABAD 380 015.

10.40 a.m. TEA

(88) 11.00 a.m. - 11.20 a.m.

PREPARATION OF LARGE MONODISPERSE LATEX PARTICLES

JOHN UGELSTAD
The University of Trondheim,
NORWAY.

(89) 11.20 a.m. — 11.40 a.m.

ELECTRICAL CONDUCTION IN THIN FILMS OF POLYVINYL-
ACETATE

V.V.R. NARASIMHA RAO AND T. BADRINARAYANA,
College of Engineering,
S.V. University,
TIRUPATI 517 502.

MORNING

(90) 11.40 a.m. - 12.00 noon

THERMODYNAMIC EVIDENCE FOR POLYMERIZATION OF ALCOHOLS

G.R. NAIDU, P.R. NAIDU AND S.V. LAKSHMAN
S.V. University,
TIRUPATI 517 502.

12.30 p.m. LUNCH.

ROOM NO 2

SESSION XXIV

PAPER SESSION

9.00 a.m. - 12.00 noon

(MISCELLANEOUS)

Chairman:

(91) 9.00 a.m. - 9.20 a.m.

RAMAN SPECTROSCOPIC STUDY OF POLYACRYLAMIDE GELS

M.K. GUPTA AND R. BANSIL,
Boston University,
Boston, Mass. 02215, U.S.A.

(92) 9.20 a.m. - 9.40 a.m.

NEW TECHNIQUES OF POLYMER CHARACTERIZATION USING THE ULTRA CENTRIFUGE

TEJRAJ M. AMINABHAVI AND PETR MUNK
The University of Texas at Austin,
Austin, Texas 78712, U.S.A.

(93) 9.40 a.m. - 10.00 a.m.

SMALL ANGLE NEUTRON SCATTERING AND QUASI-ELASTIC LIGHT SCATTERING OF POLYMER NETWORKS IN BULK AND SWOLLEN STATE

MORNING

OF
HYUK HU
University of Wisconsin,
Madison,
USA

(94) 10.00 a.m. - 10.20 a.m.

POLYMER BLENDS
JOEL BARLOW
University of Texas,
Austin, U.S.A.

n
(95) 10.20 a.m. - 10.40 a.m.

ROOM TEMPERATURE-CURING ORGANOTIN POLYMERS
R.V. SUBRAMANIAN, R.S. WILLIAMS AND K.N. SOMASE-
KHARAN,
Washington State University,
Pullman, Washington 99164
USA

DE
10.40 a.m. TEA,

(96) 11.00 a.m. - 11.20 a.m.

TO BE ANNOUNCED LATER

(97) 11.20 a.m. - 11.40 a.m.

TO BE ANNOUNCED LATER

(98) 11.40 a.m. - 12.00 noon

TO BE ANNOUNCED LATER

(99) 12.00 noon - 12.20 p.m.

TO BE ANNOUNCED LATER

12.30 p.m. Lunch.

ELECTROCHEMICAL POLYMERIZATION AND DEPOSITION ON CARBON FIBERS

R.V. SUBRAMANIAN

*Department of Materials Science and Engineering
Washington State University
Pullman, WA 99164.*

The electrodic polymerization on graphite fibres of a variety of monomers having different types of functional groups has been investigated. In addition to vinyl polymerization, some novel polymerization of cyclic functional groups have been conducted under appropriate polymerization conditions. In many instances, the grafting of the surface polymer to the fiber has been confirmed. The stereochemical configuration of poly (methyl methacrylate) resulting from electropolymerization was measured, but conclusive evidence could not be obtained for the occurrence of stereoregulation in electrochemical polymerization on graphite fiber surface. Composite specimens were prepared by the incorporation of the coated fibers in an epoxy matrix. It was demonstrated that the effect of electropolymerization on the interfacial properties of the resulting composite was manifested in variations of the measured interlaminar shear and impact strengths of the composite specimens. Implicit in these findings is the contribution of the electrochemically formed interlayer to one or more of the toughening mechanisms that are available to fiber reinforced composites.

An electrodeposition technique has also been developed for interface tailoring in graphite fiber composites. Graphite fibers running continuously as the anode through an electrolytic cell were coated with a variety of copolymers carrying carboxyl functional groups. Fortafil CG-3 fiber, free of commercial surface treatments, was used in these experiments. The copolymers employed were a series of styrene-co-maleic anhydride, olefin-co-maleic anhydride, methyl vinyl ether-co-maleic anhydride and ethylene-co-acrylic acid polymers. Unidirectional composite specimens were prepared by embedding the coated fibers in an epoxy matrix and the effect of the interphase polymer was studied through variations in their impact, interlaminar shear and flexural strengths in comparison to those of composites fabricated from commercially treated and untreated fibers. It is found that the introduction of the polymer interphase results in significant improvements in composite properties and that the extent of improvements is controlled by the nature of the polymer interphase. The molecular weight, chemical composition, and crosslinking of the interphase polymer are some of the molecular parameters modifying the effects observed.

THE CHEMICAL BONDING BETWEEN C-FIBERS AND POLYMER MATRIX IN COMPOSITES

E. FITZER, W. HUTTNER, & R. WEISS,

*Institut für Chemische Technik
Universität Karlsruhe
7500 Karlsruhe 1
West Germany*

Reinforcement of composites is only achieved by sufficient stress transfer between fibre and matrix. Such stress transfer can be realized by mechanical interlocking, physical adhesion and chemical bonding of the composite-components.

In the case of glass-fibre reinforced polymers sufficient stress transfer is only obtained by using adhesion promoters, which are able to form chemical bonds between the fibres and the matrix.

In case of C-fibre reinforced polymers various possibilities are reported in literature to achieve adhesion between the C-fibers and the polymer matrix. Mechanical interlocking and physical adhesion respectively, can be obtained by coating the fibers with silicon carbide (Simon *et al*, 1968; Fitzer *et al*, 1973; Donnet *et al*, 1977) or pyrolytic carbon (Fitzer *et al*, 1973; Donnet *et al*, 1977) or by polymer sizings (Herrick, 1968; Brie *et al*, 1970).

It is known, however, that all these means do not maximize the stress transfer between the components. In technical applications surface treatments of the C-fibers by oxidation have proved to be the best solutions to obtain good shear strengths of the composites. Various possibilities are known to oxidize the fibre surfaces, namely the anodic treatment, the wet oxidation in liquids such as nitric acid, potassium permanganate, sulfuric acid, Hummers agent or strong alkalies, and the dry oxidation at high temperatures (Herrick, 1968; Goan *et al*, 1972; DPB 2012981). For the technical scale, the anodic oxidation seems to be most advantageous. For systematic laboratory studies, the wet oxidation is applied, because this treatment can easily be carried out. By all these oxidation methods various groups of alkaline and/or acidic nature are formed on the fibre surfaces, (Boehm *et al*, 1964, 1966).

It has been shown by us previously (Fitzer *et al*, 1978; Geigl, 1979), that the acidic groups on the fibre surface, formed by wet oxidation in nitric acid, react chemically with the free hydroxyl groups of a phenolic resin precursor.

Also in the case of an epoxy matrix chemical bonds are formed in the fibre/matrix-interface as reported by Horic *et al* (1976). We have found recently (Fitzer *et al*, 1979) that in case of an epoxy prepolymer with diamine hardener, the coupling

between surface treated C-fibres and the matrix seems to be performed by the hardener.

As a consequence it was shown, that an optimized fibre surface treatment improves the yield of fibre strength and ILSS of composites with phenolic as well as with epoxy matrices. The aim of the present work is to explain the mechanism of chemical bonding in case of phenolic and epoxy matrices. The varied oxidation treatments, their influence on the fibre properties and on the mechanical behaviour of composites will be discussed in detail and methods will be described, by means of which the nature and the extent of surface groups present on surface treated C-fibres can be analysed.

The results enable us not only to propose the best surface treatment for given fibre and resin combinations, but also to find best resin modification for given industrially surface treated fibre types.

MICROFRACTOGRAPHICAL INVESTIGATIONS OF PLASTICS, SHORT FIBER RP, GRP AND CRP COMPOSITES

HANS LEIS

*Central Laboratory of
Messerschmitt Bolkow Blohm GMBH
Postfach 80 12 20. 8000 Munchen 80
Munich, West Germany*

Since the introduction of the scanning electron microscopy approximately 20 years ago, microfractography used for metal materials has seen an enormous upswing. It serves primarily to solve cases of damage and has become an indispensable aid during the entire phase of material development and the related quality assurance.

With the development of fiber-reinforced composites progressing at an ever increasing rate, we too have tried to carry out tests on the new materials using this method.

In doing so, a new analytical approach was necessary in the first place differing from the one used for the evaluation of homogenous materials. The procedure applied was as follows:

To start with, fiber-reinforced materials were subjected to static and dynamic tests applying compression-tension stresses as well as shear stresses to produce defined fractures. The factors taken into account were stress direction with respect to fiber orientation, type of fibers, fiber content and type of matrix material used.

These fractures on numerous samples are subjected to tests using a scanning electron microscope, the objective being to identify microfractographical characteristics occurring in connection with specific types of fractures and stresses. Another factor to be determined is the extent to which the fracture line is affected or influenced by the relation between fiber orientation and stress direction.

As a general rule, the fracture lines appearing on fibres and matrix can be used as an aid to determine the type of fracture occurring on fiber-reinforced composites.

Unfortunately, in practice, the high-strength fibers when undergoing fractures due to fatigue will, in general, feature the same fracture striations as caused by brittle ruptures and will not show, for instance, any strips caused by fatigue. In certain cases, however, the formation of the fracture surface of the fiber can provide information on stress direction and type. Additional information on the type of fracture is generally obtained from the fatigue striations occurring on the matrix.

Fracture investigations carried out by means of scanning electron microscope also provide data on the binding between fiber and matrix, thus permitting a qualitative rating of the interlaminar shear strength.

Many years of experience and a closely followed documentation are prerequisites for a microfractographic judgement of fracture surface of fiber-reinforced materials. For this purpose, we have been continuously working on the establishment of a type of "fracture atlas" which, apart from numerous fractographic pictures taken by the scanning electron microscope, contains the material investigated, the breaking stress, the type of fracture and the fracture characteristics analysed by an expert.

Metallography and fractography do not only play an important part in the development of fiber-reinforced composites, but also contribute to the quality assurance of these composites, to the damage analysis of fiber-reinforced structures and to a certain kind of prediction concerning the life of these materials.

**STUDIES ON THE VARIOUS PAN PRECURSORS AND ITS
BEARING ON THE ULTIMATE MECHANICAL PROPERTIES
OF CARBON FIBERS**

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Various PAN precursors have been characterized. Relationship between the primary Young's modulus of the precursor and the Young's modulus of the Carbon fibres has been established for the first time.

A novel method of stabilizing PAN for making carbon fibres is described.

**THE EFFECT OF MOLECULAR ORIENTATION ON THE TENSILE
PROPERTIES OF BUTADIEN RUBBER MODIFIED STYRENE
ACRYLONITRILE COPOLYMERS (ABS)**

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This paper deals with the relationships between molecular orientation and mechanical properties of butadien rubber modified styrene-acrylonitrile copolymers (ABS). This investigation covers the characterization of the morphology of the unoriented ABS materials, the examination of the orientation state of the stretched specimens, measurements of their mechanical properties (stress-strain behaviour, impact strength and fatigue) and a quantitative analysis of the yielding mechanisms involved.

The ABS polymers considered in this work have the same rubber content but differ mainly with regard to the volume fraction of the dispersed phase, the average particle size and the degree of interfacial adhesion between rubber and matrix. Unoriented ABS sheets were made by compression moulding at 200°C; from these sheets dumbbell shaped specimens were then cut.

The specimens were subjected to uniaxial as well as biaxial extension in the temperature range between T_g and $T_g + 30^\circ\text{C}$ and subsequently quenched in ice water. In the uniaxial stretching experiments the specimens were stretched to different draw ratios (from 0 to 500%).

Tensile tests on both unoriented and oriented specimens have been performed with an Instron machine at constant strain rate at room temperature. It is observed that the yield stress, the breaking stress and the strain hardening increase with increasing draw ratio. The elongation at rupture and the tensile toughness exhibit a maximum as a function of draw ratio. The uniaxial oriented ABS samples deform both by crazing and shear yielding at low draw ratios (0 to 50%) and only by shear yielding at higher draw ratios. The presence of the two modes of plastic deformation at low draw ratios can easily be identified; stress whitening and necking are observed. It is also observed that the impact resistance and the fatigue of the ABS materials considered are markedly improved by molecular orientation (parallel to the drawing direction).

REDOX POLYMERISATION KINETICS AND MECHANISM OF REACTIONS INITIATED BY SYSTEMS BASED ON Mn (III) COMPLEXES IN AQUEOUS AND NONAQUEOUS MEDIA

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The kinetics of polymerisation of vinyl monomers acrylonitrile methylmethacrylate and acrylamide initiated by the systems cyanoacetic acid—Mn (III) acetate in DMF and acetic acid and cyanoacetic acid-Tris-chloroquo Bipyridyl Mn (III) as well as thiodiethanol-Tris-chloroquo Bipyridyl Mn (III) in aqueous sulphuric acid have been investigated in the temperature range $30\text{--}40^\circ\text{C}$.

In DMF intermediate complex formation is evident from the kinetics. Decomposition of the complex yields primary radicals which initiate polymerisation, the efficiency of initiation being very high with acrylonitrile and methyl methacrylate but not with acrylamide. Termination is by mutual interaction in all cases. In acetic acid also oxidation proceeds through complex formation. With acrylonitrile and acrylamide the kinetics were similar although their reactivity towards primary radicals was reversed compared to DMF. With methyl methacrylate, a monomer molecule is involved in the radical production step.

In aqueous sulphuric acid with Tris-chloroquo Bipyridyl Mn (III) as oxidant there was no intermediate complex formation with either reducing agent. With TDE there was no reaction in the absence of added acid. Primary radicals from the reducing agent initiate polymerisation more effectively with methyl methacrylate than with acrylonitrile. Termination is by mutual interaction. Suitable mechanisms have been proposed to account for the observed kinetics and rate and equilibrium constants evaluated.

A KINETIC STUDY OF THE LEWIS ACID ASSISTED DECOMPOSITION OF BENZOYL PEROXIDE AND ITS IMPLICATION TO THE MECHANISM OF COMPLEX COPOLYMERIZATIONS

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The rates of decomposition of benzoyl peroxide have been studied in solvent alone and in presence of three Lewis acid, viz., boron trifluoride etherate, aluminum chloride and antimony pentachloride at the temperature range of 10-90° C. The rates have also been studied in presence of acetonitrile (to mimic the action of a complexing monomer) and an efficient radical trap such as m-dinitrobenzene. Benzoyl peroxide undergoes rapid decompositions at room temperatures or below in presence of Lewis acids such as aluminum chloride and antimony pentachloride via a polar mechanism to yield 90% phenylbenzoate and one mole of carbon dioxide. Kinetics do not indicate the presence of trappable free radicals. The implication of these results to the initiation of alternating copolymerizations of donor with acceptor monomers is discussed.

TWO COMPONENT HYDROGELS 5. THEORETICAL CONSIDERATIONS AND EXPERIMENTS

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A survey is presented on the authors work on two component hydrogels, consisting of a polymer backbone built up by one polymer component which is cross-

linked by bridges of another polymer with varying length. It is proposed that these networks in the swollen state, using water as solvent, can be treated within the framework of existing swelling and mechanical theories. Moreover, when account is taken on the two component nature of these networks in derivation of free energies of mixing and elasticity, information regarding the network composition can be derived from the equilibrium swelling and deformation behavior. In addition, NMR gives some insight into the relative affinity of each polymer for the solvent.

The effects on the equilibrium swelling behavior, the mechanical properties and the defined solvent interactions in the heterogeneous network were measured on crosslinked graft copolymers with poly (N-vinyl-2-pyrrolidone) as the backbone and poly (ethylene glycol) as the interconnecting bridge.

Conclusions derived from the two component hydrogel studies should be relevant for non-hydrophilic two component networks too.

METHYLENE BLUE AS CHAIN TERMINATOR IN FREE RADICAL POLYMERISATION. 1. POLYMERIZATION OF STYRENE, METHYL METHACRYLATE AND ACRYLAMIDE

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Methylene blue (MB), a redox dye, is found to retard the free radical polymerization of styrene and acrylamide. In doing so, MB itself is reduced and decolorised. The decolorisation process is a reversible one, the color of the dye reappearing on exposure to air. In contrast to styrene and acrylamide polymerisation, MB does not affect the free radical polymerisation of MMA. This selectivity in behaviour is expected of an electron transfer reaction. Spectrophotometric studies reveal that methylene blue remains as a monomer in the solvent mixture of styrene and DMF used in this work. An earlier view (C.S.H. Chen, *J. Polymer Sci.*, A—3, 1107, 1965) that only the aggregates of methylene blue are capable of reacting with polymer radicals has been discounted. The rate constant for the reaction of MB with polystyryl radicals has been evaluated.

GRAFTING OF ACRYLATE MONOMERS ONTO CHLORINATED RUBBER

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Grafting of chlorinated rubber with soft acrylate monomers such as ethyl acrylate (E.A.) and butyl methacrylate (BMA) was carried out in xylene at different temperatures. Isolation of graft copolymers from the crude sample was effected by means of fractional precipitation technique, knowing the γ value of the solution from M.E.K.—MeOH system. It is observed that the grafting with EA and BMA follows conventional kinetic behaviour unaffected by the presence of backbone at the present experimental conditions. The energy of activation obtained by the presence of backbone at the present experimental conditions. The energy of activation is assumed to be due to the grafting of backbone by means of chain transfer process.

Grafting efficiency and % of grafting for both the monomer systems with chlorinated rubber were determined. The decrease of G.E. and increase of % grafting with the increase in concentration of monomer initiator and temperature was adequately explained. Molecular weights of the homopolymeric samples separated from the total system were evaluated from intrinsic viscosity data. G.P.C. analysis for graft copolymer was carried out with a view to substantiate the grafting onto the chlorinated rubber.

ULTRA HIGH-STRENGTH/HIGH-MODULUS FIBERS FROM RIGID AND SEMI-RIGID POLYMERS

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Some recent developments taken from the literature concerning fibers having ultra high-strength/high-modulus (H-S/H-M) properties are reviewed. Solution spun fibers from both rigid and semi-rigid polymers are discussed as well as the newer class of melt spun fibers from aromatic polyesters and polyazomethines. The tensile properties of H-S/H-M fibers are given along with some end use applications.

STUDIES ON ACRYLIC POLYMERS WITH REFERENCE TO FIBER SPINNING

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Poly (acrylonitrile-co-methacrylate) copolymers were prepared at different temperatures. The composition of poly acrylonitrile in the copolymer was ranging from 95 to 98.12 mole percent. These polymers were characterized by viscosity and gel permeation chromatography. Finally, all these polymers were spun using a laboratory model wet spinning assembly. It is generally observed that high molecular weight polymers could be stretched upto 1:10 draw ratio which resulted in lesser diameters. Further, the tensile strength and modulus of precursor fibers and carbon fibers also depended on composition and molecular weight of the polymers.

THE FRACTURE OF ELASTOMER-MODIFIED EPOXY POLYMERS

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The use of carboxy terminated, butadiene-acrylonitrile (CTBN) to enhance the toughness of epoxy polymers is a well established technology. These resins are widely used as structural adhesives and as the matrix in fiber-reinforced composites. It has been known for sometime that the CTBN and epoxy resins react to form a dispersed phase of minute rubber particles.

In the work to be discussed, the bulk and adhesive fracture behavior of a model CTBN-epoxy polymer has been studied. The function of the elastomer parti-

cle in increasing toughness is to effectively increase the critical damage zone relative to the unmodified epoxy by 30-40X. Post-failure microscopy indicates that the particles undergo a dilatational deformation and that there is shear yielding of the epoxy matrix. In adhesive fracture, constraint of the crack tip deformation zone by the adherends reduces adhesive fracture toughness compared to the bulk toughness. Recent work on the interlaminar fracture of CTBN-epoxy matrix composites will be described.

A COMPARATIVE EVALUATION OF GLASS/CARBON/KEVLAR FIBERS AS REINFORCEMENT IN COMPOSITE PRESSURE BOTTLES

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A comparative evaluation of three reinforcing fibres namely Glass, Carbon and Kevlar was carried out in the composites group at VSSC. Their performance results were evaluated on 3.3 litre volume polar wound pressure bottles made with these fibres and an epoxy matrix. The pressure bottles were then subjected to hydro-burst test and the burst pressure data was used to compute the relative performance of the pressure vessels in terms of the ratio $\frac{PV}{W_c}$ where P = burst pressure, V = inside volume, W_c = weight of composite. The pressure vessel performance was preceded by testing of the fibre composite alone in the form of Naval Ordnance Laboratory rings.

The $\frac{PV}{W_c}$ ratio as evaluated is 1.20×10^6 cm for Kevlar/Epoxy pressure vessel, 1.02×10^6 cm for Carbon/Epoxy pressure vessel and 0.98×10^6 cm for Glass/Epoxy pressure vessel and is a convincing proof of the superior performance of Kevlar fibre in comparison with Carbon and Glass fibres.

STRUCTURES AND PROPERTIES OF RUBBER REINFORCED THERMOPLASTICS

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The properties of rubber modified thermoplastics are determined essentially by composition, molecular structure and especially morphology. The earliest products were manufactured by emulsion or melt mixing. Adhesion between the two phases—essential for good mechanics—was controlled by the chemical composition of the rubber, as opposed to the present system of grafting the rubber either in emulsion (ABS) or solution (PS). In the case of ABS and impact modified PVC the dispersion and reinforcing efficiency of the rubber particles are regulated by the degree of grafting, particle size and crosslink density.

In high impact polystyrene, which is generally produced by bulk polymerisation, morphologies and properties are determined by polymerisation parameters as well as by the structure of the rubbery modifier. The use of styrenebutadiene block copolymers as rubbery modifier in the styrene polymerisation process leads to labyrinth, capsule, rod and droplet particles.

The reinforcement mechanism of rubber modified thermoplastics is also investigated. In polystyrene and high molecular weight polymethylmethacrylate, electron microscope studies indicate that the rubber particles dissipate the impact energy by the crazing process. PVC, however, which readily undergoes shear yielding, exhibits very few crazes in the stress whitened zones. Stress whitening appears to be essentially caused by voids in the rubber particles located in shear bands. This suggests that rubber particles facilitate shearing processes as well as crazing, the exact mechanism depending on the type of the matrix.

COMPOUNDING OF GLASS FIBER REINFORCED POLYPROPYLENE AND INVESTIGATION OF ITS MECHANICAL PROPERTIES UNDER SIMPLE AND COMPLEX LOADING

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Polypropylene is one of the important thermoplastics that has been reinforced with glass fibres to give a reasonably good engineering plastic. Because of its inert nature it does not easily adhere to the glass surface and hence some coupl-

ing agent is needed to give a reasonably good bond to ensure improvement in mechanical properties.

In the present study a vinyltriethoxysilane coupling agent in polymeric form has been tried and seen to improve the properties. The results have been compared with those of an imported reinforced grade and found to be reasonably close. Tests have been carried out at (a) constant strain rate (in the instron testing machine), and (b) constant stress rate (water loading on a biaxial testing machine). Under constant strain rate, only tensile properties have been studied while under constant stress rate, the tensile, torsional and combined tensile-torsional tests have been carried out. In each of the above cases, a considerable improvement in elastic modulus has been observed. The tensile strength is improved to the extent of about 25%. There is only a slight improvement in torsional strength. Different fibre volume contents were used and their effect studied on modulus and strength.

The mechanical data for reinforced-polypropylene samples have been discussed in terms of the fibre-length distribution in the composite. Detailed analysis of tensile data suggests that at low strains, when the critical length is relatively low, the fibers contribute to a considerable extent in carrying the load which leads to a high modulus. With increasing strain the critical length increases and the load carrying capacity of the fibers is reduced. Consequently the gain in strength is relatively less. The effect of fibre length distribution in torsion and combined tension-torsion tests would be expected to be similar and the results seem to confirm this.

EFFECT OF ADDITIVES IN THE SPINNING DOPE ON THE MECHANICAL PROPERTIES OF THE PAN FIBERS

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Wet spinning of polyacrylonitrile fibers involve concentration controlled transitions like gelation and phase separation etc. To obtain fibers of good microscopic, morphological and mechanical properties gelation should precede phase separation. There are several methods to effect this—by raising solid content, by reducing solvent power, employing low coagulation bath temperature and by the use of additives.

The use of additives in the polymer solution has two fold effect on the wet spinning. They decrease viscosity of the polymer solution and effect gelation.

The effect of some additives in the spinning solution of PAN on the final properties of the fibers has been studied and the results are reported in this paper.

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SEMI-CRYSTALLINE POLY (ARYLENE ETHER SULFONE) COPOLYMERS

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New poly (arylene ether sulfone) copolymers derived from hydroquinone and/or bisphenol A with activated aromatic halides were prepared. The general scheme utilized the nucleophilic displacement of the bisphenate (s) with the halides. Statistical copolymers were prepared over the entire composition range. The pure hydroquinone polysulfone 'as made', showed a crystalline melting point of 310°C by differential scanning calorimetry (DSC). However, efforts to thermally induce crystallization from the melt were unsuccessful. Annealing times of up to 8 hours at 254°C did not result in the development of a melting endotherm. It was possible to induce crystallization via solvent treatment (acetone). This was also possible with the high hydroquinone containing statistical copolymers. The phenomena has important ramification to the problem of solvent resistance and environmental stress cracking in amorphous engineering thermoplastics. The glass transition behavior of the statistical copolymers was studied. T_g increased monotonically from about 185°C to 207°C. Model compounds were also synthesized and are being utilized to help elucidate the sequence distributions of the copolymers.

SYNTHESIS AND CHARACTERIZATION OF CERTAIN PARA- AZOAROMATIC POLYAMIDES

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The general features of para-azoaromatic polyamides which can form inherently extended chain structures have been discussed. Four coloured para-azoaromatic polyamides have been synthesised from 4, 4' azodibenzoic acid and four aromatic diamines employing both interfacial and solution polycondensation procedures. The polymers were characterized by inherent viscosity measurements, ultraviolet and Infrared spectra and solubility data. The stability of a polymer in conc. H₂ SO₄ has been discussed. The thermal behaviour of the polymers has also been observed.

MOLECULAR SIGNIFICANCE OF THE C_2 -TERM

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In an attempt to attach some molecular significance to the C_2 -term in Mooney-Rivlin plot, it is found that C_2 is dependent on both n , the number of links in the phantom chain and λ , the extension ratio. In the region of the plot where C_2 is constant, that is, before the upturn occurs, it is found that λ is proportional to $n^{1/3}$ and to $x^{1/3}$ where x is the number of monomer units per random link and that $\lambda^2 \propto (nx)^{1/3}$ where nx is the number of monomer units in the phantom chain.

SYNTHESIS OF SOME NEW METAL-CONTAINING POLYURETHANES

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New metal-containing polyurethanes were synthesised from $Mn-(HEP)_2$ and $Pb-(HEP)_2$ by condensing them with HMDI and TDI. These polymers were characterised by viscosity, IR and thermal analysis. The mechanism of degradation of the monomers $Mn-(HEP)_2$ and $Pb-(HEP)_2$ were discussed with TGA and DSC data. The thermal stability of the polymers were investigated.

ADDITION POLYIMIDES BASED ON BIS (m-AMINOPHENYL) METHYLPHOSPHINE OXIDE

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The stringent requirements of aerospace industries have led to the development of several classes of flame resistant polymeric materials. Polyimides, which exhibit outstanding thermomechanical and flammability behaviour at elevated temperatures, represent one such class of polymers. Commercial polyimides have been used for castings as adhesives and matrix resins for structural composites. Curing of these resins proceeds by thermal polymerisation of an olefinic end-group of an imide containing monomer or oligomer.

Polymers containing phosphorous in the main chain are heat and flame resistant. A literature survey has revealed that addition polyimides containing phosphorous in the backbone have not been investigated. Present studies were undertaken to study thermal behaviour of such polyimides. Maleic anhydride, dichloromaleic anhydride, citraconic anhydride and benzophenone tetracarboxylic dianhydride used in the preparations were commercially available. Bis (m-aminophenyl) methylphosphine oxide was prepared in the laboratory starting from triphenylphosphine, which was converted to methyldiphenyl-phosphine oxide by the method of Arbuzov, followed by nitration and reduction. Bismaleimides were synthesized by using the procedure of Searle. Structures of the products were determined by infrared spectroscopy. Curing of these resins was done in air for 30 min. at $290 \pm 2^\circ\text{C}$.

Amount of char and combustible gases formed in thermal decomposition are very important quantitative measures of flame resistance of polymeric materials. Char yields at 800°C may, therefore, be used as criteria, not only for evaluating thermal stability, but also flame resistance. In some of these phosphorous containing polyimides char yields in nitrogen atmosphere were as high as 70%.

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EFFECT OF THE RIGID NATURE OF THE BACKBONE ON SYNTHESIS OF POLY-P-PHENYLENETEREPHTHALAMIDE

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Poly-p-phenyleneterephthalamide is an extremely important polymer as it forms high strength, high modulus fibers. Synthesis of high molecular weight polymer is difficult owing to the rigid nature of the back bone chain. The polymerisation reaction is further complicated by the formation of liquid crystalline-anisotropic state, during the reaction. Relatively high molecular weights are however achieved at low monomer concentrations in the reaction mixture and under high speed stirring conditions. The molecular weight obtained in a reaction depends on the concentration of the monomers in the reaction mixture and the rate of stirring. The present study is concerned with finding out the onset of formation of an anisotropic state during the reaction and its effect on the polymerisation reaction. The observations have been explained on the basis of the theory of dynamics of rod like macromolecules in solution.

POLYESTERAMIDE FIBERS

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Poly (ethylene terephthalate) containing amidic and hexamethylene segments has been prepared by melt condensation by taking N, N'-bis (p-carbomethoxy benzoyl) hexamethylenediamine (BEA) as a third component along with dimethyl-terephthalate (DMT) and ethylene glycol in the initial monomer feed.

The polymers were characterized by infrared spectroscopy, nitrogen analysis and intrinsic viscosity measurements. The effect of copolymer composition on the melting point and density was also investigated. The relative thermal stability of the various polyesteramides was investigated by using dynamic thermogravimetry in nitrogen atmosphere.

Three polymer samples were spun into fibers by using melt spinning technique. The fibers were drawn to different draw ratios and then heat set. With an increase in the mol-% of BEA, an increase in initial modulus but a slight decrease in tenacity and percentage elongation was observed. The crystallinity and orientation of fibers was studied with X-ray diffraction pattern. In the drawn and heat set fibers, the density decreased on increasing the BEA content. The dye uptake and moisture regain in polyestaramides was greatly enhanced as compared to PET.

RATIONAL UTILISATION OF POLYACRYLONITRILE (PAN) FOR HIGH PERFORMANCE CARBON FIBER: A SYSTEMS APPROACH

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Polyacrylonitrile (PAN) is a well known precursor material for preparation of carbon fibres. In order to develop such high performance fibers, parametric analysis reveals the importance of various process parameters like temperature profile, residence time, furnace atmosphere and surface oxidation etc. The influence of these parameters to achieve a fiber reliability, R_f , of the final product is very critical as will be evident from sub-systems/process reliability analysis undertaken from a systems approach angle, the most effective way for rational utilisation of PAN among others. Field trial data on productionisation experiment concerning rational utilisation of PAN for high performance carbon fibre (RUPHPCF) will be presented. The impact of the application of such RUPHPCF approach for producing engineering fibres from other relevant polymeric type materials is also elucidated.

STUDIES ON AROMATIC-ALIPHATIC FIBER FORMING COPOLYESTERS

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A series of copolyesters have been synthesized by using 2-2 bis (4 hydroxyphenyl) propane (Bisphenol-A)/resorcinol as phenols and ethylene glycol (E.G) as diol with terephthaloyl chloride through interfacial polycondensation and by

dimethyl-terephthalate (DMT) through melt condensation in different mole ratios of bisphenol to glycol in the initial monomer feed. The effect of different combinations of catalysts in melt condensation is also studied.

The method of synthesis has a significant effect on melting point, viscosity, density as well as crystallinity. Use of aliphatic diol in preparation of aromatic polyesters increases the density and crystallinity while the melting point, yield and viscosity decreases in a linear fashion. Better thermal stability was observed by increased aromatic content in copolyesters. Sonic modulus and X-ray diffraction have been used for studying the molecular orientation and crystalline structure. The role of bisphenol content in these copolyesters on their tensile properties was also investigated.

POLYMERS IN TEXTILE WET PROCESSING

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From time immemorial, natural polymers such as starch and gums have been used in textiles as sizing ingredients and as thickening agents for printing and finishing. However, for man-made fibres, whose properties are quite different from cellulose and other natural fibres, the conventional materials used for sizing, printing and finishing are not quite suitable. For these operations and to a smaller extent at other points of processing polymers of various types are used. In view of the importance of polymers in textile processing, an attempt has been made to give an overview of the subject in this paper.

AN ANALYSIS OF NON LINEAR VISCOELASTIC BEHAVIOUR OF POLYPROPYLENE AND GLASS REINFORCED POLYPROPYLENE IN CREEP

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The non-linear visco-elastic behaviour of various thermoplastic materials has long ago been established. A vast field, however, remains unexplored, firstly, in finding out workable theories for actual engineering applications with their limits

of applicability specified, and secondly, in understanding the physical mechanisms which control the manifestation of non-linear visco-elastic behaviour in these polymeric materials.

An attempt to understand these phenomena has been made by performing 6 hr. isothermal creep tests on unreinforced and glass-fibre reinforced polypropylene samples under uniaxial tension. In the case of the homopolymer, experiments were performed under different stress levels and at various temperatures upto 60°C. Stress levels were chosen in such a way that maximum strain level always remained below 3%. This was done in order to achieve complete recovery during the successive recovery cycle. Validity of an equation of the form $E = E^{\circ} + E^{+}t^n$ has been tested. It is found that E° in the above equation is approximately a linear function of stress and is weakly dependent on temperature, whereas E^{+} is a non-linear function of stress and is strongly temperature-dependent. The exponent n , however, is a constant independent of both stress and temperature. With incorporation of glass fibres appreciable increase in the modulus and slowing down of time dependent deformation were achieved.

NEW FRONTIERS OF ACRYLICS IN ADHESIVES AND COATINGS

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The acrylics are an exceptionally versatile family. The acrylic monomers are easily polymerized and copolymerized to give a variety of polymers with a wide range of properties. Some novel and useful applications have been found in the areas of adhesives and coatings.

New monomer/graft polymer solutions perform as structural adhesives competing with epoxies. Anaerobic adhesives which cure in the absence of air are used for locking screws and bolts as well as parts assembly. Cyanoacrylates which set instantly find increasing use in product assembly and mechanical repair.

Acrylic emulsion-based house paints have established their market place. Excellent weatherability is the major plus factor.

Multifunctional acrylic esters are employed as cross-linkers in vinyl acetate-acrylate emulsion paints.

Radiation-cured coatings based on acrylic oligomers and monomers are non-polluting, energy saving systems, specially suited for heat sensitive substrates. Similar formulations are also employed as photopolymers in many imaging applications. Non-aqueous dispersions have replaced high-solvent acrylic lacquers in automotive top coats.

The paper will discuss in detail the technologies and applications of these new acrylic systems.

THE APPLICATION OF SPENT SULFITE LIQUOR AS AN ADHESIVE FOR PARTICLE BOARDS

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Though lignin is produced in pulp mills as a by-product in large quantities, it is mainly burnt or released into waterways, causing severe pollution problems. It has been previously found by the authors that spent sulfite liquor (SSL), when treated with hydrogen peroxide in the presence of an appropriate catalyst is intensely crosslinked by oxidative coupling to an insoluble resin. This reaction can be used for the application of SSL as an adhesive for particle boards.

We have recently found that sulfur dioxide is a very effective catalyst for this oxidative coupling reaction. It leads to particle boards with high strength properties and low swelling degrees without wax sizing. In comparison to the main conventional glue, consisting of urea formaldehyde, SSL does not release any formaldehyde from the finished boards. Furthermore, due to the highly exothermic cross-linking reaction, more homogeneous and also thicker boards can be obtained at lower press temperatures and short press times.

STUDIES TOWARDS STRUCTURE OF AROMATIC POLYIMIDES

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With the view to understand the structure of aromatic polyimides backbone, in order to improve their high temperature and electrical properties, studies have been made towards the synthesis of model compound N, N-bis-(4-phenoxy phenyl)-1, 2:4, 5 - benzene-tetracarboxdiimide. It involves condensation of pyromellitic dianhydride and 4-aminodiphenyl ether in solvent N, N-dimethyl acetamide or N, N-dimethyl formamide. Various side products formed during the reaction were isolated using column chromatography and identified by spectroscopical methods. This study reveals that the polymer backbone contains nearly 85% imide rings. The uncyclizable residues in the backbone are those derived either by chemical interaction of polymerization solvent or by modification of intermediate *ortho* amido acid. The uncyclizable nature of the latter was explained using mass and infrared spectral studies and its existence interpreted through the mechanism postulated for the reaction. Role of dipolar solvent looks to be vital for imidization step. The paper, therefore, is the compilation of the total discussion on this approach.

ADHESIVE MATERIALS USED IN MEDICINE AND DENTISTRY

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The repair and replacement of diseased or damaged body tissues using adhesive materials has a number of significant potential advantages.

For soft tissue wounds an adhesive could act as a barrier to bacteria ingress and blood loss and replace sutures. The alkyl 2-cyanoacrylates are unique in their ability to form covalent bonds to protein and, as a result, polymerise in a few seconds. They have been widely investigated as soft tissue adhesives.

No materials are known which will adhere to bone under clinical conditions, probably because of its fat content and the turn-over of cells. The prospect of long term adhesion to bone and skin is remote because it is a living tissue which is continually regenerating.

Teeth, however, are the most inert material in the body and some success has been achieved from two approaches to long term adhesion. One involves the use of aqueous polycarboxylic acids which are able to ionically complex to enamel and dentine and are formed into cements by reaction with ion leachable powders, for example, zinc oxide. The other technique involves etching enamel to open up small fissures into which self-curing monomers can penetrate and polymerise. Such monomers are usually mono or dimethacrylates to which particulate glass filler is added for restorative purposes. This acid etching procedure is also used to coat the tooth with polymer to prevent decay (fissure sealing).

ROOM-TEMPERATURE-CURING ORGANOTIN POLYMERS

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The synthesis and properties of thermoset organotin polymers cured at room temperature are described. In one method, typically, poly (styrene-co-maleic acid) is partially esterified with tributyltin oxide and then reacted with a polyfunctional aziridine. In another, diglycidyl ether of bisphenol-A is first modified by reaction with the tributyltin esters of ω -amino acids; the resulting oligomers are then cured with diethylene-triamine. The strength properties and dynamic mechanical response of the polymers were measured and correlated with the molecular structural parameters. Results of leaching of organotin species from the polymers were examined in the light of a bulk abiotic cleavage model.

PREPARATION AND BIOMEDICAL APPLICATIONS OF POLY (HYDROXY-ETHYL METHACRYLATE-METHACRYLIC ACID) HYDROGEL

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Polymeric hydrogels form an important class of modern biomaterials and are used in preparation of contact lenses, artificial organs, hemodialysis membrane and as drug carriers. Recently, in our laboratory, application of hydrogel in fertility control has been envisaged. The technique involves the use of a polymer which when injected into vas deferens lowers the pH sufficiently as to kill the spermatozoa passing through. The polymer thus provides an acidic environment for a prolonged time and also slowly erodes. The fertility may be restored after complete solubilization of polymer itself over a period of time or by flushing with a suitable solvent. This method of male contraception is thus nonsurgical, nonocclusive and reversible. The present work describes synthesis, characterization and biomedical applications of poly (hydroxyethyl methacrylate-methacrylic acid), P(HEMA-MAC) copolymer. The hydrogel containing varying ratio of HEMA:MAC was synthesised by ^{60}Co - γ radiation in methanol and tested as contraceptive in male rats. The results indicate that the system is successful in fertility control. Possibly the sperms are killed because of the low pH environment created by the gel. Further, the application of such gels for antimicrobial skin substitutes and as slowly erodible drug carriers are envisaged.

NEWEST EXPERIENCE ON CARBON FIBRE REINFORCED BONE PLATES

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Bone fractures can be healed by direct fixation of the fractured bone parts. The healing process is induced by the physiological stimulation of the bone tissue

due to the load transfer through the fixed parts of the bone by means of internal bone plates. The generally applied metal plates however may initiate a process of osteoporosis. Such bone transformation and degeneration may occur because of stress protection of the bone by the rigid metal plate, mainly due to the mismatch of elasticity between the plate and the bone. This mismatch leads to a loss of stability of 30% at the rear side of a plate-fixed corticalis and of 50% to 80% directly under the plate (Diehl *et al*, 1974). This degeneration of the bone structure is in agreement with Wolff's law. After removing the plate often refractures of the bone are therefore observed.

These disadvantages of metallic bone plates could be avoided by the use of carbon fibre reinforced composites. Such materials can be tailored to the elastic and strength requirements of the bone.

The first attempts to apply carbon fibre reinforced fixation plates with methylmethacrylate and polysulfone as matrix material were performed by Woo *et al*. (1974) and M. Kenna *et al* (1976). Such uncoated fibre reinforced polymers affect a reduced bone degeneration, as was shown in preliminary statistically unproved animal experiments.

The aim of our research was to exclude any incompatibility and toxic reactions between polymers and living tissue by using elemental carbon for plate materials which has been proved repeatedly in the last decade as an outstanding biocompatible material (Bokros, 1977). There are two ways to realize this purpose, namely carbon coatings on fibre reinforced polymers and the use of carbon/carbon composites.

The first way was reported by Aisenberg (1977) and Haubold (1977), who deposited thin carbon films on metals and polymers by sputter techniques. This method utilises the superior mechanical properties of C fibre reinforced polymers especially as far as the shear strength and fracture behaviour is concerned. The disadvantage can be seen in a limited resistance of the thin carbon films against mechanical damages, especially during implantation.

The second solution, namely the use of all carbon composites ensures unlimited biocompatibility, even after surface damage during handling. Jeknins *et al* (1977) and Fitzer *et al* (1978) proposed to use carbon/carbon composites either unidirectionally or two-directionally reinforced as material for fixation plates.

The open question, however, is whether the flexural and shear strength will be high enough to withstand the "*in vivo*" requirements of bone.

The paper will present newest experiences as well as a review about the mechanical suitability of carbon/carbon composites and carbon fibre reinforced polymer

composites for the use as internal fixation plates. In detail will be discussed the results of flexural-, shear-and torsional strength and moduli of unidirectionally, angle ply and carbon cloth reinforced composites with carbon and polymer matrix. Furthermore, the medical experiments which have been started with dogs and sheep will be reported. These experiments shall provide knowledge about the response of the bone tissue to a matched elasticity of the implant material. The goal of the work is to permit a forecast of the optimum ratio of the various mechanical properties for the selection of best material as fixation plates in order to promote bone regeneration and to avoid osteoporosis.

BIOLOGICAL TESTING OF IMPLANTABLE MATERIALS FOR MEDICAL APPLICATIONS: A PRELIMINARY REPORT

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The hazards encountered in the clinical use of medical devices and implants have been described in this paper to emphasise the need for, and relevance of carrying out appropriate toxicological investigations before such items are manufactured and marketed. Five different formulations of polyvinyl chloride (PVC), delrin and polyester fabric were subjected to various tests to determine their biocompatibility/safety, for their eventual use as components in an oxygenator and a prosthetic heart valve. The test methods together with the results obtained are described and discussed.

THERAPEUTIC SYSTEMS FROM BIODEGRADABLE POLYMERS

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Conventional methods of drug delivery, eg. by oral administration, suffer from certain drawbacks. These include the loss of biological activity of the drug

during administration and on its way to the diseased site, the resulting side effects and the need to take the dosage frequently. Therapeutic system based on biodegradable polymers eliminate many of these difficulties. Our earlier studies showed that oxidized cellulose is biocompatible and biodegradable and can be used for formulating controlled drug delivery systems. Insulin, the deficiency of which causes diabetes cannot be administered orally and has to be taken as daily injections. A depot giving prolonged insulin delivery was thus considered useful and the potential application of oxidized cellulose matrix in immobilising and releasing insulin was examined. To assess the biological activity of the released hormone, experiments on rabbits were conducted. The hypoglycemic effect due to the supply of insulin from injected immobilized insulin preparations in these animals was followed by measuring the blood glucose level at regular intervals upto a period of 16 hours. It was seen that upto this period the hypoglycemic effect is sustained indicating that there is a sustained release of insulin at least over this period, and hormone released is biologically active. Control experiments carried out simultaneously by injecting free insulin, indicated that the native hormone exerts this effect for only about 6 hours. Thus, therapeutic system based on oxidized cellulose for a sustained delivery of insulin to diabetic patients have been envisaged.

MICROBIAL DEGRADATION OF GELATIN GRAFT COPOLYMERS

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In view of the considerable interest focussed on biodegradable polymers as controlled release substances, the microbial degradation of Gelatin graft copolymers is under investigation in our laboratory. Gelatin-g-poly (methyl acrylate) is prepared in aqueous medium using $K_2 S_2 O_8$ as the initiator. The graft copolymer can be pressed into films by the compression moulding technique. The percent elongation of the films is 450 and ultimate tensile strength is 12.12 MN/m^2 . For bio-degradability testing, mineral salts medium with the polymer in question as sole source of carbon was used. *Bacillus subtilis*, *Serratia marcescens* and *Pseudomonas aeruginosa* were employed as test organisms. Degradation was followed by measuring the loss in weight periodically. Good growth was noted in all organisms. The sample inoculated with *Pseudomonas*.sp., *Bacillus*.sp., and *Serratia*. sp., showed a weight loss of 15.8%, 18.8% and 17.6% respectively after five weeks of incubation period. The susceptibility of the material to the other bacterial and fungal strains and to the mixed inocula is under investigation. The effect of percent grafting and the effect of molecular weight of side chains on the biodegradability are under investigation.

NEW RESULTS ON THE ANIONIC POLYMERIZATION OF POLAR MONOMERS

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The anionic "living" polymerization of hydrocarbon monomers offers a unique method to design macromolecules. In particular, it may result in narrow molecular weight distributions. The kinetics can be explained by assuming associates, tight or contact ion pairs, loose or solvent separated ion pairs and free anions. By choosing suitable conditions (solvent, temperature, addition of homoionic salt) the predominant presence of one particular species can be generated. The activation volume for the contact ion pair (styrene/Na⁺/THP; styrene/Cs⁺/DME) is ca. 20 cc/mole, that of the solvent separated ion pair is likely to be smaller by one order of magnitude.

With polar monomers additional effects have to be visualized namely physical ones such as solvation of the ion pair by the monomer and the polymer chain (self-solvation) and chemical ones such as side reactions resulting in termination reactions.

At low temperatures living polymerization of methacrylates is accomplished. The larger the ester group and the higher the solvation power of the solvent the more perturbing effects are reduced. The Arrhenius plot of the rate constants of polymerization is a straight line thus giving no indication for more than one active species. In contrast to methacrylates with large ester groups (t-butyl) those with small ones (methyl) show rate constants which are independent of the counter ion (Na⁺ and Cs⁺).

With increasing temperature termination reactions become increasingly important (deviation from a first order polymerization reaction, increasing broadness of the molecular weight distribution). In the presence of the monomer the termination reaction is likely to be an intramolecular one. At nearly 100% conversion termination reactions are reduced. This is not understood hitherto.

A peculiar behaviour is observed when the growing species is bifunctional. At low conversions (i.e., low degree of polymerization) an intramolecularly end-to-end associated species is the predominant one adding the monomer by a factor of 8 slower than the non-associated active species. At surprisingly high degree of polymerization the associates dissociate gradually to achieve the normal rate constant for monomer addition.

PMMA obtained by anionic polymerization is highly syndiotactic, however, the statistics for the formation of the stereo isomeric center are dependent on the counter ion (Bernoullian with Na^+ , Markov 1st order with Cs^+). The intramolecularly associated species yield a nearly perfect active polymer.

The results suggest both self-solvation by the penultimate (Na^+) or the antepenultimate (Na^+ , Cs^+) ester group of the growing chain as well as external solvation by the solvent which becomes more important as the solvation power of the solvent increases (from THF to DME) or the ester group becomes larger (from methyl to t-butyl). An association to dimeric ends is preferred when the concentration is favourable.

PRELIMINARY STUDY OF CATIONIC POLYMERIZATION OF α -METHYL-STYRENE USING $t\text{-BuCl/Et}_2\text{AlCl/CH}_2\text{Cl}_2$ SYSTEM

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α -Methyl-styrene polymerization has been carried out using $t\text{-BuCl/Et}_2\text{AlCl/CH}_2\text{Cl}_2$ system in the temperature range of 0° to -63.5°C . The effect of temperature on yield and molecular weights of poly α -methyl-styrene was determined. Based on Arrhenius plots, average activation energies of molecular weights were determined to be -9.2 ± 1.0 K. cal/mole (0° to -40°C) and 0 ± 0.5 K. cal/mole (-40° to -63.5°C). These were postulated to reflect molecular weight governing mechanisms of transfer to monomer and termination, respectively.

ANIONIC POLYMERISATION OF 2, 4-DINITROSTYRENE

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2, 4-Dinitrostyrene which is incapable to polymerise by free radical or cationic mechanism, is easily polymerised by anionic catalyst. Effect of change of alcoholate to alkali, quantity of catalyst, concentration and nature of solvent and polymerisation condition for optimum yield have been studied.

SYNTHESIS, CHARACTERIZATION AND MECHANISM OF GRAFT COPOLYMERIZATION OF METHYLMETHACRYLATE ONTO CELLULOSE NITRATE

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Grafting of methyl methacrylate onto cellulose nitrate initiated by azobisisobutyronitrile in homogeneous medium has been studied. Separation of graft polymer from the homopolymer and unreacted backbone has been done by selective solvent extraction. The effect of variables such as initiator concentration, monomer concentration and reaction time on grafting efficiency and percent grafting has been discussed. Nitrogen analysis of the samples was carried out by a colorimetric method. Graft copolymers have been characterized by GPC, DSC and viscosity measurements. Some kinetic aspects of the grafting reaction have been discussed and a suitable mechanism has been proposed.

γ -RAY INDUCED GRAFTING REACTIONS ONTO POLYPROPYLENE AND ITS ELECTROKINETIC BEHAVIOUR.

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Grafting of vinyl monomers (vinyl acetate, methacrylic acid and acrylonitrile) onto fibrous polypropylene was achieved using γ -ray irradiation technique. The amount of graft increased with the increase in the monomer concentration in the solution. Extent of acrylonitrile graft decreased with increase in the temperature of grafting (k decreased from 0.7 hr^{-1} to 0.25 hr^{-1} with decrease in temperature from 27 to 47°C) while vinyl acetate and methacrylic acid showed almost neutral behaviour towards the changes in the temperature of grafting reactions. The activation energy values (E) for vinylacetate, methacrylic acid and acrylonitrile, were

1.51, 2.30 and -12.7 Kcal/mol, respectively in the temperature range 27 -47 C. These results have been attributed to the phenomenon of chain transfer and greater amounts of homopolymer formation at higher temperatures. Polypropylene was rendered hydrophilic in character by grafting the vinyl monomers, especially methacrylic acid (moisture regain of about 0.2% for the control was raised to above 6% when the graft content of methylmethacrylic acid on polypropylene was 41%). The polypropylene substrate was rendered dyeable with disperse dyes in case of all these monomers. In addition methacrylic acid and acrylonitrile grafted polypropylene could be dyed in intense bright shades using cationic dyes.

SYNTHESIS AND CHARACTERIZATION OF MICA-VINYL GRAFT COPOLYMERS

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Graft copolymerization of methylmethacrylate (MMA) and acrylonitrile (AN) onto mica was carried out by the ceric ion method. Experiments were carried out both in the presence and in the absence of oxygen; oxygen has some detrimental effect in the grafting of AN onto mica. Mica-vinyl graft copolymers were characterized using infra-red spectra after purifying the crude graft copolymers for the removal of the occluded homopolymers. The percent grafting, grafting efficiency and the ration of R_g/R_h were determined. Mica graft copolymers were saponified by treating with aqueous alkali to convert the nitrile groups to carboxyl groups with a view to utilize these groups for coupling to collagen substrates. The leathers treated with the grafted products showed considerable overall improvement in properties such as physical appearance, feel, fullness, roundness and smoothness of the grain surface.

STUDIES IN GRAFT COPOLYMERIZATION OF VINYL MONOMERS ONTO WOOL IN PRESENCE OF VO(acac)₂ AS INITIATOR

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Methylmethacrylate (MMA) acrylic acid (AAC) and vinyl acetate (VAC) were graft copolymerized onto Himachali wool in aqueous medium by using vanadium oxyacetylacetonate as initiator. Graft copolymerization was studied at 45°, 55° and 75° for various reaction periods. Percentage of grafting was determined as functions of concentration of monomers, concentration of initiator, time and temperature. Maximum percentage of grafting for each monomer occurred at 55°. Several grafting experiments were carried out in presence of various additives which included: (i) HNO₃ (ii) DMSO and (iii) pyridine nitric acid was found to promote grafting of MMA. All the additives had adverse effects on grafting of VAC. MMA, VAC and AAC were found to differ in reactivity towards grafting and followed the order: MMA > AAC > VAc.

SURFACE AND BULK PARAMETERS AFFECTING CONTACT ELECTRIFICATION OF POLYSTYRENE

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The electrical properties (e.g., the electrical conductivity) of organic polymers involve two critical parameters: the number of charge carriers and their mobility. In discussing the conduction process, we consider the origin of the charge carriers, their number, and their energetic distribution in the surface and in the bulk of the polymer. Ultimately we should aim to relate these parameters to the chemical composition and the morphology of the polymer in order to predict the electrical properties of polymer systems and to set out to synthesize a well-defined material with specific properties.

In solving these problems we investigated the electrostatic charging of polymers due to intermittent contacts of metals with the aim to characterize the mechanisms of charge transfer and charge storage at the surface and in the bulk of atactic

polystyrene (PS). Out of these experimental data we developed a theoretical model describing the electrostatic charging of PS. Using this model, time dependent charging and discharging processes in polymers can be simulated by an analog computer. The space charge situation and its relaxation behaviour at the permanent polymer/metal contact is investigated by the help of field effect measurements. The evaluated data are consistent with the model mentioned above.

Because dark conductivity and dielectric constant depend in different ways on the applied electric field-strength, we investigated the electrostriction of PS under step-response conditions and under the influence of an alternating electric field. These experiments give a hint that at least one internal degree of freedom in PS (according to a.c. as well as d.c. field) induced changes of local order exists in PS.

GLASS TRANSITION TEMPERATURE FROM DIELECTRICS RELAXATION DATA: GLASS TRANSITION TEMPERATURE OF POLYACRYLONITRILE

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Determination of glass transition temperature of polymers from the dielectric relaxation data, i.e. the relaxation times at several temperatures, is described on the basis of WLF theory. Dielectric relaxation data obtained on polyacrylonitrile (PAN) showing loss peaks in temperature range 100 - 150°C at frequencies 10^2 - 10^5 Hz have been analysed for WLF type behaviour. The glass transition temperature ($T_g=90^\circ\text{C}$) thus found is in agreement with the value reported by dilatometric method. Further more the constants of the WLF equation, $c_1=5.7$ and $c_2=75.0$, found from this analysis for PAN are somewhat lower than the general values of these parameters.

A comparison of this method with the recently proposed method of Philips is presented. Consistent values of T_g are found by both the methods,

THEORETICAL TREATMENT OF THE KINETIC PARAMETERS OF GLASS TRANSITIONS

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The kinetic parameters associated with T_g directly from calorimetric data were calculated for the first time for some commercial polymers using Ellerstein's equation. The enthalpy change values were obtained from Differential Scanning Calorimeter measurements. The literature data (M.J. Richardson *et al*) for polystyrene was used for the calculation of E . The intercept values were not unity suggesting the inapplicability of the equation. Systematic enthalpy change measurements at different cooling rates were made with poly (ethyleneterephthalate) and poly (vinyl alcohol). The intercept for these polymers also deviated from unity. Thus the values calculated cannot be the energy of activation for glass transition as suggested by Ellerstein but actually the energy of activation for local ordering. The zero intercept values for polystyrene and poly (ethyleneterephthalate) indicates the absence of any induction period for the local ordering. The calculated E values for poly (ethylene terephthalate) exhibited a maximum when plotted against different rates of cooling. Thus the interesting conclusion is made that the maximum local ordering near T_g occurs only at an optimum cooling rate. No endothermal peak was observed in the case of poly (vinylalcohol) indicating the absence of any increase in local ordering due to the already existing order through hydrogen bonding.

ADIABATIC COMPRESSIBILITIES OF DRAG REDUCING POLYMERS

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Ultrasonic velocity and density measurements are being reported in number of aqueous solutions of drag reducing polymers over wide range of concentrations. The adiabatic compressibilities of these systems have been evaluated from ultrasonic velocity and density data.

The solvation numbers of water molecules per repeat unit of polymers have been computed using Passynsky relation. It has been found that the shear resistant of drag reducing polymers increases with the amount of solvation of water molecules.

DIELECTRIC BEHAVIOUR OF FOAMS FROM POLYSTYRENE-POLYMETHYL METHACRYLATE BLENDS AT X-BAND MICRO-WAVE FREQUENCY

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Foams have been generated from blends of polystyrene & polymethyl methacrylate of different compositions under constant solvent-nonsolvent ratio, impregnation time and heating-period. Scanning electron photomicrographs of the copper-coated foam samples reveal uniform appearance, distinct grain-boundaries and random submicronic cell size distribution. Dielectric measurements have then been made on the test specimens, cut according to the wave-guide size at 9.375 GHz X-band microwave frequency by short-circuited wave-guide method of Smith & Hippel modified by Dakin & Works. Dielectric constants are linear on direct & semi-log scales in bulk-density, volume fraction and blend-composition, obeying Wiener's inequalities. Different standard formulae have also been tried, but an empirical relationship derived on the basis of the experimental data fits best. Specific polarization is also a true function of the density. Tans lying the range 0.150-0.044 decreases with the increase of percentage of polymethylmethacrylate. An attempt has also been made to establish a correlation between the compressive strength and transverse rupture and the electrical properties of the foams.

THERMAL MODIFICATION OF POLY (VINYL CHLORIDE) AND FORMATION OF DEHYDROCHLORINATED POLY (VINYL CHLORIDE)- POLY (METHYL METHACRYLATE) POLYMER BLEND IN THE PROCESS OF FOAMING: IDENTIFICATION AND APPLICATION

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Impact resistant plastic foam of dehydrochlorinated poly (vinyl chloride) (DHPVC) - poly (methyl methacrylate) (PMMA) was prepared for cryogenic insulation in space vehicle, by the method of compression molding and chemical blowing. Impact resistance was achieved by the formation of the polymer blend dehydrochlorinated poly (vinyl chloride)—poly (methyl methacrylate), during the process of foaming the mold by chemical reaction at the temperature of 200°C. The polymer blend was separated from the plastic foam and the compatibility was investigated by Ultra violet, Infrared spectral studies and Differential Scanning Calorimetry (DSC). The compatibility of dehydrochlorinated poly (vinyl chloride) and poly (methyl methacrylate) was highlighted on the basis of allylic activation introduced in the thermally modified poly (vinyl chloride). The thermodynamic views were also correlated. The versatility of the present method for impact resistant foam was pointed out.

MECHANISM AND STRUCTURE PROPERTIES RELATIONSHIP FOR THERMO-OXIDATIVE DEGRADATION OF POLYETHYLENE DURING THERMAL AGEING

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In this investigation an attempt has been made to study the important steps of mechanism of thermo-oxidative degradation of low density polyethylene by accelerated oven ageing techniques. The oven ageing was done at 70°, 80° and 90°C in presence of air. The main oxygenated groups which have been found in this study are acidic and ketonic. Correlation between macro properties and structural changes has also been attempted.

It has been found that intrinsic viscosity and viscosity average molecular weight (Mv) decreases continuously, while tensile strength (T.S.) and elongation at break (E.B.) increase initially and then decrease to a certain level i.e. maximum upto 35.9 percent for T.S. and 68.7 percent for E.B. depending on time and temperature of ageing. The density (crystallinity) has been found to increase with the time and temperature of ageing. These properties have been found to have a direct correlation with the micro structural changes occurring during thermal ageing of polyethylene.

THE ORIGIN OF THE VARIABILITY IN THE PROPERTIES OF COMMERCIAL POLY (VINYL ALCOHOL CO-ACETATE)

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Although not documented in the literature, the variability observed between different batches of ostensibly similar poly (vinyl alcohol co-acetates) is notorious amongst those who use this product in industry. Whilst materials with higher or lower acetyl contents have their applications, polymers with a residual acetyl content of approximately 12 mole per cent are most widely used as having good surface activity combined with ease of dissolution in water. Recipes for the emulsion polymerisation of vinyl acetate (for the preparation of emulsion paints and latex adhesives) usually specify such a polyvinyl alcohol as a major component of the emulsifier. These polyvinyl alcohols also find application in the photo-engraving process for preparing blocks to enable photographs to be printed with letter press and in the production of the phosphor mosaic screens for colour television sets amongst other applications. Polyvinyl alcohols are customarily characterised by their acetyl content and by the viscosity of their 4% aqueous solutions. However these parameters alone are insufficient to ensure similar behaviour of different preparations in use.

An example of the sort of behaviour encountered is provided by two samples kindly provided by Dr. D.B. Farmer of Vinly Products Ltd., Carshalton, Surrey, England. 'Gohsenol' GH-17 is the product of Nippon Gohsei, Osaka, Japan and is an example of a standard material which is widely used. Although the acetyl content of the other sample 'B' is slightly different, it is well within the range specified for the grade (11—13 mole%) so that no significant difference in properties would

be expected for this reason. Yet when one sample was directly substituted for the other in a standard recipe for the emulsion polymerisation of vinyl acetate, the viscosity of the polyvinyl acetate latex prepared with polyvinyl alcohol 'B' (8.9 P) was only half that prepared with GH-17 (16.3 P).

Nevertheless the samples appeared to be identical under several techniques of examination. Infrared spectra were identical. No difference in crystallinity could be detected by X-ray powder diffraction. The chemical shifts in the proton-decoupled Fourier-transform ^{13}C n.m.r. spectra were identical. The ultra-violet absorbance at 210 nm (generally attributed to conjugated unsaturated ketonic structures) and at 270 nm (conjugated di-ene ketones) did differ slightly from which it could be calculated that the di-ene ketone content of GH-17 was 2.7 times that of 'B', but although the conjugated ketone content of polyvinyl alcohols does affect the rate of the vinyl acetate polymerisation, the difference in the contents of these samples is comparatively minor and the actual conjugated ketone contents are comparatively low (the diene ketone content of some commercial samples is 100 times that found for this sample of GH-17:) and it is difficult to see why the very low concentrations of these structures present (0.67 mole % mono-ene ketone and 0.04 mole % diene ketone in GH-17) should affect the viscosity of the latex prepared with these samples.

The clue to the origin of the difference between the samples was given by the ^{13}C n.m.r. spectra. Although the chemical shifts do not differ, there is a difference in the relative intensities of the methine and methylene resonances in the samples. The ratio CH_2 / CH is 1.56 for GH-17 and 1.19 for 'B'. Unfortunately although decoupling the proton and carbon-13 spins simplifies the ^{13}C spectrum which would otherwise be exceedingly difficult to interpret, it destroys the precise proportionality between the integrated intensity of the signal and the number of atoms of that type present in the structure. Decoupling also enhances the intensity of the signal because of the Nuclear Overhauser Effect by a factor of up to 2.988, mitigating somewhat the difficulty caused by the low natural abundance of carbon-13. It is usually assumed that the N.O.E. enhancement factors for the different carbon atoms in a polymer do not differ much and proton decoupled ^{13}C n.m.r. intensities have been used to calculate mean sequence lengths in copolymers. In the present case, the spectra were obtained under identical conditions on similar polymers so that the difference in intensities must mean that there are fewer methine groups in GH-17 than in 'B' (The CH_2/CH ratio would be 1.00 in a linear polymer provided that there is no difference in the N.O.E. factor between methylene and methine groups). Although there is a widespread belief that branching in polyvinyl acetate occurs exclusively through the acetyl groups when a completely hydrolysed polyvinyl alcohol would be linear, this belief seems to be based on a misapprehension. It is true that in the polymer analogous reaction in which polyvinyl acetate is converted into polyvinyl alcohol and back into polyvinyl acetate, the limiting viscosity number of the polyvinyl acetate is reduced only in the first cycle but this experiment only demons-

trates the presence of hydrolysable branches and not the absence of non-hydrolysable main-chain branches. The bond dissociation energy of tertiary hydrogen atoms is lower than those of secondary or primary hydrogen atoms and consequently transfer constant to tertiary hydrogen atoms are higher. Transfer to the methine groups of the polymer with quaternary carbon branch points increasing the CH_2/CH ratio. Quaternary carbons are difficult to detect in ^{13}C n.m.r. spectra because lack of any protons directly attached to them results in negligible N.O.E. enhancement. However, when the spectrometer is adjusted to give the greatest possible signal-to-noise ratio, a low intensity resonance can be discerned at the field expected for a quaternary carbon. The concentration of main-chain branch points is calculated as 5.2 mole % in GH-17 and 3.0 mole % in 'B', i.e. the more highly branched polyvinyl alcohol. Since there is evidence that there are only one or two long-chain branches per molecule, the majority of the branches must be short-chain branches formed by 'back-biting' by the growing polyvinyl acetate radical. The rate constant for this reaction may be critically dependent on the precise water concentration in the methanol solvent used for the polymerisation of the vinyl acetate.

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HYDROPHOBIC INTERACTIONS ON THE BINDING OF POLY-VINYLPYRROLIDONE

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A spectrophotometric method has been employed for the quantitative determination of binding in the polyvinylpyrrolidone-rose bengal system. Binding of tiron, another anionic dye onto the polymer, polyvinylpyrrolidone, has been investigated by an equilibrium dialysis method. Comparison of binding constants of the two systems indicated the importance of hydrophobic interactions in binding. Since rose bengal can serve as a fluorescent probe, a fluorimetric method has also been employed and the observed fluorescence enhancement has confirmed the significance of hydrophobic interactions in the binding of the dye onto the polymer,

KINETIC STUDIES ON THE FORMATION OF POLY (CHLORO-CYCLO PHOSPHAZENES)

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Poly (chlorocyclophosphazenes) serve as potential reactive intermediates in the formation of inorganic and hetero-organic polymer systems useful in aerospace, biomedical, textile and agro industries. Toxicity in the handling of the reactants, reaction medium and by-product, presence of a ring-chain competition kinetics and need for getting the maximum amount of the cyclic (trimer + tetramer) mixture in a minimum duration of time have prompted an in-depth study of their formation under safer reaction conditions. This paper describes these studies. A reasonably larger size of these experimental batches employed in these studies help as a simulation of the manufacturing environments.

GAMMA RADIATION INDUCED BULK POLYMERIZATION OF SOME METHYL PHENOXYMETHACRYLATES

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The kinetics of the γ -radiation induced bulk polymerization of methyl phenoxymethacrylate and methyl paracresoxymethacrylate has been studied at dose rates 0.3 and 0.075 Mrads/hr and at temperatures 0°C and 30°C. The polymerization is first order with respect to the monomer and the rate of polymerization has a direct dependence on dose rate. The activation energy values for the polymerization of methyl phenoxymethacrylate is 1, 2 K. cal/mole and for methyl paracresoxymethacrylate is 0.7 k. cal/mole. The polymerization proceeds predominantly by an ionic mechanism.

CU (DPM)₂ INITIATED VINYL POLYMERIZATION

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The behaviour of cupric dipivaloylmethide in vinyl polymerization systems was investigated with a view to understand the mechanism of initiation of polymerization. Results of polymerization reactions together with spectral investigation data are presented. The polymerization in presence of the chelate proceeds through a free radical process. The corresponding kinetic and transfer constants and activation energy values suggest a normal propagation step. With the help of spectral data an attempt is made to suggest a plausible mechanism of initiation.

STUDIES ON THE CHAIN-TRANSFER PROPERTY OF THIOUREA IN RADICAL POLYMERIZATION AND ITS TAUTOMERIC EQUILIBRIUM IN ACID AQUEOUS MEDIUM BY THE APPLICATION OF DYE-TECHNIQUE

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Chain transfer property of thiourea in radical polymerization of methylmethacrylate in acidic aqueous media has been studied by polymer end group analysis using dye-partition technique. Thiourea has been found to have a feeble chain transfer character, transfer constant with respect to polymethylmethacrylate radicals being 1.67×10^{-4} at 42° C. Incidentally, this chain transfer study led to the development of a new method for studying the tautomeric equilibrium between the thione and thiol forms of thiourea. The equilibrium is pH dependent and the equilibrium constant values at different pH's have been calculated. The thiol form of thiourea which is responsible for its chain transfer property predominates in strongly acidic media and is almost absent above pH 4. This newly developed method may be used for studying the thione thiol tautomerism of other thiourea derivatives.

**SUBSTITUENT EFFECTS IN POLYMERIZATION REACTIONS
IN TERMS OF GENERALISED SUBSTITUENT CONSTANTS F & R
AND GENERALISED WEIGHTING FACTORS f & r DEVISED BY
SWAIN & LUPTON AND WILLIAMS & NORRINGTON**

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In this investigation an approach to correlate the composite rate constants of some redox polymerization reactions (acrylonitrile-Ce (IV) - organic substrate) with a new type of multiparameter equation has been described. The multiparameter equation is based on Swain and Lupton's F and R, representing the field and resonance components of the substituents respectively, and the unique positional weighting factors f and r suggested by Williams and Norrington. The statistical parameters of the correlation involving the substituent constants (fF and rR) and the rate data have been found to be quite satisfactory, the average coefficient of determination being 0.91. The significance levels of the correlation also indicate that the present model is applicable to the kinetics of redox polymerization. The sign and magnitude of the reaction dependent regression constants α and β suggest that three different types of reaction mechanisms are operative for the substrates benzaldehyde, phenyl thiourea, acetophenone and toluene.

**NEW PROCESSING METHODS ALSO SUITED TO HIGH
TEMPERATURE PLASTICS**

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A description is given of two new processes that have been developed at the IKV for the manufacture of plastic mouldings. These processes are of particular interest because they are especially suited to high temperature plastics which can otherwise only be processed with great difficulty. Both processes are variations of the impact sintering process developed at the IKV.

Instead of the hot air used to partially melt the plastic particles in the impact sintering process, the new processes make use of UHF energy to parti-

ally heat the moulding compound. This is then followed by press moulding in both the processes. An explanation is given as to the way in which UHF energy can be used to partially heat plastics. The heating behaviour of various high temperature thermoplastics is covered in particular detail. A description is given of moulding production using the impact moulding process with a conventional die-casting machine. The mouldings produced are then subjected to an initial quality assessment.

Using a similar process, but with less pressure, it is possible to mould pre-forms that can be formed into their definitive shape directly after the impact moulding stage. Plate-like mouldings produced in this way are also subjected to an initial quality assessment.

A further variation on the impact sintering process provides a more economic way of processing thermosetting plastics. The thermosetting plastic granules cure in the centre whilst the surface remains non-cross-linked. These granules can then be used to produce mouldings with a moulding time that is independent of wall thickness. A quality assessment is likewise made on these mouldings.

DIFFUSION EFFECTS IN INITIATOR DECOMPOSITION IN HIGHLY VISCOUS AND MACROMOLECULAR SOLUTIONS

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Decomposition kinetics of single bond and multibond initiator in viscous media was studied. It was confirmed that the concept of macroviscosity cannot be used to correlate the observed viscosity effects on decomposition kinetics. From the models available in literature, microviscosities of polymer solutions and dimethyl formamide-glycerol blends were evaluated. A unified plot results when the data are replotted in this manner. The observed kinetics of decomposition of one bond initiator is influenced by the diffusive transport in the medium, which in turn is governed by the segmental motion. After a threshold chain length is reached, further increase in chain length has no influence on the diffusive transport. The observed kinetics of a single bond initiator, under such conditions, exhibits same features as that of a multibond initiator.

PROCESSING AND RHEOLOGY OF GLASS FIBER-FILLED POLYPROPYLENE

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The processing and rheological behaviour of glass fiber-filled polypropylene composites has been studied experimentally using a capillary viscometer. The elastic behaviour of the system has been investigated by exit pressure and die swell methods. Fiber breakage and fiber migration during flow have been assessed by "burn off" experiments. Initial studies show that glass fibers increase the viscosity of the polypropylene melt. The elasticity of the composite system decreases with an increase in fiber loading. Above 30 weight percent fiber loading, there is practically no effect of the die swell data of the polymer composite system. Swelling index decreases exponentially with the length-to-diameter ratio of the capillaries. Fiber migration during flow through capillaries was apparently absent, but fiber breakage during compounding, capillary extrusion and injection moulding was about as high as 50 percent.

RECENT ADVANCES IN THE UNDERSTANDING OF THE MECHANISMS OF ENVIRONMENTAL STRESS CRACKING OF POLYETHYLENE

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Although the phenomenon of Environmental Stress Cracking of polyethylene (ESC) was discovered in as early as 1946, the underlying mechanisms only started to be understood from the early 1970s. Three factors have aided this understanding: the increased knowledge of the structure and properties of the polymer in late 1950s and 1960s, the development of fracture mechanics principles to strain rate sensitive materials in the 1960s and the development of scanning electron microscopes in the 1960s.

Studies in the last 10 years have shown that there exists a unique stress intensity factor (K) - crack speed (a) relationship for ESC crack propagation and thus the ESC resistance of a material can be characterised by its K-a correlation. It has also been revealed that low stress (low K) ESC failure occurs by swelling and subsequent failure of the interlamellar regions of the polymer whereas high stress (high K) ESC failure takes place by the formation and breakdown of a craze structure. The mechanical behaviour and morphology of the polymer play important roles in the nature of the craze structure developed and sustained prior to collapse which in turn controls the ESC failure. Further, contrary to the conventional belief, it has been shown that a small amount of the ESC agent is definitely absorbed in the polymer and is distributed possibly in the interspherulitic regions, thereby exerting spreading pressure on the tie molecules and influencing the stiffness properties.

A NON-DESTRUCTIVE METHOD FOR MECHANICAL TESTING OF CEMENT-POLYMER COMPOSITE

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A non-destructive method for testing mechanical properties such as compressive strength, bending strength, strength of transverse rupture and Young's modulus have been shown to be calculated by measuring the ultrasonic pulse velocity of cement-polymer composites. Various compositions of cement mortar specimen were prepared by usual method. The cured and dried specimens were vacuum impregnated with methyl methacrylate containing benzoyl peroxide as the initiator. The impregnated specimens were polymerized at 75° C. The pulse velocity of the samples before and after impregnation were measured by an ultrasonic concrete tester. On the basis of such measurements the following empirical general relationship have been obtained:

$$\log V_1 = K_1 S + K_2$$

where V_1 is the pulse velocity (in m/sec.) of the concrete-polymer composite sample, S represents its strength under investigation, K_1 and K_2 are constants. The

values of K_1 and K_2 depend on the nature of the mechanical property to be determined. The technique thus offers a convenient non-destructive method of testing mechanical properties of unimpregnated concrete and concrete-polymer composite samples. The relationships between polymer loading and various mechanical strength have also been discussed.

ON ERRORS IN PRESSURE-HOLE MEASUREMENTS IN THE FLOW OF POLYPROPYLENE MELTS THROUGH CIRCULAR DIES

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A simple rheometric system was set up by coupling 2 and 5 mm diameters circular dies with a 25 mm diameter screw extruder. The wall normal pressure was measured through a pressure tapping drilled perpendicular to the die hole axis by means of a pressure gauge connected to the die with an oil filled tube. The melt flow behaviour of polypropylene studied with the above rheometric system was then compared with the similar results obtained by using "Brabender Plastimeter" having flush mounted melt pressure transducer and the agreement was found to be good. The tests were carried out at a temperature of 230° C and at a shear rate range of 20-4000 Sec^{-1} . The pressure gauge rheometric system showed some pressure-hole error which seems to have been eliminated by means of Bagley's correction factor.

PREPARATION OF LARGE MONODISPERSE LATEX PARTICLES

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Previous methods to make monodisperse large polymer particles in aqueous dispersions have been carried out as seed process, starting out with particles with diameter of $0.5 \mu\text{m}$. These have been swollen with monomer and polymerised with water soluble initiator. Because of the limited swelling capacity of polymer particles, this swelling of particles with subsequent polymerization has to be carried out in several steps in order to produce particles with a considerable increase in diameter. Also, the particle size one may achieve by this method has in practice been limited to $2 \mu\text{m}$ because of difficulties with coalescence and new formation of particles.

The present paper describes a newly developed method for production of monodisperse particles in the size range up to $20 \mu\text{m}$. The method implies a two step procedure. In a first step the particles are swollen with a water insoluble low molecular weight compound (2) under conditions which allow the transport of 2 through water to become absorbed in the particles. Then the monomer (1) is added under conditions where compound 2 cannot, because of its low solubility in water, become desorbed from the particles. The presence of compound 2 in the polymer particles in a v/v ratio 2 to polymer of 1:1 lead to that the swelling capacity of the particles increases to a v/v ratio up to 500 in comparison with 2:1 for pure polymer particles.

This two step swelling method allows the formation of monodisperse particles of $5 \mu\text{m}$ directly in one operation starting out from particles of $0.5 \mu\text{m}$.

Processes and applications of different types of large monodisperse particles are discussed.

WATER BORNE WIRE ENAMELS

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Wire enamel industry, as it is existing today, is largely dependent upon petrochemical sources for its raw materials. Solvents, most essentially cresols and solvent naphtha, are also from petrochemical origin. Although the traditional solvent based systems have held the field for many years, the recent survey emphasizes that environmental and safety regulations coupled with the uncertainty of supply of petrochemical based raw materials are forcing the industries towards developments in water borne coatings, high solid coatings and powder coatings.

Water based coating may be described as coating in which the resin binder is present in dissolved, emulsified or a colloidal form. Limited information is available on commercially useful water based wire enamels, but is covered by patents. Water borne acrylic wire coatings have been known for sometime, but have no specific advantages to offer.

In view of this, work was undertaken to study the preparation of water-borne polyester and polyester/imide systems and to evaluate the product in wire enamels. Specially designed polyester resin was produced by conventional techniques, converted into micronized form by grinding and dispersed in aqueous medium with the help of specific additives. The dispersion obtained could be applied on copper wire using conventional coating system and it was observed that because of high solids the required thickness of enamel could be built up with less number of passes, in addition to the advantages of cost reduction, non-toxicity and pollution control due to elimination of solvents.

Enamelled wire thus obtained were tested for adhesion, flexibility, heat shock, scrape resistance, thermo-plastic flow (cut-through temperature), dielectric strength, solvent resistance and cure test according to standard specifications and were found to pass most of the characteristic requirements of class F insulation material, (continuous operation at 155° C) when compared with conventional polyester enamel.

Work was further extended to prepare water-borne polyester-imide enamels. Polyester and polyester-imide resins were also modified using tris (2-hydroxyethyl) isocyanurate (THEIC). These resins were converted into water borne systems and

coated on the wires, by standard methods though the evaluation is in progress, they are expected to be suitable for class H insulation (180°C).

Techniques are also being worked up to develop dispersion in extremely fine particle size by direct precipitation method which would also help the molecular weight distribution control of the final resin together with stability of such water borne enamels necessary for coating operation.

POLYMER IMPREGNATION OF FERROCEMENT

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Ferrocement is a highly versatile form of reinforced concrete with well dispersed steel mesh reinforcement. The porosity in cement mortar was taken advantage of and ferrocement specimens were impregnated with styrene monomer and polymerised in-situ. The mechanical properties and failure modes of unimpregnated and impregnated ferrocement were studied. To evaluate base strength values plain cement mortar and impregnated cement mortar were also tested. The effect of polymer impregnation on fibre-matrix interface strength was evaluated.

Polymer impregnation of cement mortar results in a material with increased strength (factor of 3). On impregnating the ferrocement specimens, improvement in tensile and flexural properties is noted. Stress at first crack increases by a factor of 3 both for tensile as well as flexural specimens. Impregnated ferrocement has linear elastic behaviour upto visible crack stress. The ferrocement specimen failed in multiple fracture mode. Failure occurs by delamination. The impregnated specimen failed with single fracture and failure was controlled by the fibre fracture. Photo micrographs indicate the presence of polymer at the fibre matrix interface. Polymer impregnation leads to low water absorption and increased corrosion resistance.

CRITICAL RELIABILITY PARAMETERS IN SILICONES PROCESSING

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The important parameters in the processing of silicones have been described. The properties and applications of silicones in aerospace and electronic industries have been discussed. An equation has been formulated for the reliability of the system in terms of the reliability parameters of the individual steps in processing of silicones. The necessity of further improvement of the processing techniques to achieve better properties has been brought out in the light of the potential applications of silicones. Experimental result on aerospace grade silicone processing have revealed the value of the reliability of silicone, S_R as follows:

$$S_R \geq 0.997 \quad \dots\dots (1)$$

A new technique of relating cost reliability, C_R with S_R has been developed for economic production of such advanced silicones aiming at the following relations

$$C_R \approx S_R \approx 1.0 \quad \dots (2)$$

Further, the problems associated with achieving the reliability targets indicated in eqn. (2) will be discussed.

PHTHALIC ANHYDRIDE BASED CATION EXCHANGE RESIN FROM N-VINYL CARBAZOLE

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A condensation product based on phthalic anhydride and N-vinyl carbazole has been prepared and processed into a sulfonic acid cation exchange resin. The resin produced has been characterized by measuring its total and salt splitting capacities and by studying its thermal characteristics, rate of exchange and behaviour to pH metric titration.

COPOLYMERS OF POLYSTYRENE GLYCOL AND GLYCERYL PHTHALATE RESINS IN SURFACE COATINGS

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A new approach for synthesis of alkyds containing polystyrene chain has been described. These copolymers can be closely related to styrenated alkyde already known in the surface coating field as an improved film former.

Polystyrene glycol was first synthesized and glyceryl phthalate resins were then prepared. Polystyrene glycol replaced a part of glycerol in the esterification reaction with phthalic anhydride. The products obtained from this approach were found to exhibit better physical and chemical properties as compared to those of conventional styrenated alkyd.

RADIATION INDUCED POLYMERIZATION OF VINYLIDENE CHLORIDE IN SOLUTION

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The polymerization of vinylidene chloride in benzene, chloroform and bromoform solvents has been carried out using gamma rays as initiators. Both rates of polymerizations and molecular weights of the resultant polymer in different systems have been determined.

The rates of polymerizations R_p were found to follow the order R_p (bromoform) $>$ R_p (chloroform) $>$ R_p (benzene). The mechanism of polymerization seems to be bimolecular. The molecular weights ranged from 3000 to 7000 and followed same order.

M_v (bromoform) $>$ M_v (chloroform) $>$ M_v (benzene).

The results are explained by the chain transfer mechanism to the solvent in all the three systems studied.

ON THE USE OF THE MAYO EQUATION IN CATIONIC POLYMERIZATION

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The applicability of Mayo equation in a cationic polymerization system, where ion pair contribution to R_p is insignificant compared to free ion contribution, has been discussed. It has been shown that even under such circumstances the concentration of ion pairs relative to that of free ions may not be insignificant and that the variation of the relative concentration of these two species with total active center concentration may be large enough to render the Mayo equation inapplicable, unless care is taken to maintain a constant active center concentration independent of monomer concentration. The use of Mayo equation in Lewis acid co-initiated systems has also been discussed.

POLYMERIZABLE ULTRAVIOLET STABILIZERS

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Polymers when exposed to the atmosphere undergo deterioration. This deterioration can be prevented by use of ultraviolet stabilizers. However, these stabilizers being low molecular weight compounds have tendency to migrate out of the substrate during its service life. We have synthesised these stabilizers with reactive sites in the moiety which can be grafted to the polymer backbone during the processing of the polymer or copolymerised with the monomer during polymer formation stage. Two such stabilizers viz., 3-hydroxy-4-benzoyl-phenyl-acrylate and 3-hydroxy-4-benzoyl-phenyl-methacrylate have been synthesised and melt grafted onto polypropylene. Extraction studies have shown that 12% of-acrylate and 32% -methacrylate derivatives of 2-hydroxybenzophenone get chemically bound to the polymer backbone.

PHOTOPOLYMERIZATION OF N, N¹ -METHYLENE BISACRYLAMIDE IN AQUEOUS SOLUTION BY POTASSIUM TRISOXALATO-FERRATE (III)

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Results of a kinetic study on photopolymerization of N, N¹-methylene bisacrylamide by potassium trisoxalato-ferrate(III) in aqueous sulfuric acid medium, (pH = 0.7) by use of light of 365 nm wavelength at $30 \pm 0.1^\circ\text{C}$ are presented. All reactions were carried out under completely deaerated conditions. Certain important features of the photopolymerization are described. The rate of polymerization, $-d[M]/dt$, was followed by gravimetric estimation of polymer formed and rate of ferrous ion production, $d[\text{Fe}^{2+}]/dt$ by spectrophotometric estimations of Fe^{2+} -0-phenanthroline complex. $-d[M]/dt$ was found to be directly proportional to $[M]$ and $I^{1/2}$ universally proportional to $[C]^{1/2}$, where M, C and I refer to monomer, complex and light intensity respectively. $d[\text{Fe}^{2+}]/dt$ was found to be directly proportional to $[C]$ and I. A reaction scheme is shown that can explain the observed kinetic orders.

APPLICATION OF VARIOUS VISCOSITY THEORIES TO THE VISCOSITY DATA OF METHYL METHACRYLATE-ACRYLONITRILE RANDOM COPOLYMERS

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K_0 , Flory's constant related to unperturbed dimensions, values are evaluated for methyl methacrylate-acrylonitrile random copolymers of four different compositions, viz., 0.289 mole fraction (mf) of acrylonitrile (AN) designated as MA1 0.415 mf of AN:MA2; 0.566 mf of AN:MA3 and 0.657 mf of AN:MA4, using Flory-Fox (FF), Kurata Stockmayer (KS) and Inagaki-Ptitsyn (IP) methods and compared with the K_0 values obtained by Stockmayer-Fixman (SF) method. K_0 values are seen to be less in solvents, which have larger α -Mark Houwink (MH) exponent values. K_0 versus $1/\alpha$ yields a straight line, with a common intercept corresponding to $\alpha=0.5$, i.e. 0 condition. This appears to provide a more, reliable estimate of K_0 for this copolymer system.

COPOLYMERISATION OF STYRENE AND ACRYLONITRILE IN SUSPENSION SYSTEM: PROPERTIES OF THE SYSTEM AND THE POLYMER IN RELATION TO THE DEGREE OF CONVERSION

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Copolymerisation of styrene-acrylonitrile (SAN) in suspension is of great significance since the reaction becomes complicated due to the presence of acrylonitrile (ACN) and its partial solubility in water. Not only ACN increases the overall rate of polymerisation of styrene but also creates problems in keeping the system stable. The dissolved ACN slowly diffuses out from aqueous phase to organic phase and at the end of copolymerisation less than 0.1% was found dissolved in aqueous phase. The viscosity and surface tension of the aqueous phase during the early stages of copolymerisation could not be determined accurately because of presence of emulsion yet decrease in viscosity and pH and increase in surface tension upto about 50% conversion was observed. Beyond this conversion these values were found more or less constant. The reason for this phenomena is attributed to adsorption of stabilisers on the globules upto 50% conversion due to its tacky nature and no additional adsorption beyond this conversion.

The increase in viscosity of the organic phase was very high which was determined separately by preparing polymer-monomer solutions. However, the average molecular weight and ACN content of the polymer separated at different degree of conversion were found to be uniform.

MORPHOLOGY AND PROPERTIES OF POLYBUTYLENE TEREPHTHALATE

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Polybutylene terephthalate (PBT) is a recent addition to the engineering thermoplastic polyester materials. Its well balanced properties like mechanical strength, moldability and rapid crystallization has made it popular. This gives rise to the need for the study of its structure and properties.

Gilbert & Hybart have studied the crystallization kinetics and mechanism for a series of aromatic and aliphatic polyesters. Pratt and Hobbs have conducted a comparative study of crystallization kinetics for polyethylene terephthalate, polybutylene terephthalate and polypropylene using depolarized light intensity and DSC techniques. Pratt and Hobbs have also reported some results on skin-core morphological studies on PBT. Recently, Misra and Stein have conducted detailed and systematic studies on PBT. Most of their work was on melt crystallization. It was reported that PBT shows two types of superstructures depending upon the thermal history of the sample. It has also been reported that PBT remains transparent when crystallized from an amorphous glassy state but no details were presented. In this paper we present some properties of PBT when crystallized from its amorphous glassy state.

POLYCYCLOTTRIMERS - NOVEL THERMOSTABLE PLASTICS

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The polycyclotrimerization of difunctional isocyanates (or NCO-terminated prepolymers) induces polymer networks containing heterocyclic, thermally stable isocyanurate rings as crosslinks. The kinetic measurements of degradation of model isocyanurates showed that decomposition of isocyanurate rings starts at temperatures above 400°C. It was found that the crosslink density of polycyclotrimers can be varied by the copolycyclotrimerization of difunctional isocyanates (prepolymers) with monofunctional isocyanates. The catalysis of polycyclotrimerization of isocyanates is a key to the successful preparation of the isocyanurate based copolycyclotrimers. It was found that the structure of isocyanates, nucleophilicity of catalysts, relative permittivity of solvent system and specific solvation of catalysts play an important role in the preparation of polycyclotrimers. Copolycyclotrimers of isocyanates and their block copolymers with polyoxazolidones can find applications in preparation of high temperature resistant cellular plastics, coatings and elastomers.

RECENT EXPERIMENTS ON RUBBER-LIKE ELASTICITY

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It is possible to prepare model networks of polydimethylsiloxane (PDMS) by two highly selective techniques: (i) the end-linking of hydroxyl-terminated PDMS chains of known molecular weight and molecular weight distribution, by means of either a tetrafunctional or trifunctional silicate and (ii) the cross-linking of PDMS chains through vinyl side-chains located in known amounts and in known distribution along the chains. PDMS networks were thus obtained and studied with regard to their stress-strain isotherms in elongation and their equilibrium swelling in a thermodynamically good solvent. The results provide important information on the dependence of elastic properties on (i) the average molecular weight of the network chains, (ii) the network chain length distribution, (iii) the functionality of the network junctions and (iv) the limited extensibility of the network chains.

BASALT FIBERS

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Continuous mineral fibers, suitable for reinforcement of polymers, have been produced from basalt rocks of the Pacific Northwest. Working with a range of compositions in basalts obtained from different locations, fibers exceeding 3 GPa in strength (450,000 psi) and having a tensile modulus in the range 78-90 GPa (11-13 million psi) have been drawn. Evaluation of basalt fiber-epoxy composites has shown that the reinforcement efficiency of basalt fibers is high. The interfacial bond strength in basalt fiber-polymer systems has been investigated using a single fiber pull-out test method.

The experimental basalt fibers, about 90 μm in diameter, were specially drawn for fiber pull-out tests from basalt rock of the following compositions: SiO_2 : 49.10%; Al_2O_3 : 13.80%; TiO_2 : 3.16%; Fe_2O_3 : 4.00%; FeO : 11.98%; MnO : 0.21%; CaO : 9.43%; MgO : 5.25%; K_2O : 1.26%; Na_2O : 3.09%; P_2O_5 :

: 0.68%. The fibers were treated with a number of ionic and nonionic silane coupling agents under a variety of experimental conditions changing solution pH and concentration, ageing time, and fiber treatment time. The values of pull-out stresses were measured for treated and untreated fibers embedded both in epoxy and polyester matrix resins. The surfaces of treated and untreated fibers and those of pulled-out specimens were examined by scanning electron microscopy. Details of debonding and modes of failure were revealed in scanning electron micrographs.

CARBON FIBERS-REINFORCING COMPONENT FOR ADVANCED MATERIALS

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The high reinforcing potential of carbon fibers is more and more recognized. The types of carbon fibers available in the market and the steps leading from the reinforcing component to different composite parts are reviewed. In this respect essential aspects regarding the matrice material, semi-finished products and the engineering of composites are outlined.

For some most important carbon fibre reinforced material the requirements of the industry are compared with typical properties achieved today. The difference between both positions shows clearly the tests for the future.

Based on the promising property-spectrum of carbon fiber reinforced composites various applications are discussed. Finally, a view into the future shall give some impression, how carbon fiber consumption and price may develop.

THE POTENTIAL OF COMPOSITES WITH HOLLOW FIBERS IN AEROSPACE STRUCTURE

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Minimum weight is an essential prerequisite for the successful performance of aerospace systems. Future progress towards this goal will probably center on the optimization of load-carrying structures. In this context, the application of composite materials already plays a major role since they combine high strength and stiffness properties with low densities. A further step in this direction is the development of hollow glass and hollow carbon fibers which, imbedded in resin matrices, tend to reduce the density of such composites to less than 1 g/cm³. A promising approach also is the mixture of hollow glass and solid carbon fibers.

This paper reports on the current state of the art of hollow-fiber and mixed composites from the view point of structural applications. Following a brief discussion of preliminary considerations, experimental results are presented in the form of specific strength and stiffness parameters. All data relate to unidirectionally reinforced laminates under static loads.

THE EFFECT OF HEAT-SETTING ON THE STRUCTURE AND PROPERTIES OF POLYACRYLONITRILE FIBERS

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The structure of polyacrylonitrile fibers of different chemical composition, drawn in hot water of 100°C, was affected by tensionless heat-setting, both with dry heat and with saturated steam. For determining the changes that took place, density measurements, X-ray analysis, mechanical tests and studies of the dyeing kinetics were carried out.

The experimental results can best be explained by assuming a kind of two-phase structure, in which better ordered regions. By treating with hot air, the order was improved for all the polymers under examination, i.e. the better ordered regions were enlarged at the expense of the less ordered ones. From the point of view of X-ray analysis, this comes from the decline in the half-width of the main equatorial reflection and also from the decrease in the dyeing rate.

Treatment with saturated steam has less of an influence on the better ordered regions and the increase in the order—as established by X-ray analysis—is only more or less comparable with the hot air in the case of the fibers with the highest comonomer content. However, their effect on the less ordered regions is much greater, as is indicated by the higher relaxation, the higher shrinkage, the flattening of the stress/strain curves and the increase in the dyeing rate. In analogy with semicrystalline polymers, it can be deduced from this, that, when working with saturated steam, there is a considerable loosening of the less ordered regions, with the result that they can be more easily distinguished from those of higher order. This effect becomes more pronounced with increasing comonomer content—higher chain mobility.

The practical significance of these relationships regarding the influence of heat treatment on the fibre structure is certainly that these findings can help to answer the question of how to find the optimum procedure for heat-setting a particular textile of polyacrylonitrile fibres so as to produce the desired quality in the final article.

DEVELOPMENT OF INDIGENOUS TECHNOLOGY FOR PRODUCTION OF FIBER GLASS

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The 'E' type glass fibers possess high mechanical strength, moderately high elastic modulus, favourable electrical properties and excellent weathering resistance. These account for their extensive use in the production of fiber reinforced plastics. The major difficulties involved in melting this type of compositions are (i) excessive corrosion of alumino-silicate refractories in the melting furnace and (ii) high melting temperature and slow melting rate of the composition.

With a view to overcome these difficulties systematic studies were carried out on melting and fiberisation characteristics of glasses in the system $\text{MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2$, in relation to their composition. The devitrification range and high temperature viscosity of the glasses were measured to ascertain the melting behaviour and the temperature at which the fibers are to be drawn. The work led to the development of a modified fibre glass composition which could be melted using low cost alumino silicate refractories. The glass could be successfully fiberised from ceramic bushing at the IIT, Kanpur. The properties of the fibres compared favourably with those of the commercial 'E' glass.

The rate of melting of the glass composition could be substantially accelerated by incorporating the raw materials having high chemical reactivity and, therefore, faster melting rate. The reactive ingredients are cheap and indigenously available. The melting temperature of 'E' glass was brought down from 1550° to 1450°C and marbles were produced under commercial conditions.

An appropriate technology has been developed for production of fiber glass in small scale sector. The process involves the use of glass rods from which the fibers are directly drawn without the use of any bushing. The composite specimens prepared with these fibers were tested for their mechanical properties and the results are satisfactory. So far the fibres were produced in pilot plant scale from the 'A' type and neutral glass rods, and commercial viability of the process has been established. Further work is currently under progress for production of glass fibers from the modified 'E' glass composition developed at the Institute.

POLYMER SYSTEMS FOR CONTROLLED RELEASE OF ORGANOTIN TOXIN

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An investigation of organotin polymers capable of simultaneously providing long term fouling resistance and useful engineering properties is discussed. New synthetic routes have been developed for organotin epoxy polymers utilizing (i) the crosslinking reaction of diepoxides with the free carboxyl groups present on a base polymer partially esterified with tributyltin oxide, (ii) the copolymerization of organotin acrylates and methacrylates with vinyl monomers carrying functional

groups susceptible to crosslinking and (iii) simultaneous vinyl and epoxy crosslinking reactions. Polymer syntheses for crosslinking under ambient conditions have also been developed based on the reactions of aziridines or tributyltin esters of ω -amino acids. The network structure was varied, and the average separation, length and type epoxy crosslinks or pendant organotin groups were altered by appropriate changes in synthetic routes and reactants. Concurrent changes in measured strength, fracture toughness and dynamic mechanical behaviour of the polymer systems have been correlated with the structural variables employed. Laboratory study of leaching and biotoxicity and performance tests in marine environments have identified the organotin species released and revealed the influence of matrix characteristics on controlled release. The results are fitted to the bulk abiotic cleavage model.

NEW TECHNIQUES OF POLYMER CHARACTERIZATION USING THE ULTRACENTRIFUGE

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Two new evaluation techniques for polymer characterization using the ultracentrifuge were developed viz.,

(i) The automated reading of the interference photographs yielded an extensive data basis which made it feasible to extract more information about the polymer than in the earlier experiments. The method may be used for measurement of molecular weight of non-ideal solutions of polymers, of the preferential adsorption onto polymers in mixed solvents and under some circumstances of the polydispersity of polymer samples.

(ii) Detailed analysis of the diffusion experiment performed in the synthetic boundary cell yielded several important pieces of information.

- (a) Refractive increment of polymers at constant chemical potential.
- (b) The diffusion coefficient of polymer samples.
- (c) Mutual diffusion coefficients in solvent-solvent mixtures.

RAMAN SPECTROSCOPIC STUDY OF POLYACRYLAMIDE GELS

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Polyacrylamide gels crosslinked with N, N' bis methylene acrylamide are prepared using varying amounts of crosslinking agent and catalyst concentration. It is found that variation of catalyst concentration not only changes the rate of reaction, as believed by earlier workers (as observed by Ruchel *et al.* on the basis of SEM), but also affects the properties of gels. The decrease in the crosslinking agent and increase in catalyst concentration show similar aggregate effect on the physical appearance of gels. Their physical appearance varies from an elastic gel to a viscous fluid. The attempt has been made to explain the process of gelation using laser Raman spectroscopy. The Raman spectra of polyacrylamide, monoacrylamide and gels have been recorded in the region of 200-1800 cm^{-1} . It has been observed that gel matrix is dominantly stabilized by water polymer hydrogen bonding network. The high molecular weight polyacrylamide appears to be a limiting case of lower crosslinked gels. The higher TEMED concentration leads to very short chains, which are unable to form a gel for a given concentration of bisacrylamide.

IRREVERSIBLE PHASE TRANSITION IN MACROMOLECULES

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Melting and devitrification are rarely close to thermodynamic equilibrium in linear macromolecules. By careful study of the irreversible processes involved in these phase transitions it is possible to characterize not only the chemical nature of the material on hand but also its thermal and mechanical history. Many example of irreversible phase diagrams and hysteresis phenomena will be given.

ELECTRICAL CONDUCTION IN THIN FILMS OF POLYVINYL ACETATE

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Thin films of polyvinylacetate in the thickness range 1000 - 15000 Å were grown by solution growth technique. The current-voltage characteristics of these films were studied at different temperatures to determine the conduction mechanism. Some of the intriguing parameters such as charge carrier density, carrier mobility and the activation energies have been evaluated using these results.

THERMODYNAMIC EVIDENCE FOR POLYMERIZATION OF ALCOHOLS

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The thermodynamic property, excess volume, was measured for binary mixtures of 1-propanol, 1-butanol, 1-pentanol and 1-hexanol with the inert solvent, n-heptane. The excess property was directly measured at 303.15K using a dilatometer described by Rao and Naidu. The method offered an accuracy of $\pm 0.003 \text{ cm}^3 \text{ mol}^{-1}$. Excess volumes for the four binary mixtures are positive over the whole range of composition. These results suggest that the common component, n-heptane, exerts structure breaking effect on polymers present in pure alcohols. Thus the thermodynamic property provides evidence for the polymerization of alcohols through hydrogen bonding in the pure state. This observation is in line with similar inferences drawn about polymerization of alcohols in terms of their physical properties and spectra of their solutions.

The numerical values for excess volume of the four mixtures fall in the order: 1-propanol > 1-butanol > 1-pentanol > 1-hexanol. This order suggests that the degree of polymerization of the four alcohols decreases from 1-propanol to 1-hexanol.

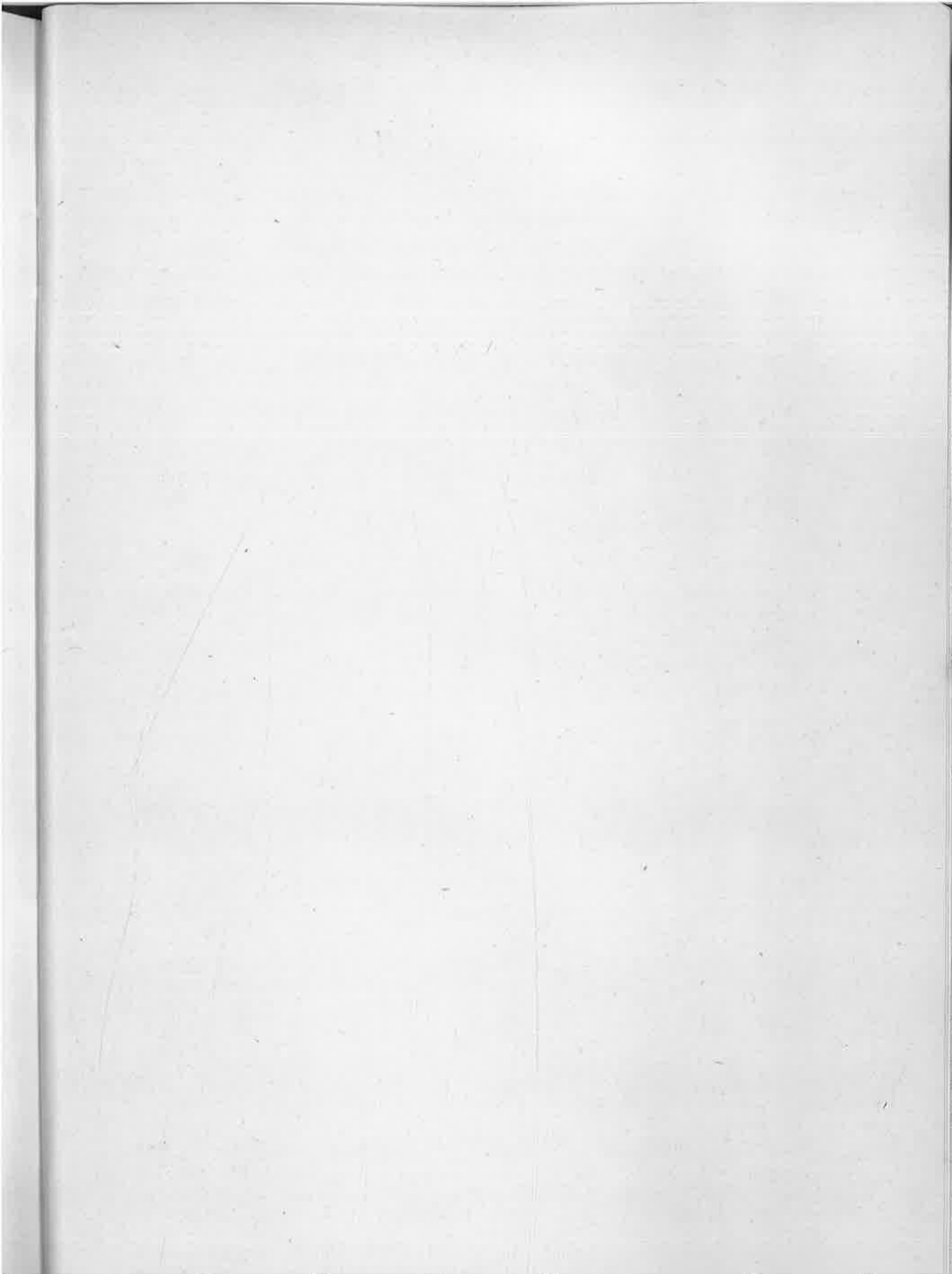
ULTRASONIC RELAXATION STUDIES IN DICYCLOHEXYLAMINE

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The ultrasonic absorption measurements have been undertaken in this laboratory in the frequency range of 0.5 to 45 MHz and in the temperature range of 333 to 413°K. Low frequency pulse gear, high frequency pulse gear and streaming techniques developed in these laboratories have been employed for the measurement of absorption. The streaming technique has been used in the frequency range 0.5 to 5 MHz with an accuracy of $\pm 5\%$. The high frequency pulse gear and low frequency pulse gear have been employed in the frequency range 5 to 45 MHz with an accuracy of $\pm 2\%$. The ultrasonic velocities are measured with an interferometer technique with an accuracy of $\pm 0.003\%$. Details of the techniques developed in the laboratories will be presented in this paper.

The absorption and velocity data obtained by using above techniques have been used to confirm relaxation in dicyclohexylamine. The energies associated with equatorial and axial conformers of dicyclohexylamine have been evaluated using the ultrasonic relaxation data. The results are compared with other substituted six-membered rings.



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