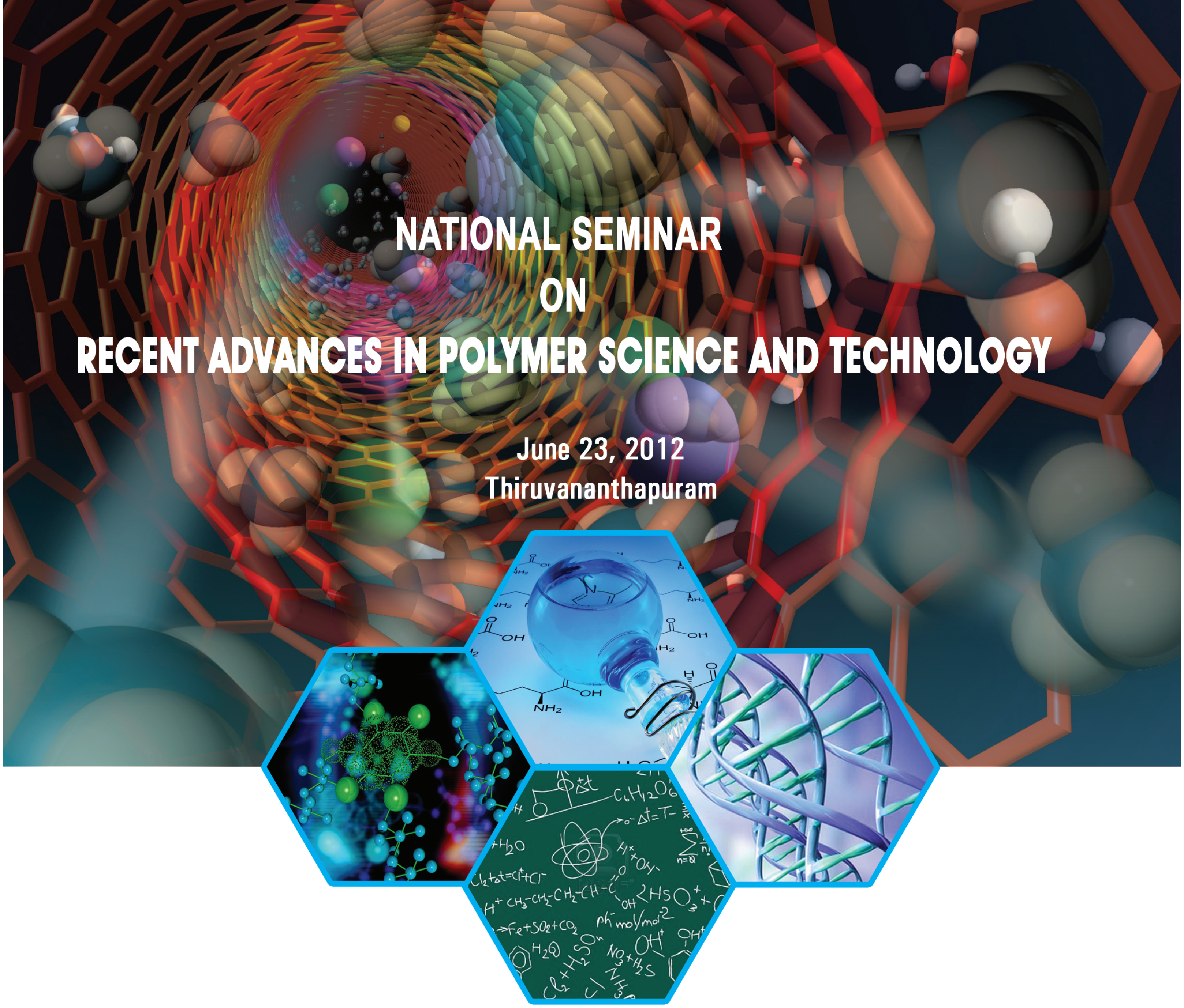

NATIONAL SEMINAR
ON
RECENT ADVANCES IN POLYMER SCIENCE AND TECHNOLOGY

June 23, 2012
Thiruvananthapuram

SOUVENIR
&
Book of Abstracts

Organized by

Society for Polymer Science India,
Thiruvananthapuram Chapter

Department of Chemistry,
Mar Ivanios College, Thiruvananthapuram

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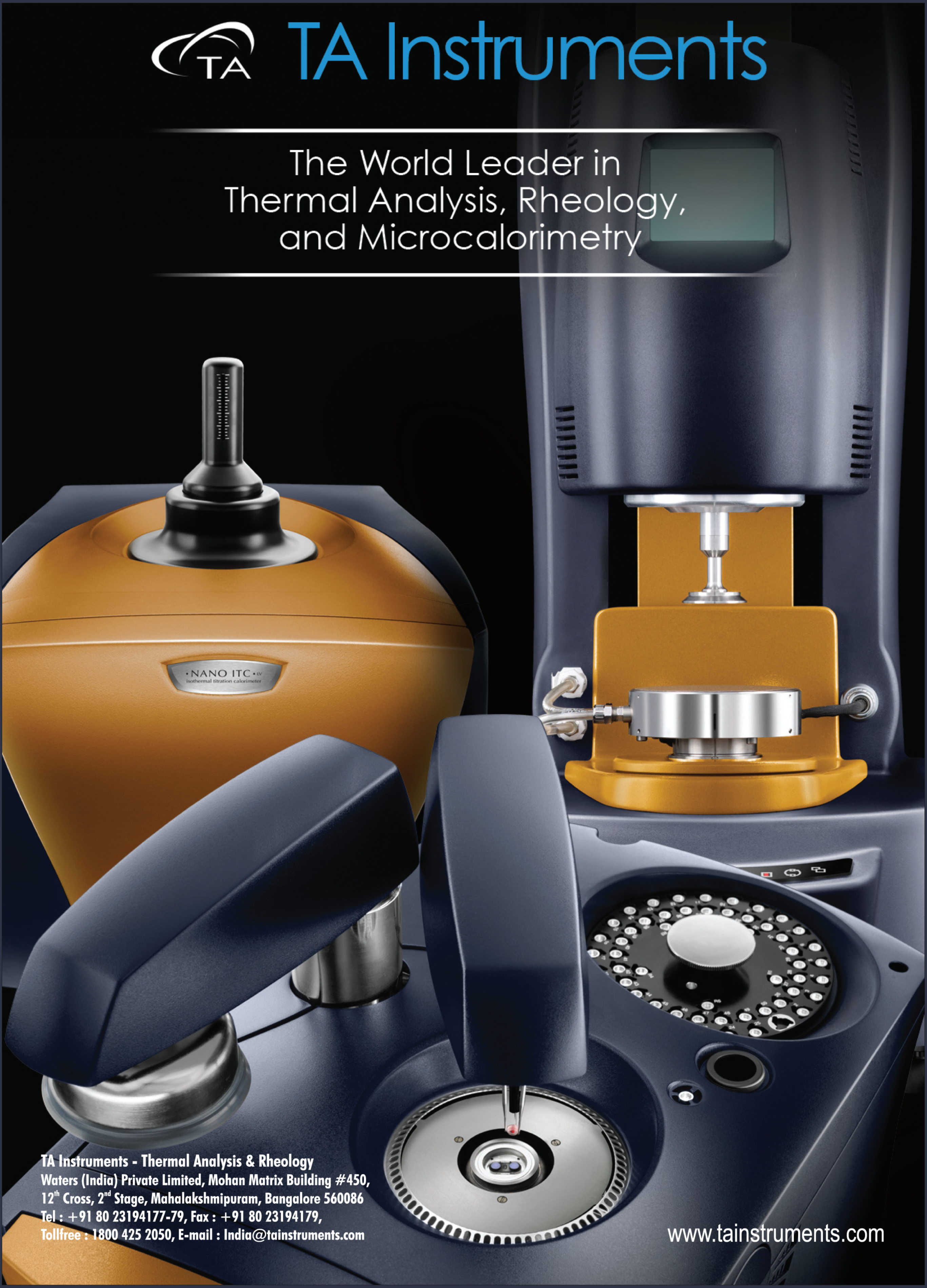
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National Seminar
on
Recent Advances in Polymer Science and Technology

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Foreword

In line with its objectives, the Society for Polymer Science India, Thiruvananthapuram chapter organizes a one-day seminar on **Recent Advances in Polymer Science and Technology** exclusively for the benefit of the student community. The national seminar is scheduled on 23rd June 2012 at Trivandrum in association with Mar Ivanios College, Trivandrum. The seminar focuses on introducing latest advances in the field of polymer science and technology/material science to postgraduate students, research scholars and young researchers by eminent scientists and researchers in this field. It also encourages contributed papers from students and researchers to be presented in the form of posters. In the seminar, the students and young researchers get a unique opportunity to interact with fellow researchers and eminent polymer/material scientists of the country. Best posters will be duly awarded in the Seminar.

Invited lectures by prominent professionals, Dr. Sivaram, Dr. Vijaya Mohanan Pillai, Prof. Bhuvanesh Gupta and Prof. Dhamodharan are expected to boost the awareness on the latest trend in the field among the youngsters and help them mould themselves in to outstanding polymer professionals in future.

The seminar could be organized with the fervor of this kind thanks to the *bon geste* of the resource persons and the support of the Kerala State Council for Science, Technology and Environment, M/s Toshniwal Brothers and M/s TA Instruments. The association of the chemistry department of Mar Ivanios College adds more academic air to the event.

I wish all the delegates an eventful day.

(C. Gouri)

Secretary, SPSI, Thiruvananthapuram Chapter

PROGRAMME

08:30 - 09:00 : Registration

09:15 – 10:30 : Inaugural Session
Inaugural Address
The Science of Polymers : Past, Present and Future
Dr. S. Sivaram
CSIR Bhatnagar Fellow,
National Chemical Laboratory, Pune

10:30 - 11:15 : Plenary Lecture -1
Design of Nanocomposites for
Polymer Electrolyte Fuel Cells
Dr.Vijayamohanan K Pillai
Director, Central Electrochemical Research Institute,
Karaikkudi

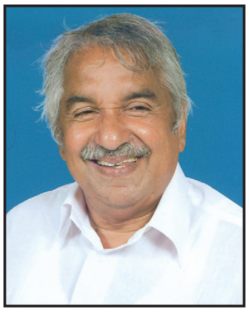
11:15 - 11:30 : Tea

11:30 - 12:15 : Plenary Lecture -2
Controlled Radical Polymerizations -Future Perspectives
Prof. R. Dhamodaran
Indian Institute of Technology, Madras

12:15 – 13:00 : Plenary Lecture - 3
Prof. Bhuvanesh Gupta
Indian Institute of Technology, Delhi

13:00 - 14:00 : Lunch
14:00 - 15:30 : Poster Session

15:30 - 16:00 : Concluding Session and Award Distribution



OOMMEN CHANDY
CHIEF MINISTER
KERALA

13/06/2012

Message

I am happy to learn that *Society for Polymer Science, Thiruvananthapuram Chapter (SPSI)* would be organizing a National Seminar in association with Mar Ivanios College on 'Recent Advances in Polymer Science and Technology' in Thiruvananthapuram.

I hope that this seminar would benefit the participants, especially students and researchers from Kerala.

Polymer science, which is a part of material science, has undergone notable advancements in the past. In modern day life, application of polymer and the use of products based on that have proven its value and advantages. I believe that the sustained contribution of SPSI in the field of Polymer Science will be of great help to the novice, the initiated and also to the researchers.

My best wishes for the successful conduct of the seminar and also for the activities of SPSI.

OOMMEN CHANDY

Office : Secretariat, Thiruvananthapuram-695 001
Phone-Office : 2333610, 2333812, 2333197, 2332148, 2333214, 2332682, 23321
Fax : (0471) 2333489 Resi : (0471) 2345600, 2342602 & (0481) 2351135

UNIVERSITY OF KERALA
Prof. A. Jayakrishnan, Ph.D., F.A.Sc.,
Vice Chancellor

Tuesday, June 12, 2012

MESSAGE

SPSI is one of the premier professional scientific societies of the country instituted with the intention of promoting advancement in the field of Polymer Science and Technology. It also serves as a forum for interaction among the polymer scientists, engineers and technologists in the R&D laboratories, universities and industries across the country. Its objective includes promoting science education and inculcating research interests among students. The Thiurvananthapuram Chapter regularly conducts workshops / seminars on specified areas for the benefit of the student community.

It is heartening to learn that in keeping with its tradition, SPSI is organizing a one day seminar on **Recent Advances in Polymer Science and Technology** exclusively for the benefit of the student community. Invited lectures by prominent persons like Dr. Sivararm, Prof Bhuvanesh Gupta, Dr. Vijaya Mohanan Pillai and Prof. Damodharan will add a different flavor to the event.

While appreciating the good gesture of SPSI, I wish the seminar all the best and the student delegates a sumptuous intellectual feast.

DR.A.JAYAKRISHNAN

hiruvananthapuram, Kerala, India-695034, *Tel:*91-471-2306634 *(O)*, 91-471-2353309 *(R)*, *Fax*-91-471-2302898,
E-mail: vicechancellor@vsnl.net, *Web:* www.keralauniversity.edu

MESSAGE

President SPSI

I am extremely pleased to note that The Society of Polymer Science, India (SPSI), Thiruvananthapuram Chapter in association with Mar Invanios College, Thiruvananthapuram is organizing a national seminar on Recent Advances in Polymer Science and Technology on 23 June 2012.

SPSI is one of the premier professional scientific societies in the country, instituted to promote professional interactions amongst polymer scientists and engineers. SPSI, since 1991 has anchored a National Symposium, held once in two years, which has become a platform to bring students, faculties and scientists working in industry together for scientific discussions. SPSI has also become a window of the Indian Polymer Science to the external world and is a founding member of Federation of Asian Polymers Societies (FAPS) comprising likeminded organizations in Japan, Korea, China, Singapore and other East Asian Countries

SPSI functions through several regional chapters. The Thiruvanathapuram Chapter is the largest and the most active amongst all our chapters. We are proud of the dedicated band of scientists who have sustained the activities of the Thiruvananthapuram Chapter over the years.

The domain of polymer science, like many other branches of science, is in a great state of flux. The character of the discipline is rapidly changing, both in industry and academia. Polymer Science should be now considered as an enabling discipline, which creates value to either biology or material science. Consequently, areas such as functional polymers, bioinspired polymers, organic polymers hybrids with inorganic materials are assuming greater importance. From an era, when polymers touched our life visibly in every walk of life, polymers are increasingly becoming invisible to us. In the future, polymers will continue to be important in many critical applications, such as, in energy conversion, human well-being, water conservation, environmental remediation, and communication and information technology. Consequently, polymer scientists will be called upon to work with scientists from many other disciplines, to create new solutions to meet the needs of the people and the planet.

Polymer Science as a discipline is less than a hundred years old. In this short span it has traversed a considerable distance and has become a ubiquitous part of our everyday life. However, the future appears even brighter, as the world searches for solutions to some of the most complex problems faced by humankind.

I wish the seminar all success.

S. Sivaram

(S. Sivaram)

MESSAGE

President

SPSI Thiruvananthapuram Chapter

The Society for Polymer Science India, Thiruvananthapuram chapter is a unique body committed to the cause of science in general, and polymer science in particular. Polymer is the best friend of man that has taken us from the stone-, bronze-, steel age to the current polymer age. Our life would never have been what it is today but for advances in the field of polymers. The revolutions in the fields of space science, biomedical, electronics, telecommunication, transportation, defense etc have become reality due to evolution in concept and practice of polymers. However, there are many technological challenges and social concerns that this branch of science is facing.

The main objectives of SPSI are promotion of polymer technology by serving as a nodal point for close coordination among researchers, industrialists, professionals, academicians, and young scientists to address the issues in this area and to alleviate fear of plastics from the minds of some.

In this backdrop, SPSI in association with Mar Ivanios College organizes a one-day national seminar on Recent Advances in Polymer Science and Technology on 23rd June 2012. The beneficiaries are principally young students and researchers.

I am sure that the seminar will be a great success and will meet its objectives.

Dr. C.P Reghunadhan Nair
President

Address for Correspondence
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Thiruvananthapuram-695022. Phone: 0471-2565689 (O), 0471-2362112 (R). Email: cp_reghunadhannair@vssc.gov.in

Estd : 1949

MAR IVANIOS COLLEGE

Re-assessed and Re-accredited (Third Cycle) with the Highest Grade, 'A' by NAAC
CPE (College with Potential for Excellence) Status conferred by UGC

Dr. K. M. Francis M.A. (Eco.), M.A. (Hist.), M.Phil., Ph.D.
Principal

MESSAGE

I am pleased to know that the Society for Polymer Science, India, Thiruvananthapuram Chapter and the Department of Chemistry, Mar Ivanios College are jointly organizing a National Seminar on Recent Advances in Polymer Science and Technology on 23 June, 2012.

Mar Ivanios College, established in 1949, is one of the pristine institutions in Kerala which has made significant contributions in the field of quality and value based higher education. This academic institution has been able to mould numerous intellectuals with a deep sense of human values and patriotism.

The Department of Chemistry in Mar Ivanios College is renowned for its meritorious output in academics normally securing the top ranks in UG and PG degree examinations conducted by the University of Kerala and in the broad area of research activities ongoing within the Department. This seminar would definitely enable the researchers and PG students to listen to and interact with some of eminent Scientists working in the field of Polymer Science and Technology. I wish the seminar all success.

With warm regards,

Dr. K.M.Francis

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E-mail : ivanios@md2.vsnl.net.in • info@mic.ac.in • Website : www.marivanioscollege.ac.in • www.mic.ac.in

PLENARY LECTURES

THE SCIENCE OF POLYMERS: PAST, PRESENT AND FUTURE

Dr. S.SIVARAM
CSIR Bhatnagar Fellow
A 201, Polymers and Advanced Materials Laboratory,
National Chemical Laboratory, Pune 411008

Polymer science is a sub-discipline of chemical science that came into existence just about a century ago. In 1909, Leo Baekeland (1863-1944) introduced a material derived from phenol and formaldehyde, called Bakelite or Novolak as a replacement for Shellac, useful as an insulating material Phenol and formaldehyde had just then become available, the former from coal tar and the latter from wood distillation. However, it took another two decades before the macromolecular hypothesis of Hermann Staudinger (1881-1965) proposed in 1920 became widely accepted by the scientific community and polymers were recognized as organic molecules with covalent bonds possessing high molecular weights. Soon several bond forming reactions that had been just discovered in the first two decades of the twentieth century were applied to polymer forming reactions, leading to the synthesis of new forms of matter called poly(ester)s, poly(amide)s, poly(urethane)s, poly(vinyl chloride)s and poly(isobutylene)s, poly(butadiene)s etc.

The utilitarian aspect of synthetic polymers was quickly recognized. Large chemical corporations set up research programs to discover new polymers with useful applications. The Second World War further provided impetus to polymer science research, especially, in academia. Synthetic rubbers, free radical chain polymerization and the science of emulsion polymerization were a product of intense wartime research.

Post 1950, polymers became the key products of the burgeoning petrochemical industry, driven by the availability of inexpensive petroleum feedstocks. Chemical building blocks such as ethylene, propylene, butadiene, benzene, toluene and styrene became available and large manufacturing capacities came up throughout the world. From mere curiosities, polymers became an indispensible part of our daily life and so ubiquitous that we no longer realize how dependent we are on polymers. Today, we consume over 200 million tons of manmade organic materials with a value of over US $1 trillion, about a third of the value of the entire chemical industry.

The lecture will trace briefly the history of polymer science as well as the growth of the industry. The polymer industry has rapidly attained technological maturity. The synthetic toolboxes available to chemists have also been substantially refined; today synthesizing a polymer molecule with precision, both at molecular and supra-molecular level is no longer a challenge.

Therefore, as we conclude the first decade of the twenty first century it is pertinent to ask what is the challenge facing polymer science? How will this science address some of the most challenging problems faced by our society? Where is technology leading? Why is there a seemingly lack of exciting discoveries at the current time? What are the barriers to introducing new materials in the market? What are the new frontiers of research? Can we define some holy grails of polymer science?

The lecture will attempt to seek some answers to these questions.

DESIGN OF NANOCOMPOSITES FOR POLYMER ELECTROLYTE FUEL CELLS

Dr. Vijayamohanan K Pillai
Central Electrochemical Research Institute
CSIR-CECRI, , Karaikudi -630 006
Email: vijay@cecri.res.in

Polymer electrolyte membrane fuel cells represent one of the most promising technologies to fulfill the enormous needs of clean energy in the near future. However, the deployment of a commercially viable technology on a larger scale requires to overcome many technical barriers including new generation of inexpensive and thermally more stable membranes, non-noble and cheaper electrocatalysts especially for the oxygen reduction reaction and less expensive manufacturing processes resulting into durable membrane-electrode assembly. Currently used persulphonic acid membrane has many limitations like limited thermal stability, inadequate proton conductivity, poor mechanical strength and tedious processing and hence needs major improvement. For example, the proton conductivity of the polymer electrolyte membranes is yet to reach the desired level, which is crucial to sustain high current density necessary for many applications. We will discuss a unique approach to increase the conductivity of the widely used polymer electrolytes like nafion and polybezimidazole membranes by an order of magnitude using nanocompositeelectrolyes incorporating suitable functionalized carbon nanotubes.

The application of sulfonic acid-functionalized multiwalled (s-MWNT) carbon nanotubes to manipulate the hydrophilic domain size of Nafion membranes is explored first as an option for tuning the proton conductivity of polymer electrolyte membranes for hydrogen-oxygen fuel cells. The electrochemical impedance experiments provide preliminary evidence of increased proton conductivity, while small-angle X-ray scattering measurements line out enhanced ionic cluster domain size in these composite membranes as the central reason for higher conductivity (70A ° for the optimum composite membrane vs 50 A ° for Nafion 115) values. Scanning electrochemical microscopy indicates synergistic interaction between the sulfonic acid functional groups present in the Nafion membrane and those on the nanotube surface. More interestingly, the nanotube-tailored Nafion membranes ameliorate the performance of fuel cells as confirmed by measurements at a single-cell level, which reveal a maximum power density of 380 mW cm-higher than those of Nafion 115 (250mWcm-^{2}) and recast Nafion (230mWcm-^{2}) membranes. Thus, in addition to providing an elegant means of controlling the ionic cluster size, the strategic approach of using CNT both as an anchoring backbone for -SO3H groups to enrich proton conductivity and as a blending agent to improve the mechanical characteristics of the Nafion phase might be helpful in alleviating many critical problems associated with the use of commercial Nafion membranes.

In a similar manner the ability of phosphonated carbon nanotubes to offer an unprecedented approach to tune both proton conductivity and mechanical stability of hybrid electrolytes based on polybenzimidazole (PBI) membrane for fuel cell applications is demonstrated next. Incorporation of functionalized MWCNT increases the proton conductivity of membranes by forming a network structure which is well reflected in the fuel cell performance of composite membranes. The composite membrane with 1% P-MWCNT loading gives a power density of 780 mW/cm2 while pristine PBI membranes show only 600 mW/cm2 revealing a 35 % improvement in performance. The enhanced performance has been attributed to the formation of proton conducting networks with a domain size of 17 nm as estimated from the small angle X-ray scattering measurements. MEA impedance measurements reveal that the reduced ORR activation is the key for the improved performance along with enhanced proton conductivity. Further, the mechanical strength measurements reveal significant improvement in the yield strength and ultimate strength. For example, the ultimate strength determined for the composite and pristine membranes is 100 and 65 MPa respectively demonstrating the superiority of the composite electrolyte that suggests the synergistic role played by P-MWCNTs. This study opens up a new strategy to systematically tune the properties of polymer electrolytes for special applications by using appropriately functionalized CNTs.

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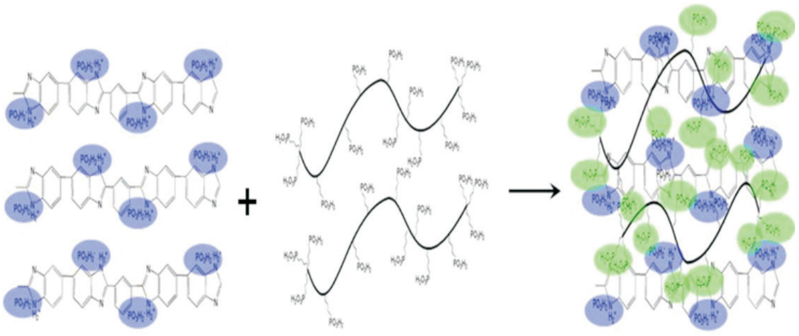
3. ImprovedPerformanceofPhosphonatedCarbon Nanotube –Polybenzimidazole Composite Membranes in Proton Exchange Membrane Fuel Cells” RamaiyanKannan,Husain N Kagalwala, Harshal D Chaudhari, Ulhas K Kharul, SreekumarKurungot, Vijayamohanan K PillaiJ. Mater. Chem 21(2011)7223



NATURAL AND SYNTHETIC POLYMERS – A PERSPECTIVE IN THE CONTEXT OF CONTROLLED RADICAL POLYMERIZATIONS

Prof. R. Dhamodharan
Department of Chemistry
Indian Institute of Technology Madras
Chennai 600 036, India
E-mail: damo@iitm.ac.in

The synthesis of new polymeric materials and the development of applications for the new polymers is a challenging area of research. As on date, the closest synthetic approach, equivalent to nature's synthesis of macromolecules, arises through living polymerizations. These involve an active initiating and propagating species such as an anion or a cation or a carbon-metal bond or a free radical. Controlled radical polymerization (CRP) methods such as ATRP, RAFT and SET have emerged as simple tools in the macromolecular synthetic library. These polymerizations are quite versatile and are applicable to a variety of monomers that are used in very large volume and can be carried out under extremely mild conditions.

Nature synthesizes quite a few macromolecules with precise primary structure (architecture). The result of a good control over primary structure results in a variety of secondary, tertiary and quaternary structures, which in turn result in excellent control over the properties. The mechanism of the same has attracted the best minds. This is exemplified by the award of the Nobel Prize in Chemistry in 2009 (understanding the structure and function of r-RNA). The primary structure of proteins consists of NCC repeat units (nitrogen-carbon reduced-carbon oxidized).

Given the vast repertoire of synthetic tools available to make a variety of bonds, it was natural to try and mimic nature and observe as to how macromolecules with control over the C-C-C- or C-C-heteroatom as the primary structure could be achieved with a view to tailor the physical properties. The first step in this direction was the living anionic polymerization of styrene (Nature, 1956). This enabled the synthesis of a macromolecule with a predominantly C-C-C primary structure with variation in the pendant group. Subsequently, a number of living polymerizations (cationic, insertion between a carbon-metal bond, group transfer) were reported. The living ionic polymerizations were seriously limited by the stringent conditions and were applicable to few monomers. The next major breakthrough was the discovery of living radical polymerization (INIFERTER; Otsu, Macro. Rapid Comm. 1982). This enabled the expansion of the scope of the reaction to a variety of monomers with a C=C. Since monomers with C=C were the major players in the market and radical polymerizations require much less stringent reaction conditions, living/controlled radical polymerization attracted attention. Several living/controlled polymerizations were invented in the previous decade. These are, Nitroxide Mediated Polymerization (NMP; D. H. Solomon, E. Rizzardo, P. CacioliU.S. Pat. 4, 581, 429, 1986), Atom Transfer Radical Polymerization (ATRP: Sawamoto et al., 1995 and Matyjaszewski et al., 1995), Radical Addition Fragmentation Transfer (RAFT; Moad, et al., 1998), and SET-LRP (Percec et al., J. Am. Chem. Soc. 2006). These methods demonstrated the possibility of synthesizing macromolecules with control over, 1) the chain length, 2) the composition and 3) the architecture (block, star, graft) along with a reasonably low polydispersity index (PDI). These polymerizations (with the exception of SET that was developed a decade later) were carried out at higher temperatures; that is, in the range 90 to 140°C.

The bulk of the literature in the area of CRP, with the exception of SET that was developed in 2007, were carried out at higher temperatures in the range 90 to 140 C. Our research has been focused on devising synthetic strategies and catalytic system for polymerizations of monomers by CRP, at ambient temperature. Ambient polymerization of monomers would enable the synthesis of complex macromolecular architectures and would push the frontiers of polymer chemistry a step towards natural polymers that are synthesized by the addition of one monomer at a time. Further, ambient temperature polymerizations would enable a one step and simple modification of surfaces through rapid polymerization from the surface.

In this seminar, our explorations on ambient temperature radical polymerizationsATRP, RAFT and SET-RAFT shall be described. We focused on the synthesis of block copolymers, at room temperature, in a test tube, by a simple and sequential addition of monomers and demonstrated the ambient temperature ATRP of a variety of acrylates and methacrylates that include tert-butyl acrylate, methyl methacrylate, benzyl methacrylate, isobornyl methacrylate, adamentyl methacrylate. The results from these studies were used to demonstrate, 1) the synthesis of block copolymers with AB, ABC, CBABC main chain architecture in the bulk as well as at an interface; 2) control the growth of thin polymeric films from a variety of surfaces. Our work on ambient temperature polymerization of monomers may enable the synthesis of complex macromolecular architectures and could push the frontiers of polymer chemistry a step towards nature's way of synthesizing polymers. We have used CRP methods to modifiy surfaces as well as in the synthesis and characterization of fluorescent homo and block polymers. These results shall be discussed in the seminar.

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AT THE INTERFACE OF POLYMERS AND BIOLOGY

Bhuvanesh Gupta, ShamayitaPatra, Jincy Joy
Bioengineering Laboratory, Department of Textile Technology
Indian Institute of Technology, New Delhi-110016

Chemistry has played a key role in designing the polymeric materials for the biomedical applications. The vision has been to develop textiles as biomaterials for wound dressings, prosthesis devices and tissue engineering applications. One of the major requirements of the materials is the biocompatibility of the material with the biological systems so that tissue reaction against the implant can be minimized. This is where the chemistry of the material needs to be monitored in such a way that it leads to required characteristics into the material without much influencing the inherent physico-chemical properties. We have been working in the field of development of polymers for different applications in medicine and surgery. These materials are modified by functionalization of the polymer surface using plasma. The interesting part of modification is that the process could be used for the polymers in any form of the material. It has been observed that the chemistry at the material surface can be easily controlled by the careful variation of the plasma conditions. Both the ionic and nonionic surfaces can be achieved by proper selection of the plasma conditions. Tissue engineering is the key area where these have demonstrated to be excellent materials as scaffolds for the cell seeding in the tissue engineering applications. This method is helpful in designing the surface structure to a desired composition and architecture that would interact with the collagen protein molecules by ionic binding under appropriate conditions. The collagen immobilized films and knittings were used for the seeding of different cells. The modified surface shows excellent growth of cells and confluence was achieved within a period of one week. We have been in the process of moving from biostable polyester to the biodegradable matrix so that the scaffold vanishes out of the scene and leaves behind an intact tissue piece for the urinary bladder tissue as well as for the blood vessels for cardiovascular systems.

Tissue engineering has become one of greatest weapons for human healthcare. Tissue engineering is an inter-disciplinary field utilizing the knowledge of material science and biochemical engineering to facilitate three-dimensional cell growth to treat or augment or replace damaged tissues or organs. It involves the intricate mechanism as shown in figure1.

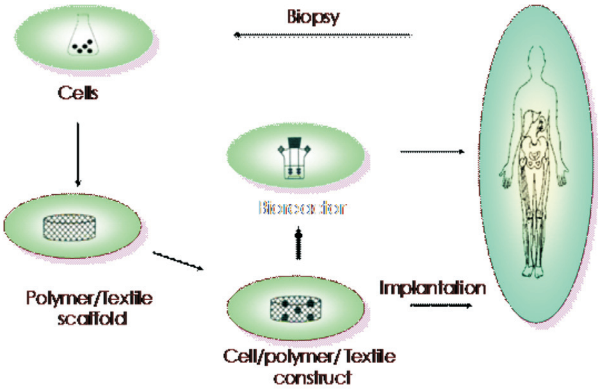


Figure1: Tissue engineering approach

Scaffolds are structural templates on which cells are seeded and with the optimized growth factors and growth medium; cells proliferate, differentiate and form tissues. Thereby the scaffold structure and properties should be such that the cells can adhere to the surface. Chemistry plays a vital role in determining the surface properties of the scaffold surface. For example cells adhere to hydrophilic surfaces and not hydrophobic surfaces. Hence a material chosen for scaffold preparation should have suitable properties or it can be modified by various routes emerging out of the knowledge of chemistry. Polymers are indispensable for tissue engineering. Polymers both natural and synthetic have tailorable properties that can be modified according to the needs of scaffold preparation. Polymers have an advantage of possessing properties that can be tailored to obtain the desired mechanical strength, porosity, biodegradability and surface chemistry.

The vision has been to develop textiles as biomaterials for wound dressings, prosthesis devices and tissue engineering applications. One of the major requirements of the materials is the biocompatibility of the material with the biological systems so that tissue reaction against the implant can be minimized. This is where the chemistry of the material needs to be monitored in such a way that it leads to required characteristics into the material without much influencing the inherent physico-chemical properties. We have been working in the field of development of polymers for different applications in medicine and surgery. These materials are modified by functionalization of the polymer surface using plasma. The interesting part of modification is that the process could be used for the polymers in any form of the material. It has been observed that the chemistry at the material surface can be easily controlled by the careful variation of the plasma conditions. With this method the bulk properties are not altered but the surface properties can be modified. Both the ionic and nonionic surfaces can be achieved by proper selection of the plasma conditions. Tissue engineering is the key area where these have demonstrated to be excellent materials as scaffolds for the cell seeding.

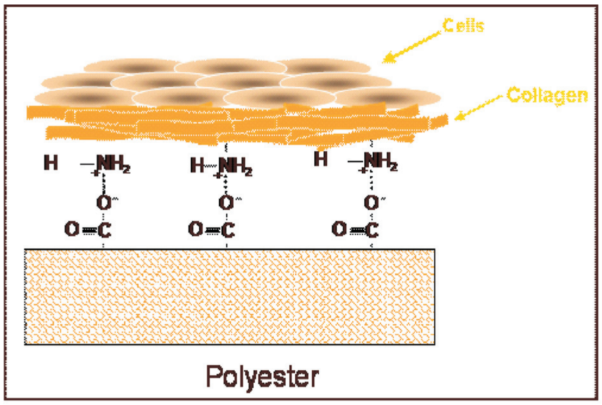


Figure2: Tissue Engineering Approach towards PET based Urinary Bladder reconstruction

Urinary bladder reconstruction is one of the challenges taken up by our group. By using the key tools of tissue engineering, the physiochemical nature of the polymers and polymeric structures were tailored to solve some burning problems in the field of human health care using the approach as shown in figure 2. One of them is urinary bladder reconstruction, which is necessary to solve some bladder related problems such as, bladder congestion, bladder tumor and bladder extrophy. To construct a patient specific product, weft knittited structures were taken, figure3, to comply with the elasticity and strength of the human urinary bladder.

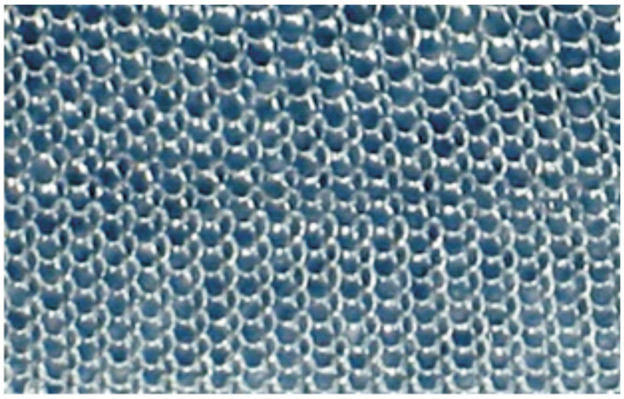


Figure 3: Weft knitted structure of PET

Polyethylterepthalate is a biostable polymer used for urinary bladder reconstruction. To improve its bioreceptivity, surface modification of this knitted structure by oxygen plasma was carried out, followed by grafting of acrylic acid, figure 4.

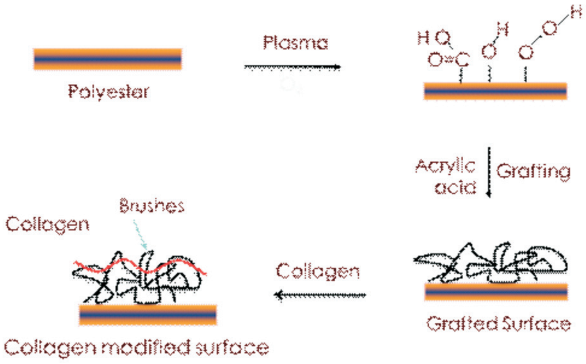


Figure 4: Functionalization of PET by O2 Plasma

Plasma generates hydrophilic peroxide and carboxylic groups on the surface, onto which acrylic acid is being grafted. Acrylic acid helps to bind collagen with the plasma treated PET surface by EDC method. The basic reason behind the acrylic acid grafting lies in collagen immobilization on the hydrophobic PET surface, so that it can give a better cell receptivity, by providing the –NH2 groups. It was observed that as the degree of grafting of acrylic acid increased, the immobilization of collagen increased coherently, figure 5.

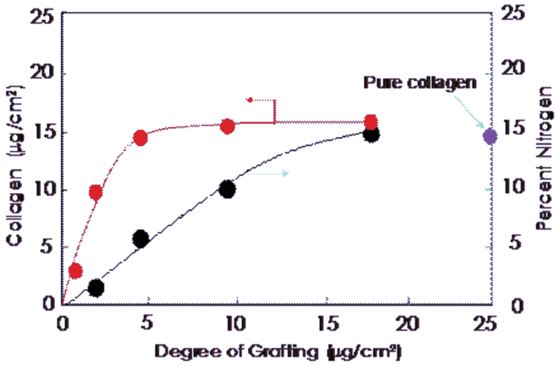


Figure 5: Effect of reaction time over Acrylic Acid grafting on surface modified PET (by O2 Plasma)

We also observed that higher the degree of grafting; greater the nitrogen content. It can be inferred that this collagen immobilized PET surface probably would show good cell receptivity. The seeding of mouse fibroblast showed excellent results as expected; as shown in figure 6.

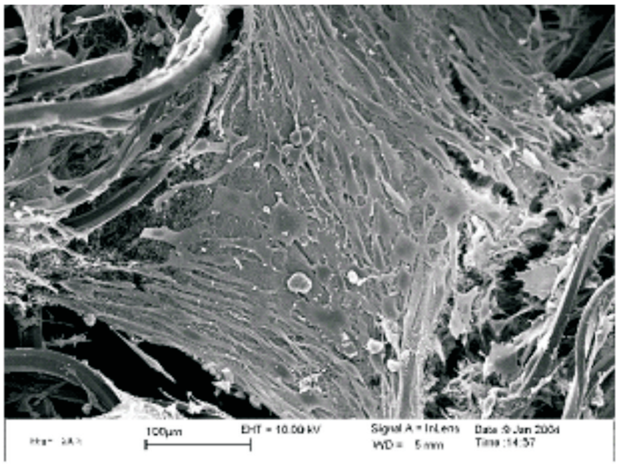
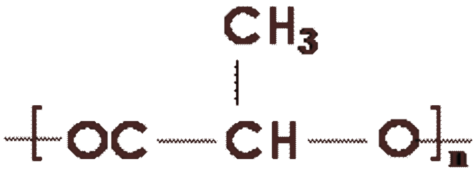


Figure 6 : SEM picture of Mouse Fibroblastcells on collagenimmobilized PET knittings.

Though collagen immobilized PET knitting have shown a very positive result, but PET is not degradable i.e. after the formation of a full viable urinary bladder on this PET scaffold, this PET knitting will remain there. Thus due to its poor biodegradable profile Polylactic acid (PLA), (figure7), was used. To sustain the mechanical compliance we have used different plied yearns, such as 2, 4, 8 plies were used.



$$\left[OC - \overset{\overset{\displaystyle CH_3}{|}}{CH} - O \right]_n$$

Figure 7: Structure of PLA for urinary bladder reconstruction.

Another major health issue lies in cardiovascular system in terms of cardiac arrhythmia or in terms of atherosclerosis. 80 million patients are waiting for blood vessel grafting in USA only (2010). The scenario is much severe in India where 100 million patients (10% of total population) are suffering from the same problem. To solve this bitter problem, two major approaches were followed; one being textile method such as flat sheet method, braided textile scaffolds for their simplicity and economically viability and the other being salt leaching method. The basic tissue engineering approach still remains the same, figure 8. The surface of the polymer was modified by plasma treatment followed by immobilization of gelatin, to provide better cell attachment.

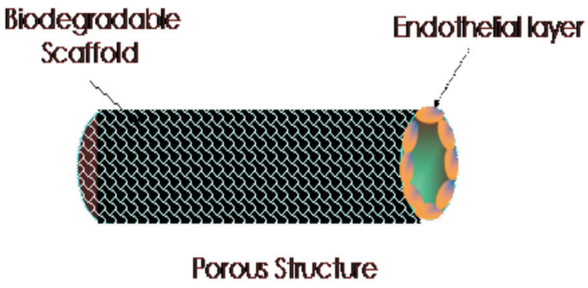


Figure 8 – Basic Tissue Engineering Approach for blood vessel regeneration

The difference in urinary bladder and blood vessel lies in their ultimate purpose. So, for blood vessel reconstruction, braided tubular structures were chosen. This will give us mechanical compliance. For braided structure polycaprolactone (PCL) was used for its easy machinability, better biocompatibility and excellent biodegradability. PCL is FDA approved polymer for health care related usage. Thereby braided structures of PCL were prepared and for biomolecule immobilization, the braided structure was dip coated into the gelatin solution. To get a porous structure, this composite structure was further freeze dried.

In a second approach, PCL porous tube structures were prepared, figure 9, by dip coating. Further the PCL structure was modified by carbon dioxide (CO2) plasma to generate –COOH group. These –COOH groups were intended to hold gelatin by ionic bond through its –NH2 groups, to provide better cell adherence.

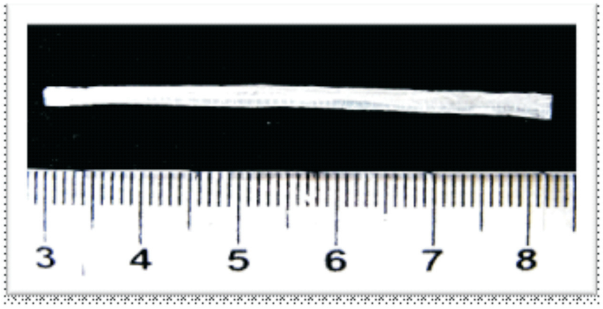


Figure 9 – Porous PCL tubularscaffold

With such excellent porosity and cytocompatibility due to gelatin immobilization, leading to appreciable cell adherence justifying itself as a viable scaffold.

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NANOMATERIALS AND POLYMER NANOCOMPOSITES

Characterization of Deacetylated Chitosan and Chitosan Nanofibres

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Chitin is the second most abundant natural amino polysaccharide,made up of β-(1→4) linked 2-acetamido 2-deoxy β- D-glucose. This renewable resource is found many naturally occurring organisms such as fungi, yeast, and is the principal component in the exoskeleton of sea crustaceans such as shrimp and crab. The process of deacetylation involves the removal of acetyl groups from the molecular chain of chitin, leaving behind a compound (chitosan) with a high degree chemical reactive amino group (-NH2). This makes the degree of deacetylation (DD) an important property in chitosan production as it affects the physicochemical properties, hence determines its appropriate applications. Chitosan possesses exceptional chemical and biological qualities that can be used in a wide variety of industrial and medical applications. In this work chitin is converted to chitosan and its characterization, chitosan nanofibres were prepared by electrospinning technique. The spun samples were characterized by using SEM analysis.

Key words: chitin, chitosan, deacetylation, electrospinning

Utilization of Pineapple Leaf Wastes as a Potential Source for Nanocellulose

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Isolation of cellulose nanoparticles (CNPs) from renewable resources is becoming an important area of research. These novel nature based materials have garnered interest from the scientific community because of their high strength and stiffness combined withlow weight, biocompatibility and renewability. Steam explosion process is employed for the extraction of nanocellulose from pineapple leaf wastes. Characterization of the fibres by Fourier transform infrared (FTIR) spectra, scanning electron microscopy (SEM) and X-ray diffraction (XRD) supports the evidence for the successful isolation of nanocellulose from pineapple leaf. Thermogravimetric analysis (TGA) revealed that the isolated nanocellulose exhibit improved thermal properties than the raw fiber. The obtained nanocellulose may have the potential applications in the fields of nanocomposites as a reinforcing agent, as well as in biomedical, tissue engineering, pharmaceutical and optical industries as additives.

Keywords: Nanocellulose; Steam explosion; Pineapple leaf.

Polymer nanocomposites based on blends: Effect of vinyl silane modified kaolin clay on Polypropylene/ Polystyrene Nanocomposites

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Polymer blending is an effective way to combine the properties of individual components together. Polypropylene (PP) and polystyrene (PS) are two of the widely used plastics and their blends have also received considerable attention. However, PP and PS are widely regarded as immiscible due to lack of interfacial adhesion between the components. Several problems of these blends may be caused by poor compatibility of the components. Properties of such blends can be improved by using compatabilizers such as homopolymer, graft, block or star copolymer. In recent years, a new concept of compatibilization by using nanoparticles such as nanoclays, nanotubes etc have been introduced. Traditionally clays have been used as fillers in polymer systems due to the improved physical and mechanical properties of the resulting polymer composite .A large quantity of polymer-clay composites have been successfully synthesized through the integration of clay in a wide variety of polymer matrices. The first demonstration of polymer clay nanocomposites was reported by Kojima and co-workers. Since the early 1990 polymer blends have been used as the matrices of polymer nanocomposites. Yan Zhu et al found out that MMT clay can plays a significant role in reducing the dispersed domain sizes in PP/PS blends. The results showed that the organoclay platelets tend to form knife like structure in the PS domain under the shear stress of the continuous PP phase during compounding. Kyunyl Kim et al successfully prepared PP/PS clay nanocomposites by continuous compounding with high intensity ultrasonic waves during extrusion process which enhance the interfacial interaction between the immiscible polymer blend. SuprakasSinha Ray et al studied the role of Closite 20 A as an interfacial modifier in PS/PP or PS /PP-g-MA blends. The results clearly indicate that C20A acts at the same time as a nanofiller and also as a modifier.

Kaolin clay, potential nanofiller, is not widely used for polymer modification. In this work it is proposed to modify kaolin clay by using triethoxy vinyl silane. XRD, TGA and BET surface area is used to characterize the modified kaolin clay. The results show that property of unmodified clay is improved by adding triethoxy vinyl silane. The modified kaolin nanoclay was added as a modifier in PP/PS blend. Polypropylene and polystyrene / clay Nanocomposites were prepared through melt intercalation technique using Thermo HaakeRheochord mixer at 1800Cwith a rotor speed of 50 rpm and mixing time was fixed at 8 min. After mixing the melt was pressed in a hydraulic press cut into pieces. Samples for mechanical studies were prepared using Injection mould. The mechanical properties like tensile properties and flexural properties were studied. PP/ PS Nanocomposites were characterized using XRD, TGA. The flow properties were evaluated using MFI. Results show that nanoclays can be used to improve various mechanical and thermal properties of PP/PS blend. XRD result shows a slight increase in d spacing which confirms partial intercalation.TGA studies show that the thermal stability of PP/PS clay nanocomposites is improved by modification. SEM images show good dispersion of modified kaolin in PP/PS blend. This study shows that polymer nanocomposites can be developed from PP/PS blends using modified kaolin clay.

Thiolated Chitosan- Polyethylene Glycol Blend/ Montmorillonite Nanocomposite Formulations for the Oral Delivery of Insulin

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1. Introduction

Chitosan (CS), a polysaacharide obtained by the alkaline deacetylation of chitin derived from the exoskeleton of crustaceans has emerged as a useful drug delivery matrix because of its polycationic nature, biodegradability, biocompatibility and mucoadhesiveness. The chemical modification of CS by conjugating various functional groups allow the control of the hydrophilicity and the solubility at neutral and basic pH, thereby opening new oppurtunities to expand the application of this biopolymer. ThiolatedChitosans (TCS) constitute an integral part of designated" thiomers", which show various promising properties such as mucoadheshion, efflux pump inhibition, permeation enhancement, insitu gelling capacity and controlled drug release1. In contrast to unmodified chitosans, these novel polymers are capable of forming covalent bonds with the mucus forming constituents. Hence TCS mimic the natural behaviour of secreted mucus glycoproteins, which are also covalently anchored in the mucus layer by disulphide bonds. Polyethyleneglycol (PEG) is a biodegradable polymer with excellent biocompatibility and non toxicity, often blended or compounded with other polymers to be used in the fields of controlled drug release2. Montmorillonite (MMT), a potent detoxifier, which belongs to the structural family known as the 2:1 phyllosilicate can provide mucoadhesive capability for the nanoparticle to cross the GI barrier.

The peptide insulin, used for the management of Diabetes Mellitus is administered parenterally by subcutaneous injection resulting in low level of compliance due to pain. The oral route is considered to be the most acceptable and convenient route of drug administration and it represents an exciting challenge for drug delivery scientists particularly with the prospect of delivering the hormone physiologically to the liver, replicating the dynamics of endogenous release, rather than creating universally high supraphysiological peripheral concentrations as with the parenternal route. Drug-loaded nanocomposites of biodegradable polymers have great potential to provide an ideal solution for delivering the peptide via oral route. In the present work, we report on the preparation of a novel nanocomposite formulation, i.e., biodegradable Thiolated Chitosan-Polyethylene Glycol (TCS-PEG) blend incorporated with medical clay, MMT called TCS-PEG/MMT nanocomposites for oral delivery of insulin. The different stages of the preparation of ternary blend were characterised using FT-IR,XRD,SEM techniques and the effects of pH on insulin loading and controlled release were studied.

2. Experimental

2.1. Preparation of TCS-PEG/MMT nanocomposites

Scheme-1 represents the preparation of TCS. The blend of TCS and PEG were prepared by casting a mixture of the solutions and to this blend solution MMT of different compositions were added. The cast films were allowed to dry at room temperature for three days and were collected for characterization. Scheme 2 shows the intercalation of TCS-PEG blend inside the galleries of MMT clay.

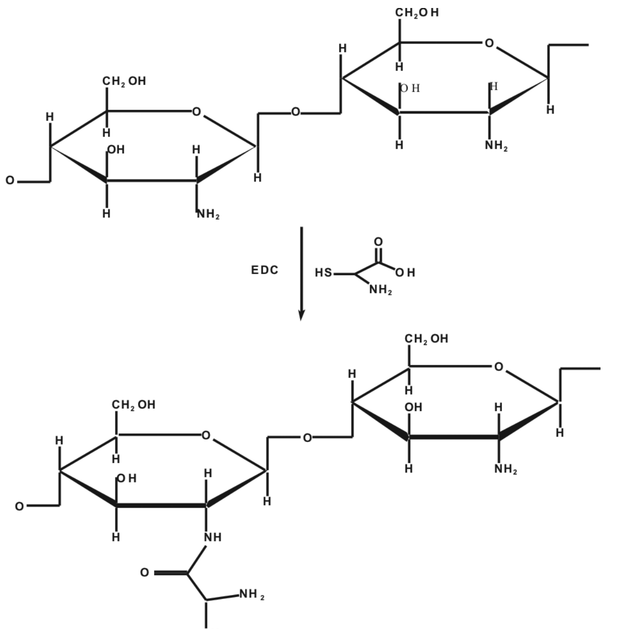
2.2. Insulin loading on TCS-PEG/MMT nanocomposites

Insulin was loaded into the nanocomposites by diffusion loading method. Scheme 3 represents the loading of insulin into the drug carrier vehicle and its controlled release at different pH conditions.

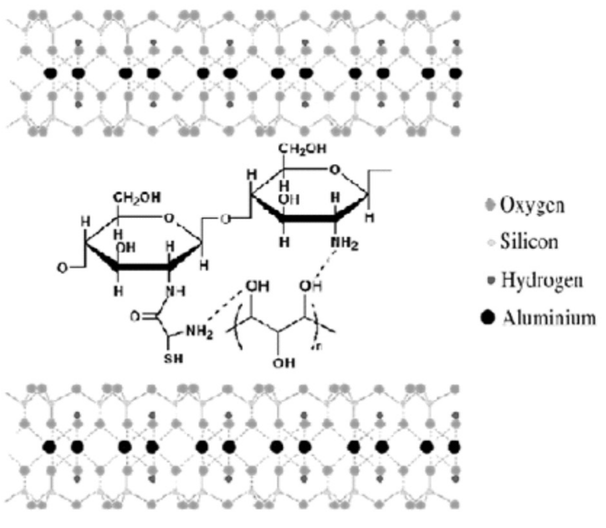
3. Results and discussion

The primary process involving the modification of chitosan by introducing a thiol moiety was successfully carried out and L- Cysteine (CYS) was attached covalently to the primary amino groups of chitosan under the formation of amide bonds. The carboxylic acid moieties of CYS were activated by EDC forming an O-acyl urea derivative as intermediate product which reacts with the primary amino groups of chitosan. The lyophilized TCS- CYS conjugates appeared as white, odorless powder of fibrous structure. Results demonstrated that pH has profound effect on thiolation. Thiolation was carried out from pH 3 to 5 and effective attachment of thiol groups was observed at pH 5 and decreased above pH 5. The reason for this observation can be the oxidation of sulfhydryl groups during the coupling reaction, which is favored at high pH values.

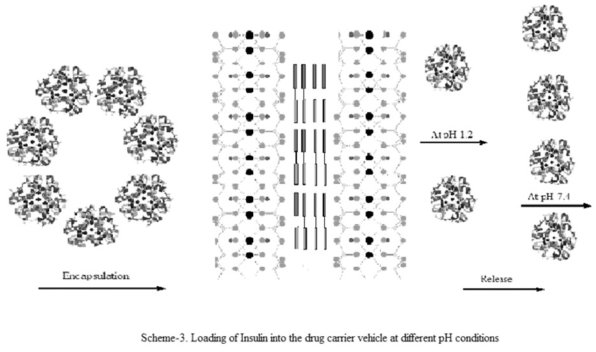
The characteristic vibration peak of chitosan and its derivative were clearly observed and the broad peak at 3440cm-1 was assigned to –OH and –NH stretching vibration and the weak peak at 2920cm-1 was attributed to –CH stretch. The peak at 1030cm-1 was due to the C-O-C stretching and the saccharine structure. In the spectra of thiolated chitosan derivative, distinct absorption peak at 1732cm-1 correspond to the carbonyl groups of CYS and the decreased peak at 1590cm-1 assigned to –NH blending implied that the modification was done successfully. The characteristic absorption band at 1100cm-1 of PEG was attributed to the bending vibration of C-O and two absorption bands at 1340 and 2890cm-1 were attributed to the bending vibration of C-H respectively. The absorption band around 3430cm-1 concerned the stretching vibration of N-H group bonded to O-H group shifted to a lower wave number at 3419cm-1 and became wide suggesting an increase in the hydrogen bonding. These changes show a strong evidence of the intermolecular interactions and good molecular compatibility between TCS and PEG. The change in gallery height of the blend was investigated by WAXD experiments. The insertion

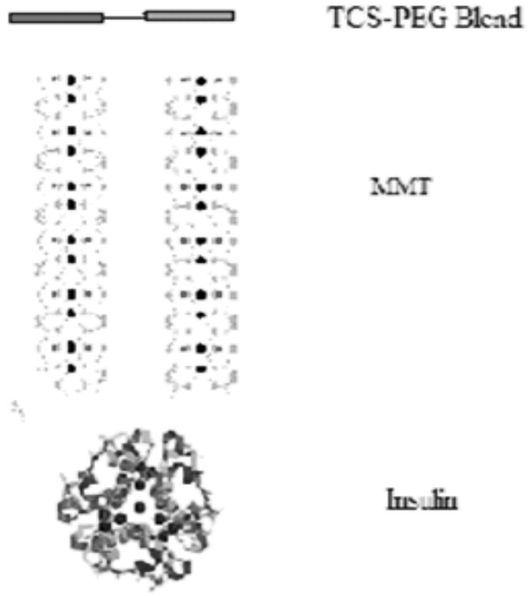


Scheme.1 Preparation of Thiolated Chitosan



Scheme 2. Intercalation of TCS-PEG blend inside the galleries of MMT clay





Scheme.1 Preparation of Thiolated Chitosan

of Polymer blend into the clay galleries forces the platelets apart and increases the d-spacing, resulting in a shift of diffraction peak to low angles. The release of insulin from various insulin-loaded nanocomposites was captured. Results showed that only 5% insulin is released after 2h incubation in the simulating gastric condition and after 4h incubation in the simulating intestinal conditions, 30% of the initial amount was released. When the loading was carried out at basic pH (7.4), the release profile enhanced to 67%, which shows that the release was much pronounced in the basic medium than in the acidic medium.

4. Conclusion

Controlled drug delivery devices that utilize biodegradable polymers are enjoying high resurgence of interest, as there is no need for the surgical removal of the device. The results of the present investigation show that TCS-PEG/MMT nanocomposite formulation represents a good candidate as a drug carrier vehicle for the oral delivery of insulin.

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Nano Kaolin Clay as a Modifier for Glass Fiber Reinforced Thermoplastics

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Fiber-reinforced composites have generated considerable interest, both in terms of industrial applications and fundamental researchwherein the performance, along with the cost effectiveness, is crucial for various end-use applications.Polyolefin nanocomposites have gained considerable commercial viability for automobile applications because of their low density and high modulus. Nanocomposites based on three phase systems containing nanoclay, glass fibers, and polymer matrices have not been widely explored.Glass fiber reinforced PS /HDPE composite and hybrid amino silane modified nano kaolin clay- fiber reinforced composites were prepared by melt-blending technique followed by injection molding. Moulded specimens were analysed by XRD, together with characterization of thermal and mechanical properties. The mechanical behavior of these materials and the changes as a result of the incorporation of both nanosize kaolin clay and glass fibers were investigated. Composites were prepared with a glass fibre content of 10, 20, and 30 %. The proportion of the nano size kaolin clay platelets was fixed at 2 %. Hybrid clay-fiber reinforced PS/HDPE blend composite possess better tensile, flexural properties.Tensile modulus was enhanced with the incorporation of glass fiber and further increased with an introduction of nanoclay. Flexural strength and flexural modulus are both enhanced with an increase in fiber loading. The addition of clay nanoparticles further improved these properties. It also posses better, storage modulus, and glass transition temperature. SEM studies reveal that the nanoclay acts as a molecular bridge between the nonpolar matrix and polar fiber and thus enhances the interfacial adhesion between them.

A Comparative study of Natural Rubber Latex /Carbon Nanotube dispersion using different surfactants

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Carbon Nanotube (CNT) based Natural rubber Latex nanocomposites have been fabricated through solution casting method. In order to achieve fine dispersion of nanotubes and facilitate strong interfacial adhesion with the polymer matrix, multi walled nanotubes (MWNTs) were treated with surfactants of different charges, such as sodium dodecyl sulphate (anionic), cetyltrimethyl ammonium bromide (cationic) and Tween 20(non-ionic), prior to the dispersion in Latex medium. Results showed that the agglomeration and entanglement of the nanotubes were greatly reduced upon the addition of sodium dodecyl sulphate. Among the three surfactants CTAB and SDS provide minimum and maximum dispersion, respectively.Transmission electron microscopy and contact angle measurements have evidenced the compatibility of sodium dodecyl sulphate with MWCNT/NR latex in which a promising dispersion and adhesion has been observed at the MWCNT-latex interface. The change in dynamic mechanical properties with temperature, mixing time and Payne effect are studied on the Latex composites filled with surfactant-MWCNT. We used two models to explain Payne effect i.e Kraus model (filler-filler interactions) and Maier and Göritz model (rubber-filler interactions).

Keywords: Natural rubber Latex, surfactant, Carbon Nanotube, Payne Effect, Dispersion.

Polymer-Grafted-Magnetite/Nanocellulose Superabsorbent Composites for the Selective Separation and Recovery of Immunoglobulin from Aqueous Solutions

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1. Introduction

Immunoglobulin (γ-globulin) is a large Y-shaped protein used by the immune system to identify and neutralize foreign objects such as bacteria and viruses, and hence its recovery is inevitable in biomedical applications. In this study, a novel hydrogel, poly(methacrylic acid–co–vinyl sulfonic acid)–grafted-magnetite/nanocellulose composite (P(MAA-co-VSA)-g-MNCC) was synthesized by graft copolymerization technique. The hydrogel was well-characterized using TG, XRD, SEM and FTIR techniques. The antibody, Immunoglobulin (IgG) was immobilized onto P(MAA-co-VSA)-g-MNCC, under different optimized conditions. The present study was proposed to utilize the cation exchange capacity of the carboxyl and sulfonyl groups from the adsorbent surface to recover IgG from aqueous solutions. Studies on separation of IgG from mixture of proteins were carried out to ensure its better applicability in the biotechnological and biomedical fields.

2. Experimental

2.1. Preparation of P(MAA-co-VSA)-g-MNCC

The general procedure adopted for the preparation of P(MAA-co-VSA)-g-MNCC consists of three steps.

Step 1. Extraction of nanocellulose (NC) from saw dust
In the pres ent work, cellulose was first extracted by acid-alkali treatment of saw dust (collected from Local saw mill, Trivandrum) and subsequent bleaching using 5.0 % hydrogen peroxide (Mulinari and Da Silva, 2008). The bleached cellulose (5.0 g) was added to 250 mL distilled water and 140 mL conc. H_2SO_4 wasdropped to itwithout cause heating. After complete addition, the mixture was heated at 50 ^{o}C for 2 h. The hot reaction mixture was quenched using crushed ice and the obtained white colloidal nanocellulose (NC) was centrifuged and freeze-dried.

Step 2. Preparation of magnetite nanocellulose composite (MNCC)

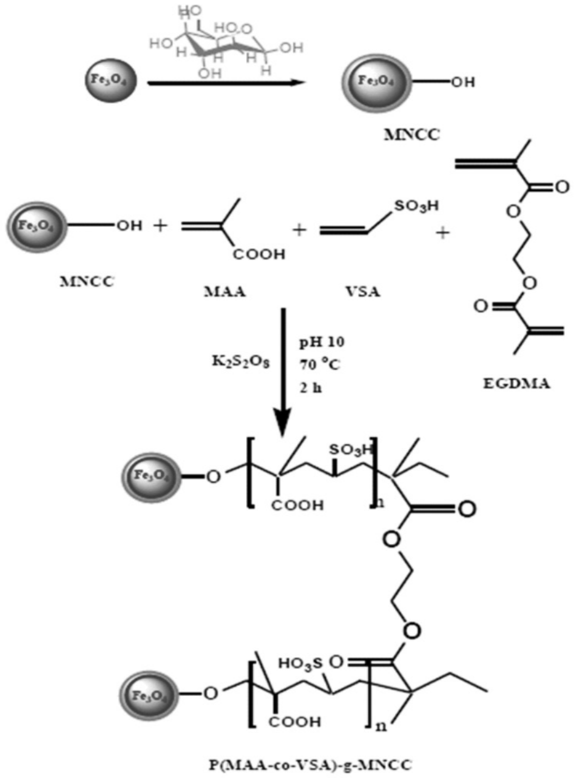
The MNCC was prepared by co-precipitating Fe(II) and Fe(III) ions in aqueous solution containing NC with ammonia. Briefly, about 1.5 g of NC was added to 200 mL distilled water and stirred for 10 min. To the mixture, 1.49 g $FeCl_3 \cdot 6H_2O$ and 0.765 g $FeSO_4 \cdot 7H_2O$ were added to form a source of iron, and heated at 60 °C. Chemical precipitation was achieved by adding 8.0 M ammonia solution drop wise with vigorous stirring and a constant pH of 10, upon which an orange color suspension obtained was changed to a black precipitate. After incubation for 4 h at 60 °C the mixture was cooled to room temperature with stirring, and the resulting MNCC particles were separated magnetically. The product thus obtained was washed several times with distilled water, finally with ethanol and dried.

Step 3. Preparation of P(MAA-co-VSA)-g-MNCC

The general procedure adopted for the preparation of P(MAA-co-VSA)-g-MNCC is illustrated in Scheme 1. Typically, about 0.5 g of MNCC was stirred well with 100 mL distilled water (60 °C, 20 min). $K_2S_2O_8$ (0.004 M, 0.92 g) was added and kept at 60 °C for 10 min. After cooling the suspension to 40 °C, a mixture of MAA (0.1 M, 8.5 mL), VSA (0.1 M, 7.8 mL) and EGDMA (0.015 M, 2.83 mL) were added. The pH was adjusted by NaOH to 10. The temperature was risen to 70 °C and maintained for 2 h to complete the reaction. The obtained product was filtered and washed repeatedly with distilled water and ethanol to remove excess chemicals and then dried in vacuum at 70 °C. The dried sample was then grounded and sieved to obtain -80 +230 mesh size particles (average diameter of 0.096 mm) and used throughout the studies.

3. Results and Conclusions

A cellulose-based hydrogel, P(MAA-co-VSA)-g-MNCC was synthesized by graft copolymerization of MAA and VSA onto MNCC, in the presence of EGDMA as cross linking agent and $K_2S_2O_8$ as free radical initiator. The amount of sulfonyl and carboxyl functional groups in P(MAA-co-VSA)-g-MNCC was estimated to be 1.92 and 1.36 meq/g, respectively, was an evidence for proper grafting of PMAA and PVSA onto MNCC. The zero point charge of cellulose and P(MAA-co-VSA)-g-MNCC was observed at pH 5.5 and 3.6, respectively. The adsorbent was well-characterized by means of TG, XRD, SEM and FTIR techniques. TG curves show an enhanced thermal stability of P(MAA-co-VSA)-g-MNCC with respect to Cellulose and can be used at high temperature conditions. The average crystallite size of NC and MNCC calculated from XRD pattern was 25.0 and 23.8 nm, respectively. Swelling capacity of P(MAA-co-VSA)-g-MNCC was found to be increased with increase in pH and temperature. The efficiency of P(MAA-co-VSA)-g-MNCC in the recovery of IgG was tested by batch adsorption technique. The optimum pH for maximum adsorption was found to be 6.8 with the adsorption percentage of 98.4 % (12.3 mg/g) and 96.8 % (24.2 mg/g) for an initial IgG concentration of 25 and 50 mg/L, respectively. Electrostatic interaction has played an important role in the adsorption process of IgG onto P(MAA-co-VSA)-g-MNCC. Equilibrium was achieved within 3 h. IgG adsorption on P(MAA-co-VSA)-g-MNCC follows a pseudo-second-order kinetic model, which is based on ion-exchange mechanism followed by complexation. The adsorption isotherm results were well-fitted into Sips and Langmuir isotherm models, which confirm monolayer coverage process at higher concentrations. The maximum adsorption capacity according to Langmuir model was found to be 203.78 mg/g at 30 ^{o}C. The adsorption capacity towards IgG was found to increase with increase in temperature from 10 to 40 ^{o}C, indicating endothermic nature of adsorption. Gibbs free energy possesses negative values for all interactions, indicating the spontaneous nature of adsorption. The positive values of ΔH^0 and ΔS^0 indicate the endothermic nature of adsorption and increased randomness at the solid-liquid interface, respectively. Adsorption capacity was found to be increased with increase in salt concentration. Satisfactory results were obtained from the attempts for the selective separation of IgG from mixture of proteins. The adsorbed IgG was effectively regenerated using 0.1 M KSCN. The present investigation shows that P(MAA-co-VSA)-g-MNCC can be used as an effective adsorbent for the selective separation and recovery of IgG molecules from aqueous solutions.



Scheme 1. *Proposed reaction mechanism for synthesis of P(MAA-co-VSA)-g-MNCC.*

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Stress relaxation behavior of Natural rubber (NR)/ Nitrile rubber (NBR) blend nanocomposites.

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Key words: Stretched-exponential relaxation, stress relaxation immiscible rubber blends,nanoclay,compatibilizing, blend morphology

Abstract: Blends of two different polymers have significant influence in industrial applications. Understanding the role of nanofillers in immiscible blends is one of the key factors that researchers put their efforts into. While dealing with the service performance it is necessary to study the time dependent properties like stress relaxation and creep. Here we have prepared different compositions of natural rubber (NR) and nitrile rubber (NBR) blend nanocompositevulcanazite with both high and low clay loading in an attempt to study the effect of nanoclay on the stress relaxation behavior of these elastomer blends. The effects of clay loading, blend composition, filler polarity, and temperature on stress relaxation were carefully measured. A two stage stress relaxation steps was observed in all blend composition. Blend nanocomposite with higher filler loading showed higher rate of relaxation rate due to the presence of more number of filler-filler interactions. At a higher temperature of 70 ^{0}C the viscosity ratio was found to influence the reinforcement and consequently relaxation rate of the 50/50 blend nanocomposite. The nature of clay was also found to influence the relaxation rate due to the difference in interaction. It was found that the rearrangements of the polymer chains are dependent on the blend composition, temperature filler/polymer interactions etc. The stretched- exponential Kolrousches equation was used to model the relaxation behavior. It was found that the experimental curve fitted well with the theoretical model.

EFFECT OF TERMINAL VINYL SILYLATION OF MONTMORILLONITE ON THE SELF ASSEMBLING CHARACTERISTICS OF POLYSTYRENE-CLAY NANOCOMPOSITES

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Polymer–clay nanocomposites have attracted great interest because of its remarkable thermal, mechanical and barrier properties due to dispersion of silicate layers having thickness of 1nm and lateral dimension of several nanometers in a polymer matrix. Nanocomposites with radically different morphologies, properties and applications can be produced by the control of the organisation of the silicate layers at larger scale by tuning of polymer–clay interactions. Polystyrene-clay nanocomposite particles which exhibited concentration dependent self assembling properties in THF were synthesised by *in situ* intercalative polymerisation of styrene with terminal vinyl silyl modified organoclay. The characterisation of vesicles was done by SEM and TEM. The thermal characteristics were studied by TGA and DSC measurements. Microvesicles of diameter >3µm were obtained from dilute solution concentration of 2.5mg mL^{-1}. The formation of large micro vesicles observed may be attributed to the edge-edge binding of the silicate layers by the terminal vinyl silyl modification.

ELECTRO-OPTIC POLYNILINE- POLYTITANATE HYBRID NANOCOMPOSITES FOR PHOTOCATALYTIC APPLICATIONS

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Design of hybrid nanocomposites by co-assembling organic and inorganic precursors in the molecular level by control over the interfaces, structure and morphology is a challenging task. Such hybrid materials are receiving importance because the synergism between the components often gives rise to properties that are superior to the sum of those of the individual components. Harnessing the advantages of both the components requires fine tuning of the spatial assembly of individual domains and their interfaces. Nanocrystalline titanium dioxide has unique physico-chemical properties and can be used in advanced coating, cosmetic, sensor, solar cell, and photocatalyst applications.[1-8] Clays are layered materials having large surface area, high cation exchange capacity and can adsorb organic substances either on their external surfaces or within their interlaminar spaces by interaction or substitution. Preparation of titanate intercalated clays is receiving importance since they are having mesoporous structure, high adsorption ability, stable photocatalytic activity and large specific surface area. [9,10] Recently, TiO2 pillared clays have studied for their photocatalytic activity on degradation of some organic pollutants in water.11 They can enhance the electron transfer between host and guest and can also impart high thermo-mechanical stability for the formed composite. Several methods have been developed to prepare TiO2–clay composites. They are usually prepared by the exchange of Ca^{2+}, Na^{+}, and K^{+} present in the clay gallery by OH-Ti cation species.

Conjugated polymers with extended π- electron systems such as polyaniline, polythiophene, polypyrrole and their derivatives have shown great promises due to their high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers, and good stability.26 Polyaniline (PANI) is one of the most important conducting polymers because of its unique opto-electrical properties, ease of preparation, excellent environmental stability and tunable conductivity via special proton doping mechanism.27,28 Therefore, conjugated polymers with wide band gap inorganic semiconductors are receiving importance for optical, electronic, photocatalytic and photoelectric conversion applications.29-32 Conducting PANI behaves as a p-type semiconductor with a band gap absorption edge that can extend into the range of visible light, exhibits good environmental stability and has been used in varieties of applications.

Thus p-n junctions can be realized by intercalating p-type conducting polymer into the n-type polytitanatefunctionalisednanoclay layers. This should allow overcoming the drawbacks of the latter, such as its poor response to visible light, high rate of electron-hole recombination apart from controlling the configuration of the polymer by the host layers and may enhance stability of the polymer from leaching and thermal decomposition. In addition to the photocatalytic properties, a successful candidate for a global scale catalyst material need to be non-toxic, inexpensive, stable and widely available.Thus, the preparation of polyaniline- polytitanate-clay composite is receiving importance since it can exhibit unique properties arising from the synergetic effects of electrically conductive PANI, semiconducting and photocatalytic effect of polytitanate, absorbability and high aspect ratio of nanoclays. The complementary band gaps of the organic and inorganic components can be exploited to achieve functional materials. In the present work, nanostructured polyaniline-clay-polyhydroxytitanate composite (PPTC) was prepared by in-situ emulsion polymerization of aniline in presence of polytitanate ion intercalated clay at room temperature. PPTC was characterized for their particle size using dynamic light scattering measurement (~100 nm). Chemical and opto-electronic characterization using FTIR and UV-visible spectroscopy, respectively. Morphological studies using SEM, TEM and PLM analysis revealed tubular structure of PPTC. Electrical conductivity measurement using four probe methods observed to be ~2S/cm. The strong interaction between polytitanate ion and PANI was manifested from the studies made by FTIR spectroscopy. Photocatalytic activities of PPTC were studied by performing photodecolorization studies using methylene blue and methyl orange in presence of PHT and PPTC under natural light. Decolorization efficiency of the catalyst was monitored by performing UV-Vis spectral studies at different intervals of time. Under visible light irradiation, PANI generated $\pi - \pi^*$ transition, delivering the excited electrons into the conduction band of titanate, and the electrons transferred to an adsorbed electron acceptor to generate oxygenate radicals to degrade pollutants. The observed high photocatalytic activity arising from the synergistic effect between titanate and polyaniline, which promoted the migration efficiency of the photogenerated carriers on the interface of PANI and titanate. This modified photocatalyst will be a promising material for the environmental purification and also photovoltaic applications. The mechanism for the decolonization of the dyes by the photogene rated carriers at the interface of PANI and titanate ion is shown in figure 1.

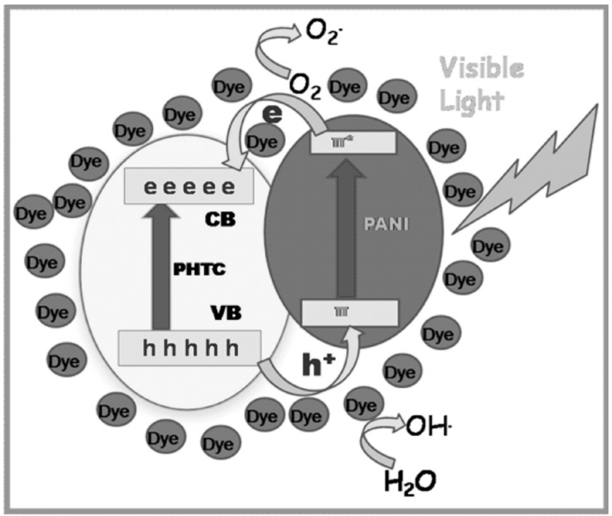

Figure 1. Mechanism for the photodegradation of dye in presence of PPTC

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Studies on the beneficial properties of Sol-gel Ceramic Nano Hybrid Fillers for Advanced Epoxy Polymers Electrical Insulators

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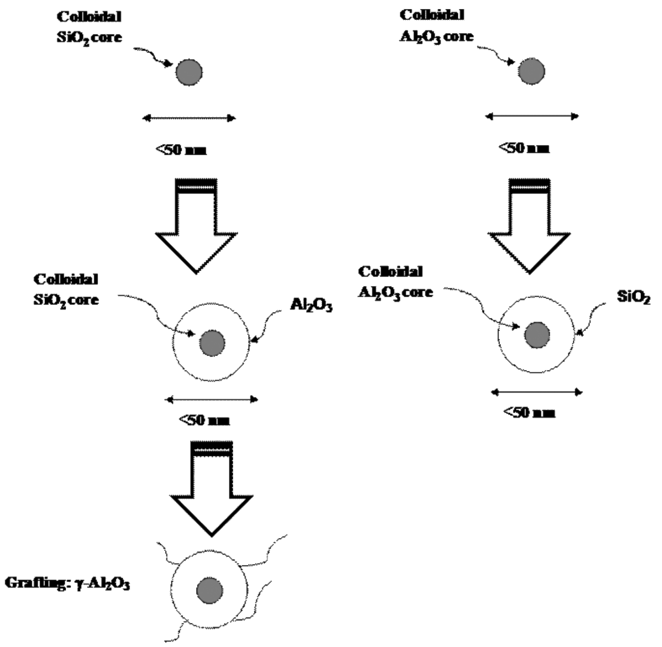
Epoxy polymers have been considered as Future Electrical Insulators due to their excellent low dielectric nature, low temperature processing, high mechanical strength and easy availability at cheaper cost. However, a drawback noticed in epoxy polymer for any insulator application is its poor thermal conducting property. Composite approach is earlier suggested as promising technique to obtain enhanced thermal conductivity. Addition of thermally conducting ceramic phases such as AlN, Al2O3, BeO, and carbon allotropes like CNTs, Graphite as fillers into epoxy polymer matrix was reported and demonstrated for high thermal conductivity. Unfortunately the improvement of thermal conductivity is observed at the expense of mechanical strength degradation and increased dielectric constant, electrical conductivity which is undesirable.

Use of surface modified, core-shell type nano composite hybrid fillers can produce high performance, advanced epoxy insulators. Hence in this work sol gel assisted ceramic-polymer nano hybrid fillers have been designed and introduced into epoxy resins to make ceramic-polymer nanocomposites.

In a typical work, Epoxy resin was procured from Huntsman Company and micron and nano size silica and alumina particles procured from Aldrich. The micro, nano and micro/nano blends taken in the ration of 10-80 wt% were incorporated into epoxy resin and cured using the hardener mixed in the ratio of 110:80. A routine solution mixing, casting and elevated temperature curing was followed to prepare the samples. Hybrid nanofillers were processed through sol gel technique in which silica and alumina layers were made on the surface of nano/nano and nano/micro ceramic fillers. In addition to that a different surface functional groups were also attached by chemical treatment.



The beneficial properties of hybrid nano fillers compared to single phase alumina, silica micro/nano fillers were studied with respect to rheology, thermal stability, glass transition and dielectric properties. The schematic representation of the different steps involved n the work is shown in Fig. 1. The efficiency of sol gel nano ceramic hybrid fillers has been systematically analyzed and reported.

Effect of functionalization and thermal exfoliation on the properties of polyimide-graphene nanocomposites

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This paper investigates the effect of functionalization and thermal exfoliation of graphene on the mechanical, dynamic mechanical and electrical properties of polyimide-graphenenanocomposite films. Graphene platelets were functionalized by modified Hummer's method and incorporated to the polyamic acid in different concentrations and imidized to polyimide-graphene films. Similarly, graphene, functionalized to different extent was thermally exfoliated at different temperatures, was used for the preparation of polyimide-graphene films.. It was found that the properties of graphene polyimide films depend on the combined effect of extent of functionalization and thermal exfoliation conditions. The studies have shown that functionalization for longer duration as well as thermal exfoliation at higher temperatures for longer duration are required for making polyimide-graphene films with good mechanical, dynamic mechanical and viscoelastic characteristics.

Key words: graphene, functionalization, thermal exfoliation, polyimide.

1. Introduction

Polyimide (PI) is an important polymer in space applications because of its excellent thermal stability, good mechanical properties, good resistant to solvents and excellent optical transparency. Though polyimide is widely used in space applications such as in satellites and spacecrafts, it needs to be rendered conductive to mitigate the electrical charges generated in the space environment. It can be made surface conductive by using current technologies such as providing indium tin oxide (ITO) coating, the future programmes demand bulk conductivity for such films without losing optical and mechanical properties. Nanotechnology aids in such situations where these films can be made bulk conductive with the addition of a very small percentage of suitable nanofillers thereby not compromising on optical and mechanical properties. Graphene, an allotrope of carbon, is an ideal nanomaterial to meet this challenge. Substantial mechanical and electrical properties of graphene gained as an ineluctable filler material for light weight super strong polymer nanocomposites including those based on polyimides.

This poster reports synthesis of graphene oxide nanoplatelets and development of polyimide-graphene films. Graphene oxide was synthesized using modified hummers method and acid functionalized followed by thermal reduction of the functionalized graphene. Electrical, mechanical and viscoelastic properties of PI-graphenenanocomposite films were studied by varying the graphene loading, functionalization method, extent of functionalization as well as the thermal exfoliation conditions. It is found that graphene, suitably exfoliated and functionalized improves the functional properties of polyimide films.

2. Experimental

Graphene was synthesized from graphite flakes using modified hummers process [1]. The final product was dried and used as the filler material. Acid functionalization of graphene was done in conc. HNO_3 by reflux reaction for 30, 60 and 90 min duration. The creation of too many functional groups can generate defects in graphene platelets which can reduce the electrical conductivity of the PI- graphenenanocomposites. Therefore, thermal reduction of the functionalized graphene was attempted to control the defects and to improve the conductivity. This method also reduces the number of layers present in the functionalized graphene. Thermal reduction is done at a temperature of 400°C and 600°C for 2hr and 8hr duration [1] under inert atmosphere.

PI-graphene films were prepared by direct sonication of graphene in polyamic acid followed by film casing on glass plates. The imidization was done by heating the solution in inert atmosphere at the following temperature conditions: 65°C for 1.30 hrs., 110°C for 2hrs, 150°C for 1hr and 300°C for 1hr.

3. Characterization

Spectroscopic analyses of the films were done using FTIR and Raman spectroscopy. The morphological studies were done using JEOL SEM. Mechanical properties were studied using Instron UTM. The viscoelastic properties are done using TA Instruments' DMA Q800. The electrical properties were studied using Trek surface resistivity meter.

4. Results and discussion

4.1 Synthesis of graphene

Fig. 1(a)-(c) are the Raman spectra of graphite flake with 15 layers, 5 layers and graphene synthesized in laboratory respectively. The peak shifts present Raman spectra indicate the reduction in number of layers in graphite, which will help confirming whether graphene is formed by the synthesis route. As the number of layers decreases, the 2D band will shift to lower wave numbers. Broadening of the 2D band also takes place as the number of layers decrease. The peak shifts given in the Table 1 indicate that graphene synthesized in the laboratory has layers less than 5 numbers because wave number of 2D band is the lowest here. From Fig. 1(c), it is also evident that the broadest 2D is band is observed for the synthesized graphene. Thus it is evident that the synthesis route adopted resulted in graphene with platelets less than 5.

Table 1: Peak positions in Raman Spectra for the graphite flakes and graphene synthesized

Specimen	2D Band peak position
15 layer graphene	2701
5 layer graphene	2691
Synthesized graphene	2676

Inducing defects in graphene will increase the intensity of the D band observed in the wave number region 1330-1360. Comparing Fig. 1(a) to 1(c), it is evident that the highest peak intensity is shown by the synthesized graphene, which indicates that functionalization of graphene has taken place [4]. FTIR spectrum shown in Fig. (1d) also confirms this observation. The presence of peak at wavenumber 3413 corresponds to the presence of -OH group occurred during functionalization. The slight shift in OH group is due to the presence of hydrogen bonding.

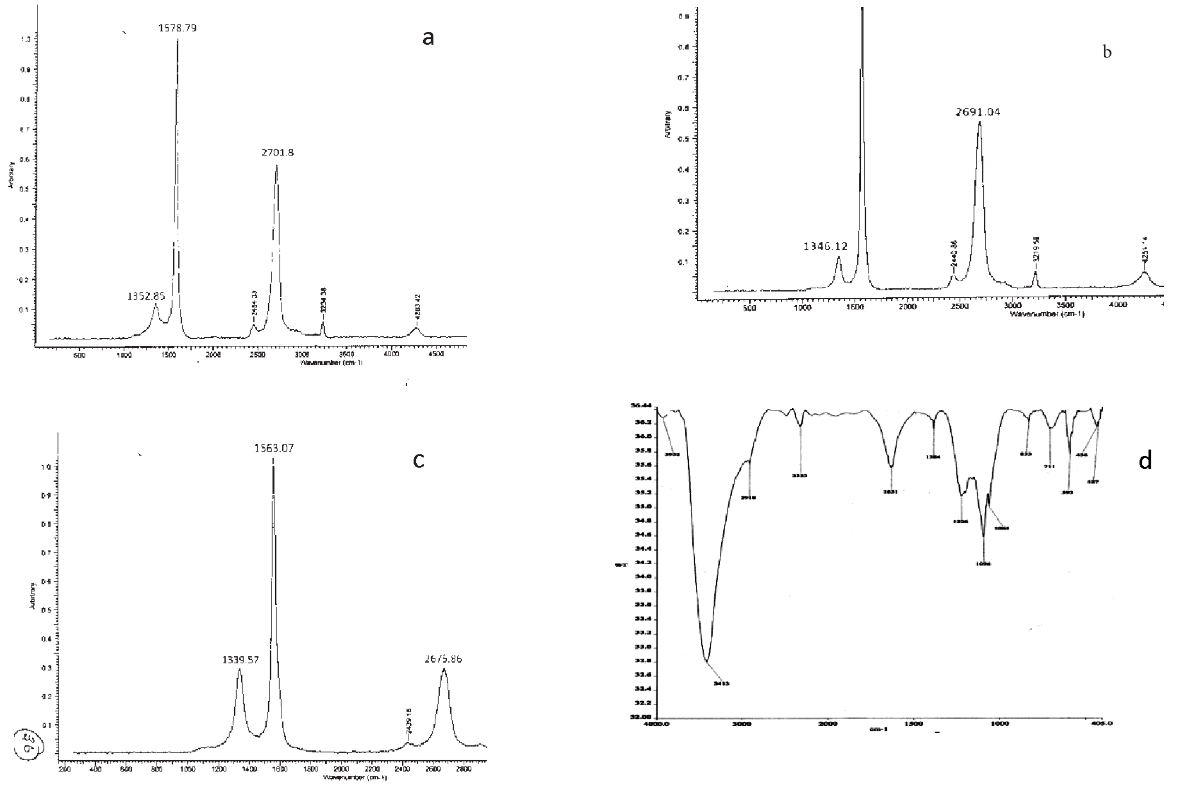


Fig. 1. (a) Raman spectrum of graphite with 15 layers; (b) Raman spectrum of graphite with 5 layers; (c) Raman spectrum of synthesized graphene and (d) FTIR spectrum of functionalized graphene

4.2 Optical transparency of the films

Functionalization of graphene will attach functional groups on the surface of graphene. These functional groups will act as new sites for bonding with the polyimide matrices which will improve the chemical bonding thereby improving the mechanical properties. One of the important points to be noted is that at 0.5wt. % addition of the functionalized graphene, the optical transparency of the films is retained. As filler concentration increases, the film becomes darker (Fig. 2). At 0.9 wt%, the dispersion of the filler is found uniform.

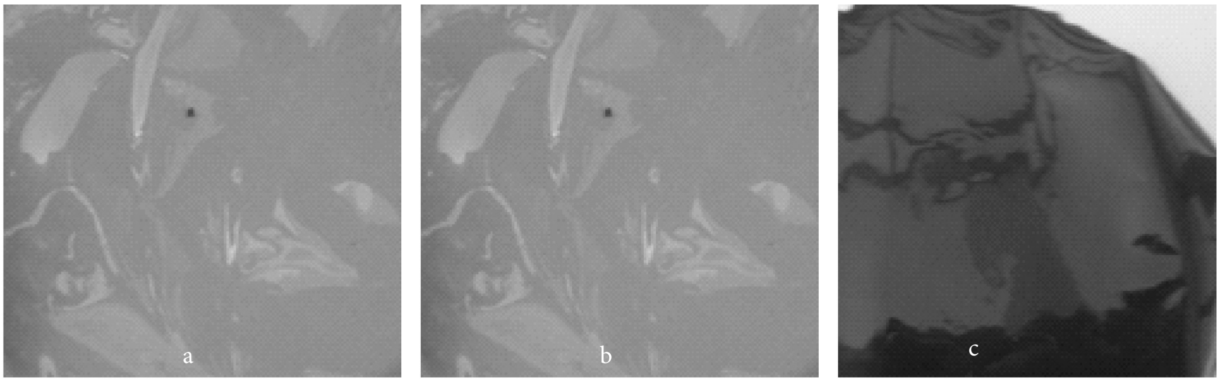


Fig. 2.Photographs of PI films. (a) neat PI film; (b) PI with 0.5 wt% functionalized graphene and (c) PI with 0.9 wt% functionalized graphene

1.3 Mechanical properties of the films

Table 2 shows that the tensile strength of the polyimide-graphenenanocomposite enhances up to 30% (for 0.5 wt% graphene loading) compared to the neat polyimide film. As the functionalization time increases, there is a slight reduction in tensile strength. It is found that 30 min functionalization is the optimum for optimum mechanical properties. However, when the functionalized graphene is thermally exfoliated, longer extent of functionalization also contribute to the exfoliation of graphene layers. As is evident from Table 3, the highest mechanical properties are shown by the film containing 90 min functionalized graphene, thermally exfoliated at 600 °C for 8 hours. This shows that vigorous conditions like longer duration of functionalization and higher temperature of thermal exfoliation are required for separating the individual graphene layers from the bulk. The representative stress-strain curves of the films are shown in Figs. 3(a) and 3(b).

Sample details*	Functionalization time (min)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
Neat PI film	0	93 ± 14	3 ± 0.2	10 ± 4
0.3% FGS/PI	30	94 ± 4	2 ± 0.0	9 ± 2
0.5% FGS/PI	30	106 ± 5	3 ± 0.0	13 ± 4
0.9% FGS/PI	30	92 ± 1	2 ± 0.1	9 ± 2
0.9% FGS/PI	60	93 ± 11	2 ± 0.2	10 ± 4
0.9% FGS/PI	90	85 ± 1	2 ± 0.1	13 ± 1

**FGS – functionalized graphene sheets*

Table 3 Mechanical properties of thermally exfoliated graphene loaded PI films

Sample details	Functionalization time (min)	Exfoliation condition	Tensile strength(MPa)	Tensile modulus (GPa)	Elongation at break (%)
0.9% FGS/PI	30	400°C,2hr	88 ± 11	2 ± 0.2	18 ± 8
0.9% FGS/PI	30	600°C,2hr	70 ± 17	2 ± 0.2	7 ± 4
0.9% FGS/PI	30	600°C,8hr	95 ± 8	3 ± 0.1	6.0 ± 1
0.9% FGS/PI	60	400°C,2hr	54 ± 4	2 ± 0.3	12 ± 2
0.9% FGS/PI	60	600°C,2hr	96 ± 2	3 ± 0.3	10 ± 3
0.9% FGS/PI	60	600°C,8hr	89 ± 9	3 ± 0.4	8 ± 1
0.9% FGS/PI	90	400°C,2hr	94 ± 8	2 ± 0.1	10 ± 2
0.9% FGS/PI	90	600°C,2hr	98 ± 2	3 ± 0.2	10 ± 3
0.9% FGS/PI	90	600°C,8hr	120 ± 12	2 ± 0.2	19 ± 4

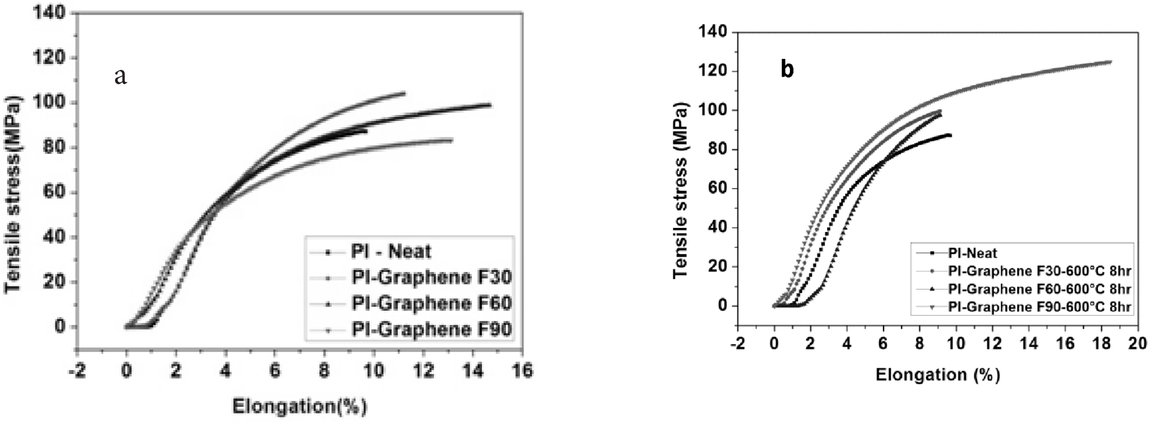
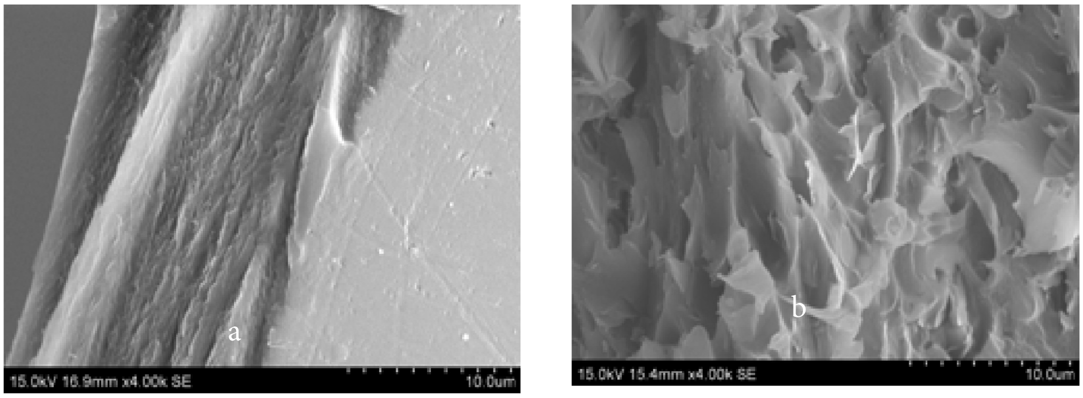


Fig. 3 Stress-strain curves of (a) PI-graphene films with graphene functionalized for different duration and (b) thermally exfoliated graphene incorporated PI films

The fracture surface morphology of the films has been studied by using scanning electron microscopy (SEM). From the SEM micrographs given in Fig. 4, it is evident that the interaction between graphene and polyimide matrix has been enhanced with functionalization of graphene (Fig. 4(a) vis-à-vis Fig. 4(b)).



4.4 Studies on the viscoelastic properties of the films.

Fig. 5(a) shows the variation in storage modulus and tan δ with increasing graphene loading for the films based on functionalized graphene (30 min functionalization). It is evident that the optimum loading of graphene in this case is 0.5 wt% after which there is no significant change in the storage modulus. At the same time at higher temperature (above 370 °C), storage modulus of the 0.5 wt% graphene loaded film is higher than that of 0.9 wt% loaded film. This further confirms the observations made in the mechanical property measurements. Tan δ shows a positive shift of more than 10 °C for the film loaded with 0.5 wt% functionalized graphene.

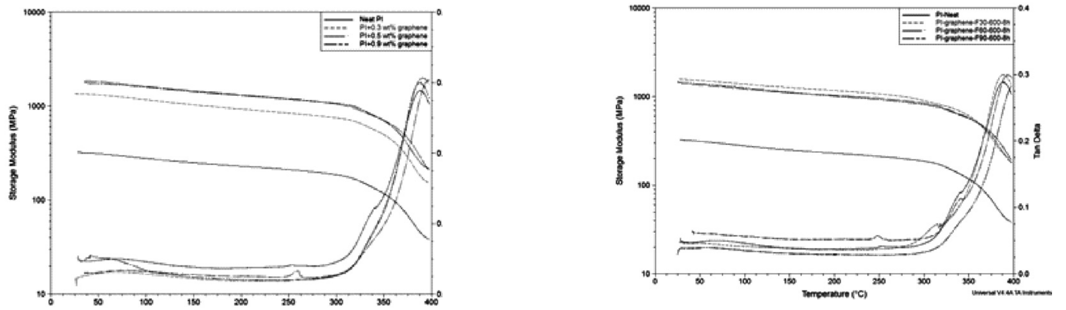


Fig. 5 (a) Variation in storage modulus and tan δ with increasing graphene loading; (b) variation in storage modulus and tan δ with different extent of functionalization for the thermally exfoliated graphene

Thermal exfoliation also improves the viscoelastic characteristics of the film (Fig. 5(b)). There is one order increase in storage modulus when functionalized graphene is thermally exfoliated. As observed in the mechanical property analysis, the extent of functionalization and thermal exfoliation affect the dynamic mechanical properties of the film, especially at higher temperatures. Though 30 min functionalized graphene, thermally exfoliated for 8 hours at 600 °C gives higher storage modulus up to 350 °C, 90 min functionalized graphene thermally exfoliated for the same duration gives higher storage modulus above 350 °C. The tan δ also shifts to more than 10 °C (> 400 °C) for these films.

4.5 Electrical properties of the films

The surface resistivity of the PI-graphene nanocomposite has shown a two oder reduction in resistivity. In presence of graphene, the films have achieved the electrical conductivity with minimum loss in transperancy as shown in Fig. 2. The surface resistivity of the selected films are given in Table 4.

Table 4 Electrical properties of the films

Type of film	Graphene loading (wt%)	Surface resistivity (Ω/□)
Neat PI films	0	2.02 x 10^{13}
PI- graphene F 30*	0.5	2.43 x 10^{12}
PI-graphene F 90**	0.9	3.10 x 10^{11}
PI-graphene F 90-600-8hr***	0.9	2.12x 10^{11}

** graphenefunctionlized for 30 min*
*** graphenefunctionlized for 90 min*
**** graphene functionalized for 90 min thermally exfoliated at 600 °C for 8 hours*

5. Conclusions

It is demonstrated that modifying nano-graphene sheets and incorporating them in polyimide matrix can give better dispersion and improved mechanical, dynamic mechanical and electrical properties. The optical transparency of the polyimide film can be retained up to 0.5 wt.% loading of graphene. There is 30% improvement in tensile strength when 0.5 wt% graphene, functionalized for 30 min., is incorporated into polyimide matrix. The high temperature storage modulus also is the highest for this film with a positive shift (more than 10 °C) in tan δ. The studies have shown that thermal exfoliation of functionalized graphene has significant effect on the mechanical and dynamic mechanical characteristics of the films. Graphene sheets, functionalized for maximum duration (90 min in this study) and thermally exfoliated to the highest temperature and duration (600 °C and 8 hours respectively in this study) displayed the highest mechanical properties and high temperature storage modulus. Fracture surface morphology of the film significantly changes in presence of modified graphene. The surface resistivity of the films found decreasing in presence of graphene.

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PREPARATION AND CHARACTERIZATION OF GRAPHENE/PDMS NANOCOMPOSITES

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Introduction

Graphene, the one atom thick, two-dimensional single layer of graphite, is emerging as a rising star in the field of material science because of its prominent intrinsic properties. Nanocomposites utilizing graphene materials as nanofillers offer opportunities to impart unprecedented enhancement in mechanical and thermal properties to polymers at very low loading. Poly(dimethyl siloxane) (PDMS) is the most widely used silicon-based organic polymer, and is particularly known for its unusual rheological properties. PDMS is optically clear, and, in general, is considered to be inert, non-toxic and non-flammable. Graphene/PDMS composites are potential candidates for many practical applications including light triggered actuators. In this work, Graphene/PDMS composites are prepared and their properties are evaluated.

Experimental

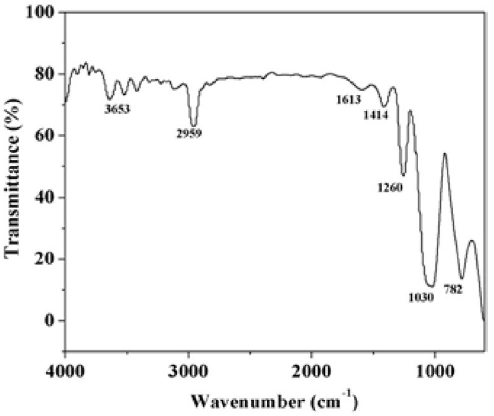
Graphite oxide was synthesized from graphite flakes by improved Hummer's method using H2SO4/H3PO4 mixture as the oxidizing agents. The resultant graphite oxide was then readily exfoliated to completely water dispersed graphene oxide (GO) by ultra-sonication, which was dried in an air oven at 100oC to get GO sheet. Thermal reduction of graphene oxide was done in a preheated muffle furnace at 850oC for 1 min. The graphene powder was sonicated in Dimethyl formamide for 2h and dispersed in Hydroxyl terminated poly(dimethyl siloxane) using an automatic mortar grinder for 5h to get a homogenous dispersion and was cross linked by using tetra ethyl orthosilicate and dibutyl tin dilaurate as cross linking agent and catalyst respectively. The slurry was then cast on a stainless steel mould at room temperature and kept for 12h to cure. The sample was then post cured at 150oC in an air oven for 4h. Composites were prepared with varying weight percentage of filler loading from 0 - 1.0 wt%.

Graphene oxide and graphene were characterized by X-ray diffraction (XRD) studies, Fourier transform infra red spectroscopy, Thermo gravimetric analysis under air and nitrogen at a heating rate of 10oC/min and Scanning electron microscopy. Mechanical properties of the composites and hardness of the samples were also measured.

Results and Discussions

The conversion of Graphite to Graphite Oxide was confirmed by XRD. The FT- IR spectrum of the graphene - PDMS nanocomposites(Fig. 1) shows peaks at 3653 cm-1 due to - OH stretching vibration of adsorbed water molecule, peak at 2959 cm-1 is due to C-H stretching of CH3 and aromatic C=C gives peak at 1613 cm-1. CH3 asymmetric deformation of Si -CH3 gives peak at 1414 cm-1, peak at 1260 cm-1 is due to CH3 symmetric deformation of Si -CH3, Si-O- Si stretching vibration gives peak at 1030 cm-1, which is the highly intense peak. Peak at 782 cm-1 is due to Si-C stretching and CH3 rocking motion. There is no peak corresponding to C=O indicating the absence of DMF solvent. Hence it is confirmed that DMF is completely evaporated when the sample is post cured at 150 oC for 4h.

TGA of graphene- PDMS composites were done in air and nitrogen atmosphere (Fig.2). There is a remarkable difference in the degradation pattern of the composite in air and nitrogen atmosphere. In nitrogen atmosphere, the degradation starts at 400oC and peak degradation occurs at 540oC. The percentage residue is around 1.3%. In nitrogen atmosphere, PDMS completely degraded by forming volatile cyclic oligomer. In the air atmosphere, degradation starts at a temperature of 310oC and maximum degradation occurs at 459oC. The percentage residue remaining at 800oC was 28.1%. The higher residue is due to the formation of silica by the oxidation of PDMS in air.



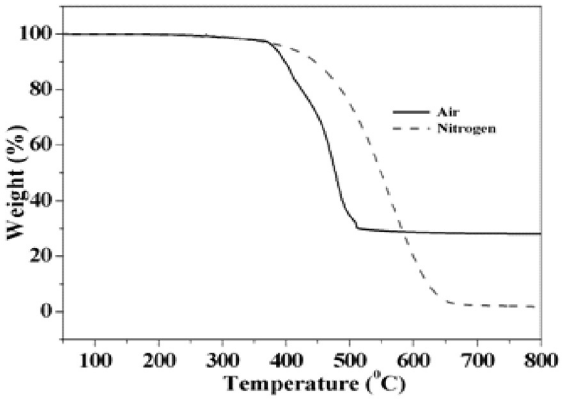


Fig.1:*FT-IR of Graphene/PDMS nanocomposites* ***Fig. 2:****TGA of Graphene-PDMS nanocomposite*

SEM of the composites **(Fig. 3)** shows a uniform distribution of graphene in PDMS matrix

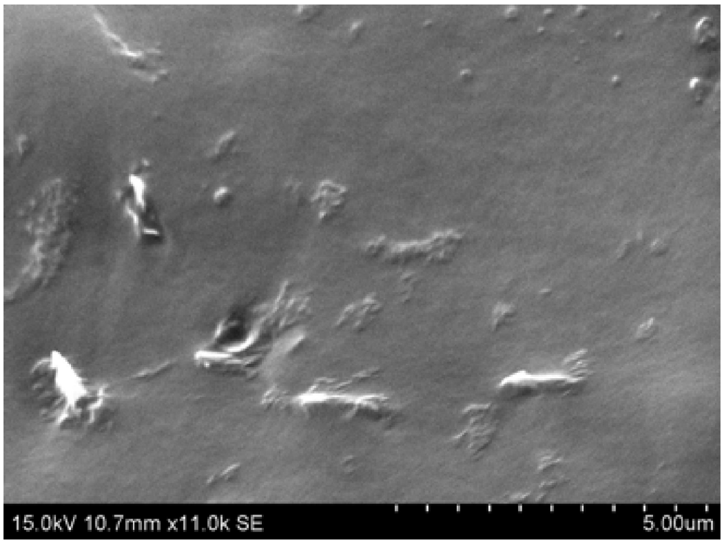


Fig. 3: *SEM of Graphene-PDMS nanocomposites*

The mechanical characteristics of the graphene - PDMS nanocomposites are given in table 1. The tensile strength of the PDMS is improved by the addition of the graphene filler without affecting much the elongation which is good for the actuation properties of the graphene - PDMS nanocomposite. Hardness of the composite is less compared to virgin PDMS.

Table 1 Mechanical characteristic of graphene- PDMS composite

Loading of graphene [wt %]	Tensile Strength [N/mm^2]	Elongation at break [%]	Young's modulus [N/mm^2]	Hardness [Shore A]
0	0.832	261	0.318	32
0.3	1.100		0.591	23
0.7	1.379	353	0.390	23
1.0	1.051	246	0.420	26

Conclusion

Graphene/PDMS nanocomposites were prepared by casting method. The nanocomposites were characterized by FT-IR, TGA and SEM analysis. The mechanical properties of the nanocomposites showed an improvement over virgin PDMS even at very low graphene loading.

Acknowledgement

The authors acknowledge the financial support of Department of Science and Technology (DST), Govt. of India

Photomechanical actuation of Styrene – Isoprene – Styrene block copolymer/ graphene nanocomposites

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Introduction

Graphene is an atomically thick, two-dimensional (2-D) sheet composed of sp^2 carbon atoms arranged in a honeycomb structure. It is the building block of many other allotropes of carbon having different dimensionalities like fullerenes, carbon nanotubes and graphite. Since their discovery, these materials have attracted a lot of research intention.Carbon nanotubes and graphene have showed the potential to replace silicon as a material for electronic devices. Nanocomposites utilizing graphene materials as nanofillers offer opportunities to impart unprecedented enhancement in mechanical and thermal properties to polymers at very low loading. Fillers for polymer composites are expected to enhance the properties of the polymer and develop a composite with properties combining that of the polymer and filler. Styrene- Isoprene-Styrene (SIS) is a tri block copolymer.It is an elastic and flexible material. SIS has properties of good flexibility adhesive strength and cohesion force. Photomechanical actuation of Graphene/ SIS composite is a new arena of research. Materials that can reversibly change their mechanical propertiesupon application of external stimuli are used as actuators. In the present work the actuation behavior of graphene filled SIS nanocomposite in the presence of IR light is investigated.

Methodology

Graphite oxide was synthesized from graphite by improved Hummer's method using H_2SO_4/ H_3PO_4 mixture as the oxidizing agents. The resultant graphite oxide was then readily exfoliated to completely water dispersed graphene oxide (GO) by ultra-sonication, which was dried in an air oven at 100^0C to get GO sheet. Thermal reduction of graphene oxide was done in a preheated muffle furnace at 1000^0C for 1 min.The graphene powder was sonicated in Toluene for 4h to ensure proper dispersion.Polystyrene-block-Poly-Isoprene-block-Polystyrene was dissolved in toluene by sonication, for about 1 to 2hrs. The amount of solvent added was optimized. Both SIS and graphene in toluene were mixed together and sonicated for 1hr. The resultant mixture was casted and thin sheets of composites were obtained after solvent evaporation. Photomechanical actuation employs an infrared light to trigger the graphene/SIS nanocomposite. An Infra red (IR) exposure of 15 seconds was given to the sample fixed on clamps. Actuation measurements were carried out in an in vitro muscle test apparatus. Mechanical properties of the nanocomposites were studied.

Result and discussion

XRD pattern of graphite, graphite oxide and graphene prepared thermal reduction method were given in figure 1. The XRD pattern of graphite powder exhibits a characteristic peak of graphite at 2θ = 26.3^0. After oxidation, the characteristic peak of graphite is shifted to 2θ = 11.2^0. This corresponds to the diffraction peak of graphite oxide.

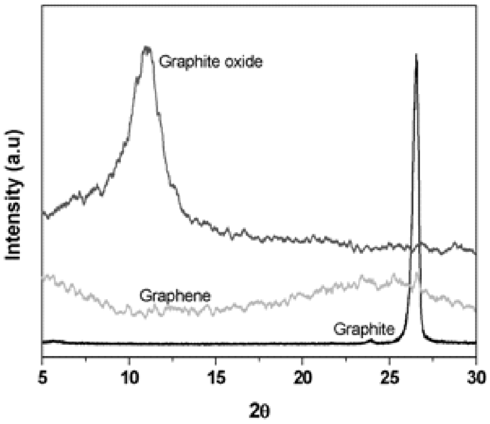

Fig. 1: *XRD pattern GO,Graphene&Graphite*

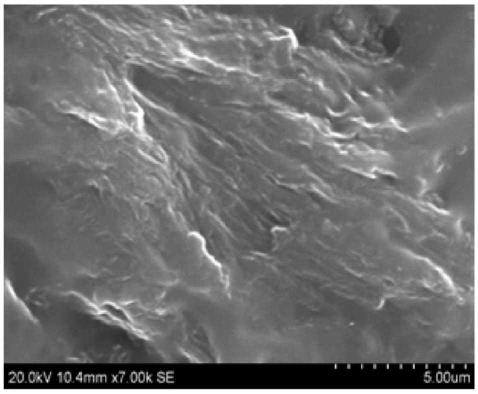

Fig 2: *SEM image of 2wt% Graphene/ SISnanocomposite*

SEM image of the fractured surface of 2wt% graphene/SIS composite was given in Fig. 2. The graphene sheets protruded from the matrix can be seen in the image. The photomechanical actuation studies of different weight percentages of Graphene/SIS nanocomposite was done using IR source, kept at a distance of 25 cm. A typical photomechanical actuation behavior of 1.5 wt. % Graphene/SIS nanocomposite with different prestrains is given in Fig.3. At lower prestrains the nanocomposites shows expansion. At 10% prestrain, there was no noticeable contraction or expansion. Further as the prestrain was increased, the composite exhibited a contraction. The sample returns to its original position on removal of IR source.

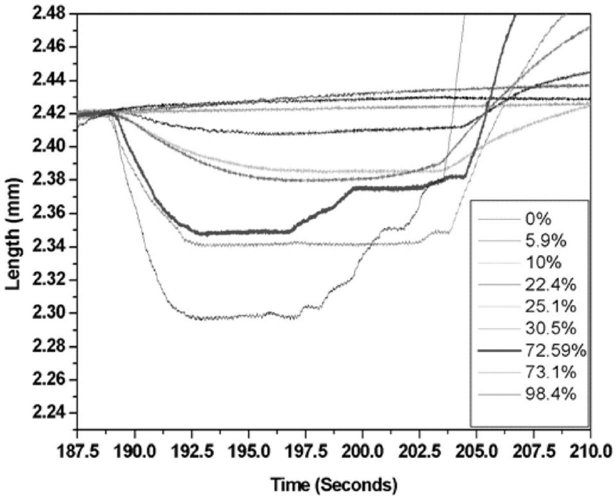

Fig 3: Actuation response of 1.5 wt% G/SIS composite at different prestrains

Conclusion

The exceptional electronic and mechanical properties madegraphene a suitable material for technological applications. Hence synthesis of high quality graphene is thus a necessity. In the presentwork, graphene oxide was prepared through improved Hummer's synthesis method and thermal reduction was employed to obtain graphene. Graphene/ SIS nanocomposites were prepared by slip casting and the process conditions were optimized. Photomechanical actuation studies of Graphene/SIS composites were conducted. These nanocomposites exhibited good IR response.

Acknowledgement

The authors acknowledge the financial support of Department of Science and Technology (DST), Govt. of India

The results showed a very good agreement within the whole conversion range for the unfilled and all the filled systems.

Effect of copper nanoparticles on the cure kinetics of an epoxy/ cycloaliphatic amine system

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The effects of copper nanoparticles on the cure kinetics of DGEBA-based epoxy resin / aliphatic amine system were studied. Cure kinetics studies were carried out by performing dynamic and isothermal differential scanning calorimetric (DSC) experiments. The dynamic DSC experiments were carried out at four different heating rates. Dynamic kinetic modeling was performed using Kissinger and Ozawa approaches. Since these methods are based exclusively on the maximum rate of cure, which occurs approximately at the beginning of the cure reaction, the activation energy calculated using these methods is valid only for the initial stage of the cure. A plausible reaction mechanism which involves the effect of the nanoparticle as an accelerator of the cure reaction was proposed. The Isothermal DSC scans were carried out at three different temperatures. The experimental data showed an autocatalytic behavior of the reaction, and the isothermal modeling was carried out by Kamal autocatalytic model.

P(VDF-TrFE)/$BaTiO_3$ Polymer Nanocomposite with Enhanced β Phase for Ferroelectric Applications

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We report the impact of BaTiO3 nanoparticle on the β phase of poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)]. β phase formation on the material enhances the ferroelectric properties of the sample. Poly(vinylidene fluoride-trifluoroethylene) is one of the most promising PVDF ferroelectric copolymer. The increase in crystalline properties of PVDF by copolymerization with TrFE results in higher polarization characteristics under an applied electric field, which is very crucial for electrical applications [1].This enhancement originates from the electro negativity between fluorine, carbon and hydrogen. Fluorine side attracts most of the electrons and hence results in polarisation [2, 3]. Out of the four phases, α, β, γ and δ, the β phase has large spontaneous polarization. Hence the enhancement of β phase is very important.

The dielectric, ferroelectric and piezoelectric properties of P(VDF) polymers can be increased by blending them with functional inorganic powders like lead zirconium titanate or barium titanate[4-8]. BaTiO3 is one of the most important electro ceramic materials among all ferroelectric materials, with very high dielectric constant.The main aim of this work is to show that there is enhancement in the β phase intensity in the P (VDF-TrFE)/BaTiO3nanocomposite. Different analysis techniques like XRD, FTIR and Atomic Force Microscopy (AFM) were done and it all shows that the addition of BaTiO3 enhances the β phase of PVDF-TrFE and hence the ferroelectricity.

P (VDF-TrFE) copolymer powder with 70/30 mol was obtained from Solvay Solaxis, Italy. BaTiO3nanopowder (size <100nm) was added to solvent Methyl Ethyl Ketone (MEK) to get solutions of different concentrations like 0.2%, 0.4%, 0.6% and 0.8%. To this we add P(VDF-TrFE) to make P (VDF-TrFE)/BaTiO3nano composite. Different analysis techniques like XRD, FTIR and AFM were done and it all shows that the addition of BaTiO3 enhances the β phase of PVDF-TrFE and hence the ferroelectricity.

FTIR studies were carried out to investigate the formation of β-phase and also to study the chemical interactions of BaTiO3 nanoparticles with P (VDF-TrFE) with a Nicolet Magna-750 FTIR spectrometer.The characteristic vibration bands of P (VDF-TrFE) and its nanocomposites were analysed within the frequency range of 400-4000cm-1. Figure 1 shows the peaks representing the β-phase. Peaks at 1288 cm-1 and 1184 cm-1 represent the asymmetric and symmetric vibrations of C-F bonds. Vibrations associated with the C-F asymmetric stretch at 1288 cm-1are very much sensitive to ferroelectric crystallinity. The Peaks at 850 cm-1 and 885 cm-1 associates with the C-F symmetric stretch and C-H2 in plane rocking deformations respectively. The above all bonds are highly sensitive to dipole orientation towards the applied electric field.From the FTIR analysis it can be concluded that the β-phase (850, 1288, 1400 cm-1) has been developed in the matrix and its composites.

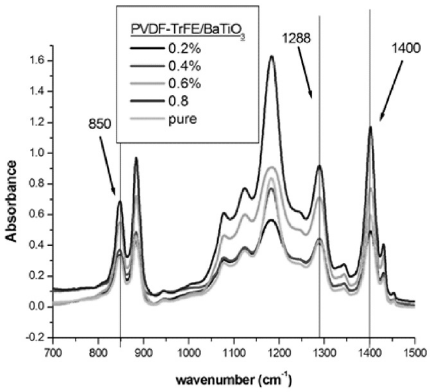


Fig 1: FT-IR spectrum of P (VDF-TrFE)/BaTiO$_3$ samples showing the β phase peaks at 850cm^{-1}, 1288cm^{-1} and 1400 cm^{-1}

The XRD spectra of the nanocomposites are depicted below in figure 2. The diffraction peaks at 2θ=19.9o corresponds to (110) and (200) orientation planes of polar β phase. From the spectra it can be observed that there is a peak shift towards lower angles, due to the enhancement of β phase. In support with the FTIR analysis, the XRD analysis also confirmed the enhancement of β phase by the introduction of ferroelectric nanoparticle to the matrix

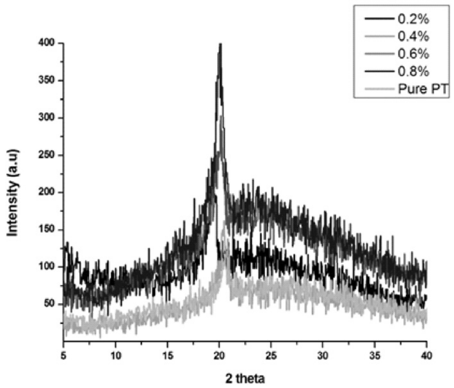
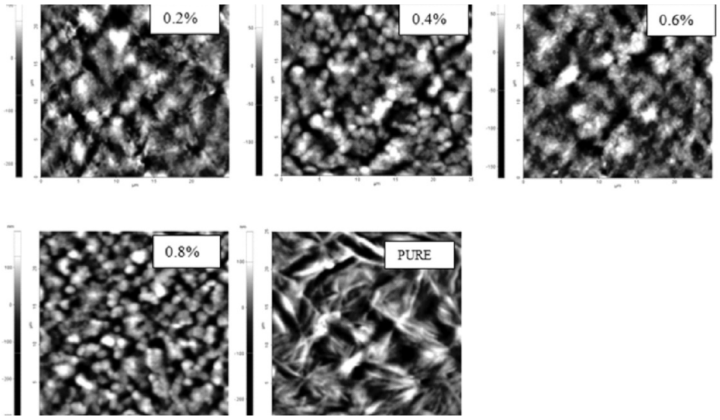


Fig 2: XRD spectrum of PT-BT samples showing the β phase peaks at 2ϑ=19.9 ^{o}C

Atomic Force Microscopy (AFM) analysis was done to study topography and roughness of the materials. Topography images are shown in figure 3 below. Surface roughness of the material has been calculated from the topography images. The roughness values of the composites are shown in figure 4. Introduction of the nano particle to the matrix leads to a smooth surface, which corresponds to β phase.



*3 : The AFM images of P (VDF-TrFE)/BaTiO$_3$ samples showing the effect of BaTiO$_3$ in PVDF-TrFE . (Scan size: 25*25 µm, Scan mode: Non-contact mode)*

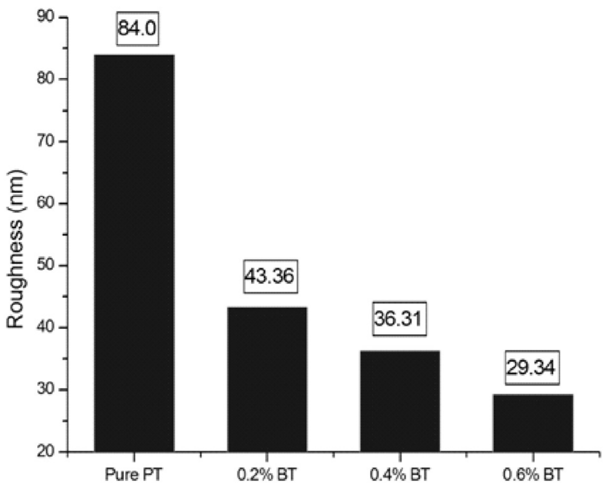


Fig 4: Graph showing the surface roughness of P (VDF-TrFE)/BaTiO$_3$ samples done using AFM.

To conclude, P(VDF-TrFE)/ BaTiO3nanocomposites have been prepared with increased β phase. Enhancement in β phase has been confirmed with different characterising techniques. This enhancement is found by checking out the presence of β phase in the samples. The physical study of these samples where done with the help of AFM. Decrease in roughness shows the enhancement of β phase. The results obtained from FT-IR and also XRD justifies the presence of β phase. Thus there will be enhancement in the ferroelectric properties. . The results obtained from these studies are superior or comparable with the existing literature. This property can be used in many applications like memory, FeFET, ferroelectric capacitors etc...

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Polarization Switching Behaviour of Ferroelectric P(VDF-TrFE)/ $BaTiO_3$nanocomposite using Piezoresponse Force Microscopy

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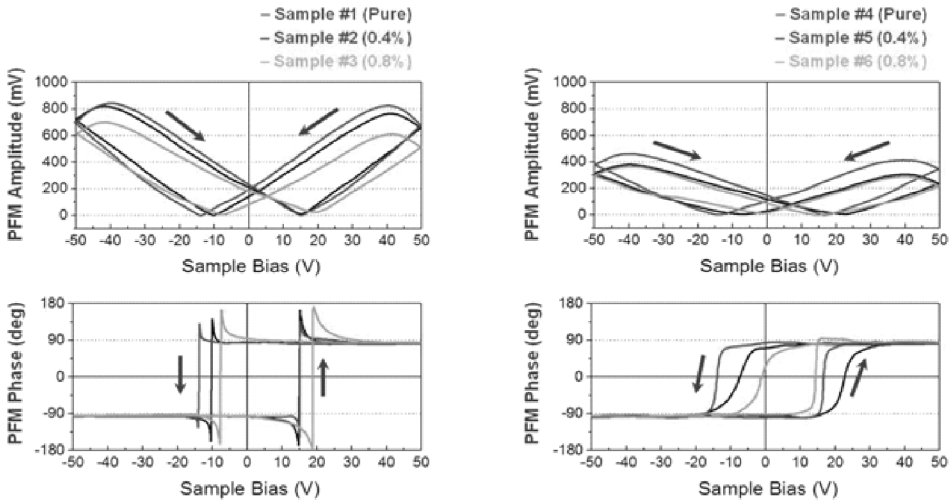
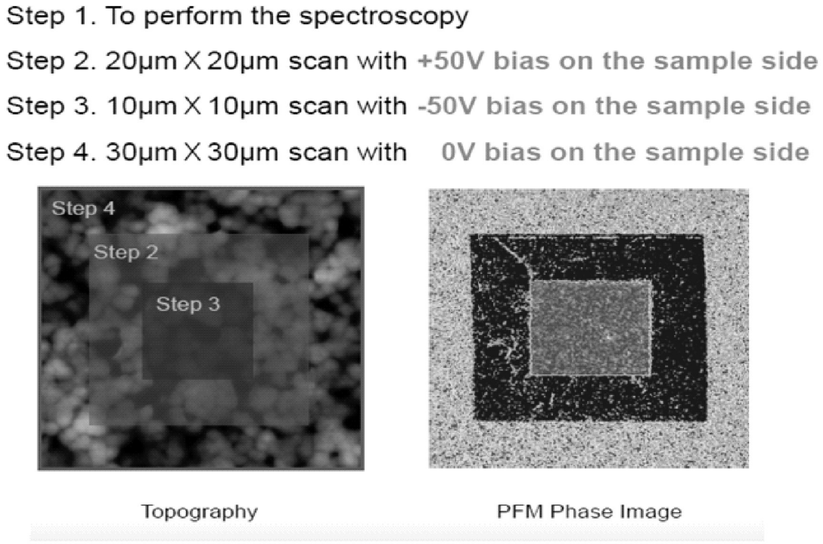
In the present work, we have reported the ferroelectric properties of P(VDF-TrFE)/BaTi03 using Piezoresponse Force Microscopy (PFM). Poly(vinylidenedifluride-trifluroethylene), P(VDF-TrFE), is among the most well-studied organic ferroelectric.The high polarization of the poly(vinylidene fluoride-trifluoroethylene) copolymer originates from the large difference in electronegativity between fluorine, carbon andhydrogen (Pauling's value for fluorine, carbon and hydrogen are 4.0, 2.5 and 2.1, respectively) [1]. Most of the electronsare attracted to the fluorine side of the chain and polarization is created. Similar to poly(vinylidene fluoride)[PVDF], poly(vinylidene fluoride-trifluoroethylene) has four known phases; phase I (α), phase II (β), phase III (γ) andphase IV (δ) . The β phase is the all-trans zig-zag planar configuration, which generates the largest polarizationalong the b axis (parallel to C, F dipole moment). There has always been interest in improving the dielectric, ferroelectric and piezoelectric properties of PVDF co-polymer by blending them with functional inorganic powders like lead zirconium titanate or barium titanate [2-6]. BaTiO3 is one of the most important electro ceramic materials among all ferroelectric materials, with very high dielectric constant.

P (VDF-TrFE) copolymer powder with 70/30 mol was obtained from Solvay Solaxis, Italy. BaTiO3nanopowder (size <100nm) was added to solvent Methyl Ethyl Ketone (MEK) to get solutions of different concentrations like 0.4% and 0.8%. To this we add P(VDF-TrFE) to make P (VDF-TrFE)/BaTiO3nano composite. For a comparative study we have analysed pure P(VDF-TrFE) also. P (VDF-TrFE)/BaTiO3 samples where spin coated on copper plate and also one set on glass plate.

Piezoresponse force microscopy PFM has been shownto be a powerful technique and has been widely used to studynanoscaleferroelectricity and piezoelectricity. Common application of PFM includes local characterization of electromechanical properties of materials, including detailed domain mapping and study of domain switching dynamics. Our samples were subjected to PFM analysis. Figures 1 show the hysteresis phase loopand the piezoresponse amplitude loop acquired with the PFM for samples coated on copper plate as well as glass plate. The result is more accurate for the sample coated on copper plate. The sweep direction for acquiring the hysteresis loop was from -50V → +50V → -50V and with a sweep rate of 20sec. A square loop in the hysteresisphase loop and a classic "butterfly shape" amplitude loopwere observed, which implied the existence of well defined polarizations [7]. The PFM image clearly shows the domain switching in the samples. Figure 2 shows the procedure for doing polarisation switching and figure 3 shows the PFM images of samples on copperplate after polarisation switching has done.



Figures 1: show the hysteresis phase loop and the piezoresponse amplitude loop acquired with the PFM for samples coated on copper plateand glass plate



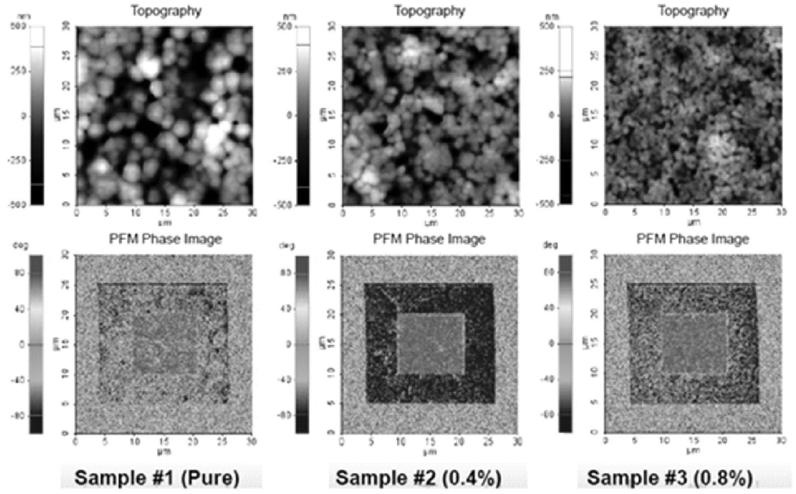
Step 1. To perform the spectroscopy

Step 2. 20μm X 20μm scan with +50V bias on the sample side

Step 3. 10μm X 10μm scan with -50V bias on the sample side

Step 4. 30μm X 30μm scan with 0V bias on the sample side

Figures 2: Step wise procedure for doing polarisation switching



Figures 3: Polarisation switching of copper plate samples

Thus to conclude we have analysed the P(VDF-TrFE)/BaTiO samples using PFM . We were able to acquire the topography and domain images of the samples. The polarization hysteresis curves and polarization switching images confirms the presence of ferroelectric property in the composite. The above results clearly explains the effect of addition of ferroelectric BaTiO3 to ferroelectric P(VDF-TrFE).

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SYNTHESIS OF CdS NANOCRYSTALS USING EXPANDED POLYSTYRENE WASTE

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Semiconducting nanocrystals shows novel optical and charge transfer properties which are useful for technological applications. Composites of semiconducting nanocrystals in polymers have lot of applications such as biological imaging, photocatalysis, solar cells, optical switching etc. These properties originate from the luminescent and nonlinear optical properties of the composite. In situ synthesis of nanocrystals in polymers reduce the chances of aggregation. Several studies describe the direct synthesis of nanocrystals in polymer matrix. Du et al synthesized CdS quantum dots in sulfonated polystyrene. Wang Y. et al have reported a third order non- linearity of CdSnanocrystals embedded in Nafion films. Incorporation of CdS nanoparticles into polymer –blend membranes of poly(styrenephosphonate diethyl ester) (PSP) and cellulose acetate has also been reported.The present work proposes the synthesis of CdSnanocrystals over functionalized polystyrene recovered from waste thermocol . Advantage of this nanoCdS synthesis is that the method does not need surfactant or capping molecules to prevent aggregation .The polymer acts as a template for the synthesis of nanocrystals.

Polystyrene recovered from the waste thermocol using dichloromethane. Sulfonation of the polystyrene recovered from waste thermocol was done using con. H2SO4 in presence of Ag2SO4 catalyst in dichloroethane solvent. The precipitated sulfonatedpolystyrene(SPS) washed several times with water and dried in vacuum oven at 600C. The SPS is insoluble in water and soluble in Toluene/Methanol mixture. In water it swells to form a gel. The CdSnanocrystals were attached to the resultant sulfonated polystyrene(SPS) gel in aqueous solution through the -SO3H functional group in two steps. In the first step Cd2+ was attached to the SPS by ion exchange mechanism. The excess Cd2+ ions were removed by washing with water till the washings were free from Cd2+ ions. In the second step CdSnanocrystals were generated by adding Na2Ssolution. The resultant yellow nanocomposite was characterized by SEM, FESEM, FTIR and XRD measurements.

This in situ synthesis of CdSnanocrystals in sulfonated polystyrene is a simple method for the formation of CdS-SPS nanocomposite from waste expanded polystyrene.

OPTICAL AND ENERGY APPLICATIONS, SMART POLYMERS

DESIGN, DEVELOPMENT AND EVALUATION OF NOVEL POLYMER ANALOGOUS ORGANIC SENSITIZERS FOR DSSC

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Introduction

Dye- Sensitized Solar Cells (DSSC) provide an economically viable alternative to the state- of-the-art, wafer-based p-n junction photovoltaic devices. They are expected to gain growing market shares in the years to come, owing to the potential for realization of flexible, thin film photovoltaic devices with moderate efficiency (5-10%), which can be processed under non- vacuum conditions, at temperatures from 30°C to 450°C. Present paper is focused on the molecular design and development of novel dye sensitizers and study of their suitability for application in DSSC.

Design of novel dye sensitizer using theoretical modeling

The photovoltaic performance of solar cells was fine-tuned by appropriately selecting the dye, based on Density Function Theory (DFT) and time dependent DFT (TD-DFT) computational methods. The electronic effects of varying substituents in the dye molecules have been evaluated and geometry optimizations and time dependent calculations were performed using DFT with the B3LYP functional and 6-31+G(d,p) basis set. The molecular structure and absorption spectra of the synthesized dyes were calculated in the gas phase using the Guassian 09W computational package. Figure 1 shows the optimized structure for two dyes chosen for the present study.

Synthesis and characterization of dyes

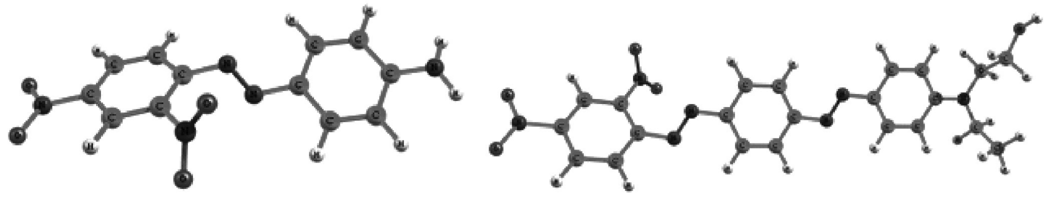

Fig.1. Optimized structure of the dyes

The theoretically optimized dyes were synthesized by appropriate synthesis strategy. Fig.2 shows their chemical structures.

The synthesized dyes were characterized by FTIR, UV-Visible spectroscopy, emission spectroscopy,

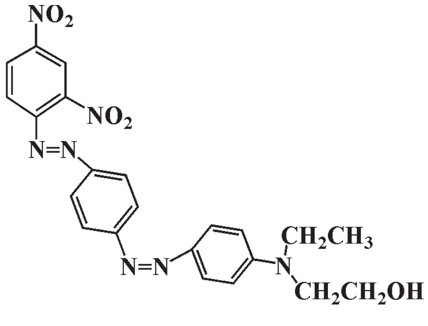

Fig.2a. 2-((4-((4-((2,4- dinitro phenyl) diazenyl) phenyl) diazenyl)phenyl)(ethyl)amino) ethanol

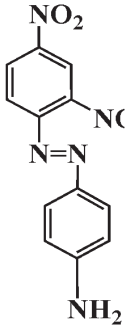

Fig.2b. 4-((2,4-dinitrophenyl)diazenyl)benzamine

NMR, elemental analysis, solar absorptance and melting point.

Electrochemical evaluation of the dyes

Sensitizer for DSSC needs to satisfy the requirements of having matching energy levels with those of titanium dioxide semi conductor and the electrolyte. Lowest Unoccupied Molecular Orbit (LUMO) of dye needs to be higher than the edge of conduction band of the semiconductor, for an efficient electron injection. The oxidation potential of dye should be more positive than the redox potential of electrolyte for accepting electrons and regenerate from the oxidized state. The energy level of developed dye, evaluated by CV and fluorescence spectroscopy satisfies the above conditions. HOMO – LUMO energy levels of dye were estimated using cyclic voltammetry, at a scan rate of 50 mV/s. It was found that the energy levels are suitable for application in DSSC. Bandgapof the dye is calculated to be 1.99 eV which is comparable to the commercial dye, N3, widely used in DSSC. Schematic representation of the energy levels of sensitizers, TiO2 and electrolyte and the photoelectrochemical system is shown in Fig.3.

Photophysical evaluation

The light absorption spectrum of the sensitizing materials ranges from UV region to near IR region, with an absorption peak at the visible region. Thus, the developed dye has an absorption maximum of 540 nm with absorption ranging from UV region to IR region with enhanced molar extinction coefficient (compared to the popular commercial dye, cis-bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato ruthenium(II) (N3)) indicating superior light harvesting capability. The solar absorptance of the dye is 0.72 (vs 0.75 for N3). Influence of solvent on the absorption wavelengths were correlated to the solvent-dye interaction. The reason for lower absorption wavelength compared to the theoretically predicted value was ascribed to the solvent-dye molecule interaction since the theoretical prediction was done in the gas phase, where no such interactions are envisaged.

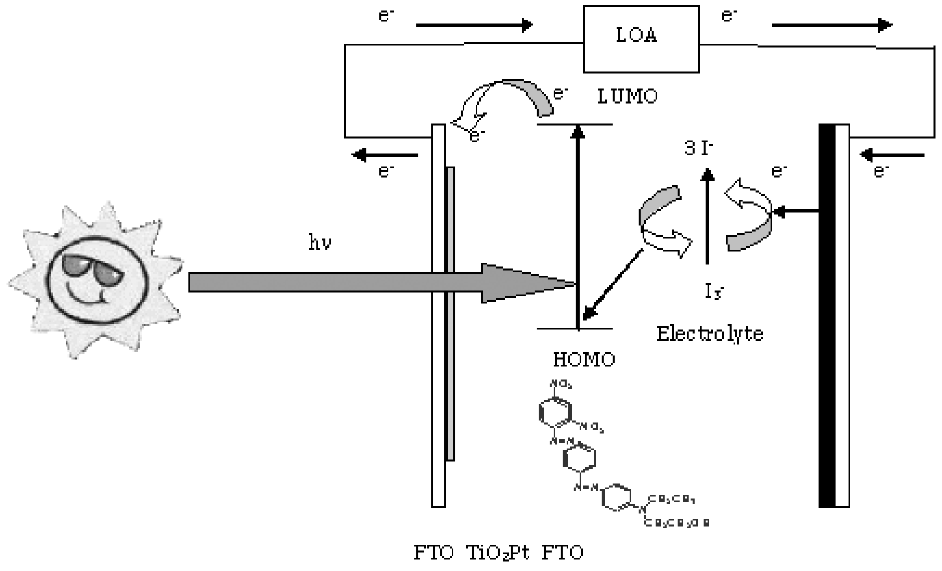

Fig.3. Schematic diagram of DSSC using TiO$_2$ as electrode and developed dye as sensitizer

Dye adsorption/retention studies

It was found that, the retention of the dye on TiO2 surface is lower for the synthesized dyes due to lower affinity of the dye towards TiO2. Thus, only 10% retention was observed (for N3 dye, retention is 50 %). Modification of the dyes with suitable adsorption promoting groups is in progress.

Conclusion

Novel conjugated dye sensitizers were designed and developed for application in DSSC. The dyes exhibited superior performance with respect to molar extinction coefficient and lower band gap and comparable solar absorptance compared to state-of-the-art dyes used in DSSC. These dyes can be probably grafted in to polymer back bone to form polymeric analogue of DSSC.

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Electro - optic Polyaniline - polytitanate Hybrid NanoComposites for Photocatalytic applications

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Design of hybrid nanocomposites by co-assembling organic and inorganic precursors in the molecular level by control over the interfaces, structure and morphology is a challenging task. Such hybrid materials are receiving importance because the synergism between the components often gives rise to properties that are superior to the sum of those of the individual components. Harnessing the advantages of both the components requires fine tuning of the spatial assembly of individual domains and their interfaces. Nanocrystalline titanium dioxide has unique physico-chemical properties and can be used in advanced coating, cosmetic, sensor, solar cell, and photocatalyst applications.1-8 Clays are layered materials having large surface area, high cation exchange capacity and can adsorb organic substances either on their external surfaces or within their interlaminar spaces by interaction or substitution. Preparation of titanate intercalated clays is receiving importance since they are having mesoporous structure, high adsorption ability, stable photocatalytic activity and large specific surface area. 9,10 Recently, TiO2 pillared clays have studied for their photocatalytic activity on degradation of some organic pollutants in water.11 They can enhance the electron transfer between host and guest and can also impart high thermo-mechanical stability for the formed composite. Several methods have been developed to prepare TiO2–clay composites. They are usually prepared by the exchange of Ca2+, Na+, and K+ present in the clay gallery by OH-Ti cation species.

Conjugated polymers with extended π- electron systems such as polyaniline, polythiophene, polypyrrole and their derivatives have shown great promises due to their high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers, and good stability.26 Polyaniline (PANI) is one of the most important conducting polymers because of its unique opto-electrical properties, ease of preparation, excellent environmental stability and tunable conductivity via special proton doping mechanism.27,28 Therefore, conjugated polymers with wide band gap inorganic semiconductors are receiving importance for optical, electronic, photocatalytic and photoelectric conversion applications.29-32 Conducting PANI behaves as a p-type semiconductor with a band gap absorption edge that can extend into the range of visible light, exhibits good environmental stability and has been used in varieties of applications.

Thus p-n junctions can be realized by intercalating p-type conducting polymer into the n-type polytitanatefunctionalisednanoclay layers. This should allow overcoming the drawbacks of the latter, such as its poor response to visible light, high rate of electron-hole recombination apart from controlling the configuration of the polymer by the host layers and may enhance stability of the polymer from leaching and thermal decomposition. In addition to the photocatalytic properties, a successful candidate for a global scale catalyst material need to be non-toxic, inexpensive, stable and widely available.Thus, the preparation of polyaniline- polytitanate-clay composite is receiving importance since it can exhibit unique properties arising from the synergetic effects of electrically conductive PANI, semiconducting and photocatalytic effect of polytitanate, absorbability and high aspect ratio of nanoclays. The complementary band gaps of the organic and inorganic components can be exploited to achieve functional materials. In the present work, nanostructured polyaniline-clay-polyhydroxytitanate composite (PPTC) was prepared by in-situ emulsion polymerization of aniline in presence of polytitanate ion intercalated clay at room temperature. PPTC was characterized for their particle size using dynamic light scattering measurement (~100 nm). Chemical and opto-electronic characterization using FTIR and UV-visible spectroscopy, respectively. Morphological studies using SEM, TEM and PLM analysis revealed tubular structure of PPTC. Electrical conductivity measurement using four probe methods observed to be ~2S/cm. The strong interaction between polytitanate ion and PANI was manifested from the studies made by FTIR spectroscopy. Photocatalytic activities of PPTC were studied by performing photodecolorization studies using methylene blue and methyl orange in presence of PHT and PPTC under natural light. Decolorization efficiency of the catalyst was monitored by performing UV-Vis spectral studies at different intervals of time. Under visible light irradiation, PANI generated $\pi - \pi^*$ transition, delivering the excited electrons into the conduction band of titanate, and the electrons transferred to an adsorbed electron acceptor to generate oxygenate radicals to degrade pollutants. The observed high photocatalytic activity arising from the synergistic effect between titanate and polyaniline, which promoted the migration efficiency of the photogenerated carriers on the interface of PANI and titanate. This modified photocatalyst will be a promising material for the environmental purification and also photovoltaic applications. The mechanism for the decolonization of the dyes by the photogene rated carriers at the interface of PANI and titanate ion is shown in figure 1.

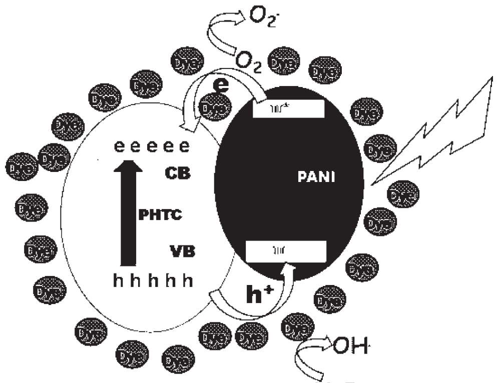

Figure 1. Mechanism for the photodegradation of dye in presence of PPTC

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Optical characterization of Erbium doped PMMA and PMMA/ EVA polymer network

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INTRODUCTION

Many organometallic complexes and compounds of lanthanides exhibits extraordinary photo luminescent properties. The erbium doped polymeric systems have received much attention due to their potential application in the manufacturing of waveguide amplifiers due to their small size, low cost, simple processing and compatible with silicon substrate [1-4]. The performance of the polymer waveguide can be improved by choosing the suitable fabrication technique and the polymeric system which gives better performance. Many researchers reported the use of erbium doped polymers for the manufacturing of erbium doped wave guide amplifiers. Polymers are very promising material for the manufacturing of waveguide amplifiers due to the great compatibility with the large variety of organic molecules and organometallic molecules allows the different combination of properties like light emission, amplification and non linear response. The synthesis of erbium containing polymers is the key source for NIR light emitting devices [5].

MATERIALS AND METHODS

Poly (methyl methacrylate) (molecular weight 120,000 gmol-1), 2,2'-bipyridine and europium nitrate pentahydrate (99.9% on the metal basis) were obtained from Aldrich, UK. Glacial acetic acid, hydrogen peroxide, acetone, chloroform and methanol (AR grade) were obtained from Fischer Scientific, UK.

Preparation of erbium (2,2'-bipyridine-N,N-dioxide)2(NO3)3.

Initially, 2,2'-bipyridine-N,N-dioxide was dissolved in hot methanol. Erbium nitrate pentahydrate, dissolved in methanol, was then added drop-wise. The mixed solution was heated at 60°C for three hours, then cooled and the product precipitated by adding diethyl ether.

Preparation of complex doped thin films

The complex doped PMMA thin films were prepared by solution casting technique. For this, known amounts of the rare earth complex, erbium (2,2'-bipyridine-N,N-dioxide)2(NO3)3, and PMMA were dissolved in chloroform. The amount of PMMA used was 100g/L. A small amount of methanol was added to the PMMA/complex solution to ensure the complete dissolution of chelate. The solution was stirred for 12 hours and then poured on to a glass mold. The wet film was then carefully stored to allow the solvent to evaporate. The thin films were then kept in an oven at 50°C for 12 hours.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The IR spectra of the 2,2'-bipyridine-N,N-dioxide ligand and the erbium complex are shown in Figure 1. The N-O stretching vibration, usually occurring at 1246 cm-1, is shifted to a lower value by 35 cm-1, with a notable splitting of the signal. The N-O bending vibrations, usually occurring at 835 cm-1 and 850 cm-1, appear at 834 and 848 cm-1 respectively. These shifts arise from changes incurred in the nature of the nitrogen-oxygen bonding as a result of coordination. The formation of the oxygen-metal atom bonds increases the demand for electrons at the donor oxygen atoms and thereby decreases the double bond character of the nitrogen-oxygen bond in the resonance structure of the ligand molecule.

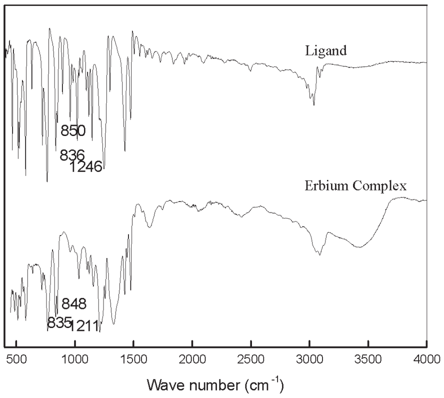

Figure 1. The IR spectra of erbium complex and ligand

The erbium complex doped polymers were analyzed by infrared spectroscopy. Figure 1 shows the infrared red spectra of complex doped polymeric systems. The peaks at 2994 and 2950 are caused by the stretching vibrations of the CH3 nd CH2 bonds. This is an indication of the hydrocarbon rich CHx of PMMA layers. The absorption band corresponds to O-H bond is not seen in the infrared spectrum of the fabricated layers indicate the absence of O-H bond in the composite systems. The O-H groups present in the composite system cuases problem by hindering the emission at 1530nm. There is likelihood for the presence of O-H vibrations in the sample since the erbium complex and the chemicals used for the manufacturing of the composite are hygroscopic in nature. If the erbium emission is hindered by the O-H vibrations due to the hygroscopic nature of the components, this can overcome by the use of protective ambient atmosphere.

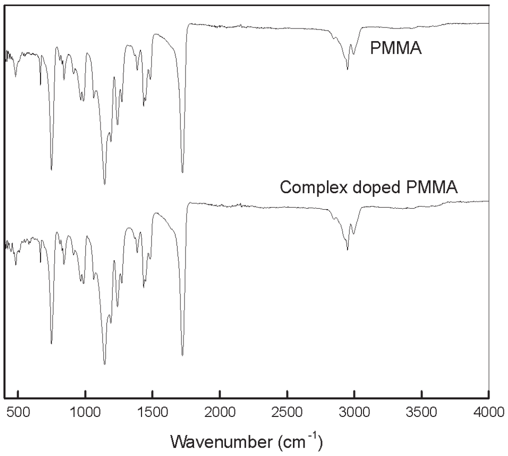

Figure 2. The IR spectra of PMMA and complex doped PMMA

Photoluminescence studies

Laser excitation operating at wavelength λex=880nm with Eex=500mW at room temperature was used to detect the sample luminescence in the range of 1500 to 1600nm. Figure presents the luminescence of the complex doped PMMA in the range of 1500 to 1600nm which is due to the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$. The full width half maximum of this peak is considered as the figure of merit for the utility of the optically active materials. The full width half maximum of the 1wt% complex doped PMMA is 24nm, which is the value expected at the good quality optically active materials.

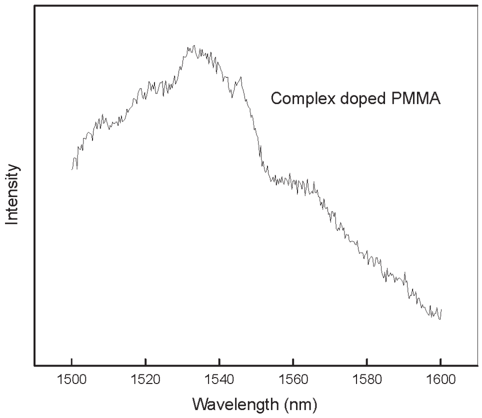

Figure 3. Emission spectrum of erbium complex doped PMMA

CONCLUSIONS

Erbium (2,2’-bipyridine-N,N-dioxide)2(NO3)3 complex-doped PMMA thin films were developed by a solution based casting technique. The IR studies on complex show that the occurrence of coordination of bPyO2 molecule to the central metal atom through the oxygen atoms. The Luminescence analysis reveals that the material developed is suitable for the fabrication of a good quality optically active material.

ACKNOWLEDGEMENTS

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PTFE content and transport properties of gas diffusion layer of PEM Fuel Cell

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Fuel Cell is an electrochemical device which produces clean energy, along with pure water as the byproduct, at efficiencies much higher than the present day engines. There are different types of fuel cells. Among them, Polymer Electrolyte Membrane Fuel Cell or the Proton Exchange Membrane Fuel Cell (PEMFC) is considered to be the most suitable type for portable applications, including automobile motive power [1].

Main parts of a PEMFC are the Polymer Electrolyte Membrane, Bipolar Plate which houses the Gas Channels (GCs), Gas Diffusion Layer (GDL) and Catalyst Layer (CL). Polymer Electrolyte Membrane is an electrolyte in the solid form which enables conduction of ions between anode and cathode. The gas channels distribute the reactant gases. The gas diffusion layer helps in distributing the gases uniformly over the catalyst layer. GDL also plays a key role in the removal of the product water. The reactions of conversion of Hydrogen into H+ ion and electron as well combination of Oxygen with H+ ions and electrons to form water occur inside catalyst layers.

Hydration of membrane plays a significant role in the performance of the PEMFC. At the same time, the presence of excess water results in a reduction in performance. Removal of excess product water is essential for ensuring good performance of the PEMFC. Generally PTFE coating is given to GDL to modify its transport properties, towards reactant gases and product water, to meet Fuel Cell needs optimally. It also provides reinforcement to the GDL. PTFE tends to reduce the pore volume available for the movement of gases and water through the gas diffusion layer. Extent of PTFE coating plays an important role in deciding the performance characteristics of a Fuel Cell. It has to facilitate easy water removal, sufficient membrane hydration and sufficient movement of the gases.

Studies were conducted to evaluate performance of Fuel Cell with GDL having different PTFE content. Voltage – Current characteristics of the cell is the resultant of all the physicochemical processes within the cell. It was attempted to study and assess the contribution of factors such as reduction in porosity due to PTFE coating as well as modification of surface property, especially hydrophobicity. While the former has the potential to reduce the free volume and passage of gases, the latter facilitates ejection of water by increasing hydrophobicity. These aspects were modeled and the effects were quantified for varying conditions.

Variation of concentration of the oxygen gas available at the catalyst layer side of the gas diffusion layer was estimated for different PTFE content by correcting the values of porosity. To model these, we have considered the Fick's and Knudsen diffusion mechanisms. Porosity and tortuosity of the gas diffusion layer were suitably corrected. Bruggeman relation was used to capture the variation in tortuosity. The concentration of Oxygen gas at the catalyst layer was found out for different porosities. Porosity variation within the range of 0.5 to 0.8 was considered based on the fact that the porosity of GDL without PTFE coating is 0.8. Corrections for different PTFE contents – 10%, 20% and 30% by volume, were effected. The variation of concentration of oxygen available at the CL side was plotted as given in Fig. 1 below.

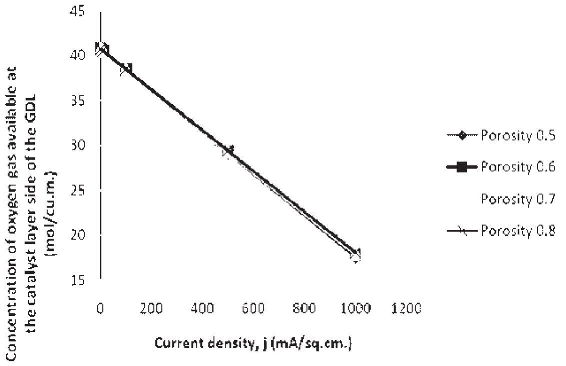

Fig. 1 The variation of the concentration of oxygen gas available at the CL side of the GDL with current density for different values of porosity of the GDL

As already mentioned, PTFE imparts modification in hydrophobic nature of GDL which is reflected as change in contact angle. From the one dimensional analytical solution of liquid water transport through the GDL, the variation of liquid saturation within the GDL for varying dimensionless thickness can be plotted [2] for two different contact angle. Contact angles chosen are representative of extreme conditions. The liquid saturation is defined as the portion of the pore volume filled with liquid.

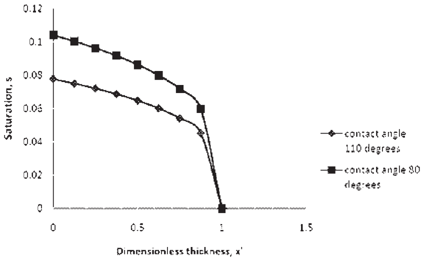

Fig. 2 Liquid saturation profiles across GDL predicted by 1D analytical solution of liquid water transport for different contact angle

Experimental studies were conducted on PEMFCs with GDLs having different PTFE contents. The experiments were conducted using GDLs with 10%, 25%, 40% and 55% by mass. The results were plotted as shown below.

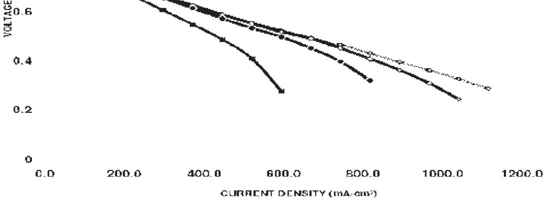

Fig. 3 The polarisation curves for PEMFC with GDLs having different PTFE contents at room temperature conditions

Fig. 1 brings out the variation of concentration of oxygen gas available at the catalyst layer with respect to the changes in current density, for different PTFE content. The change in PTFE content modifies the pore volume available for the transport of different species. The study reveals that variation of PTFE content and resulting change in porosity has negligible effect on the level of concentration of Oxygen at the catalyst layer. But at the same time, the impact on water removal appears to be more pronounced. From Fig. 2, we can see that the liquid saturation is more if the contact angle is less and vice versa. A contact angle, θ<90º corresponds to a hydrophilic GDL and a contact angle, θ>90º corresponds to a hydrophobic GDL. Low PTFE content facilitates higher water content within the GDL whereas high PTFE content provides low water content and easy water removal. From Fig. 3, we can see that higher PTFE corresponds to lower voltage level for the same current density of operation.

The study brings out the impact of two contrasting mechanisms of importance in Fuel Cell. These are related to gas and water transport where PTFE coating plays a decisive role. Extent of coating imparts changes in performance. Modeling of the phenomena reveals that gas transport remains relatively unaffected. Whereas, PTFE induced changes in hydrophobicity has important effect on the water retention and transport within GDL.

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Electrospun lithium titanate ultrafine fibres for applications in lithium-ion batteries

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Spinel lithium titanate($Li_4Ti_5O_{12}$)is a very promising anode material for Li-ion batteries owing to its great merit of zero-strain characteristic during Li+ insertion/extraction and absence of irreversible capacity loss during the initial charge-discharge cycles. The material shows a very flat charge-discharge plateau at 1.55 V vs. Li, which is above the reduction potential of most of the electrolytes used in Li-ion cells.

Electrospinning has emerged as an effective method for the preparation of ultrathin polymer fibres and membranes. Recently, this technique has been employed for the synthesis of advanced materials (anode, cathode and polymer electrolytes) for Li-ion batteries. In this paper, we report the synthesis of phase pure $Li_4Ti_5O_{12}$ by combining the advantages of sol-gel and electrospinning techniques. Theelectrospinningof sol-gel precursor containing polyvinylpyrrolidone (PVP) was optimised to get bead-free, fibrous mat of $Li_4Ti_5O_{12}$ precursor. Thermal analysisof the electrospun precursor directed the heat treatment procedure and crystalline $Li_4Ti_5O_{12}$ in ultrafine fibre form was synthesized by sintering the precursor at 800 °Cin air for 4 h. The material was characterized by X-ray diffraction, Raman spectroscopy and Scanning Electron Microscopy (Figure 1 (a), (b) and (c) respectively).

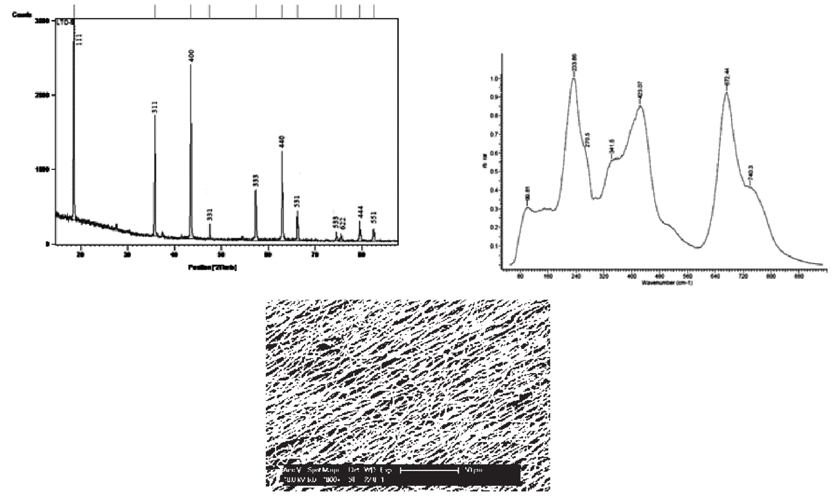

Figure 1 (a) X-ray diffraction pattern, (b) raman spectrum and (c) SEM image of electrospunLi4Ti5O12

Electrospunlithium titanate was subsequently evaluated as an anode material using Li metal as counter electrode. The charge-discharge curves show that the material exhibited an extremely flat discharge plateau at 1.55 V and a charge plateau at 1.57 V as illustrated in Figure 2. The synthesized material exhibited an initial discharge capacity of 163 mAhg-1and a charge capacity of 150 mAhg-1 in the range of 1.0-3.0 V. Over 90% of theinitial capacity of the cell remained even after 30cycles.The $Li_4Ti_5O_{12}$ in the form of ultrafine fibre exhibited high specific capacity with good cycle performance, suitable for applications in Li-ion batteries.

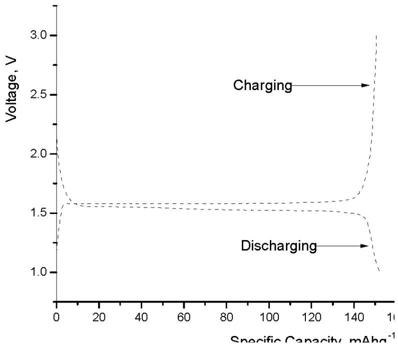

Figure 2 Typical Charge-discharge curve of electrospun$Li_4Ti_5O_{12}$

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Shape Memory Polymer Based onCyanate ester-Epoxy resin; Dependency of Nature of Switching Segment

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Thermoset polymers showing shape memory properties were synthesized by reacting bisphenol A dicyanate (BADC) and diglycidyl ether of bisphenol A (DGEBA) with different switching segments such as phenol telechelic poly(tetramethyleneoxide) (PTOH), poly(ε-caprolactone) (PCLOH) and poly(propylene) glycol (PPGOH). The cure characteristics of the blend were evaluated by DSC and FTIR. Blend with fixed proportion of DGEBA/PTOH/BADC, DGEBA/PCLOH/BADC and DGEBA/PPGOH/BADC, were studied for their flexural, dynamic mechanical and thermal properties. The flexural strength and thermal stability found to increase in the order PPG-20<PCL-20<PTMO-20. PCL-20 shows higher storage modulus than the other two systems, but it drops suddenly after 80 °C. The observed transition temperature (Ttrans) were in the orderPPG-20<PCL-20<PTMO-20. The shape recovery properties were proportional to the modulus ratio (Eg/Er), the recovery time showed an inverse relationship with it. The transition temperature and shape recovery varied with different switching segments. These epoxy-cyanate ester-PTOH systems possess better shape memory property compared with other two systems.

1. Introduction

Thermo-responsive shape memory polymers (SMPs) have the capability for changing their shapes from a temporary shape to a permanent shape upon application of an external thermal stimulus. It evinces great interest due to the adaptability for shape change when temperature switches from below to above the transition temperature. They provide great potential for application in self-deployable structures for space applications, micron-sized actuators, orthodontic applications, medical treatment etc. Shape memory thermoset blends have rarely been reported.

Our approach to derive shape memory epoxy is to incorporate various switching segments (SwS) such aspoly(tetramethyleneoxide) (PTMO) , poly(ε-caprolactone) diol (PCL) and poly(propylene) glycol (PPG) in polymer matrix as this group confers shape memory property to the system and to study their impact in the SMP properties.

This work reports the synthesis of a shape memory epoxy-cyanate ester resin system based on diglycidyl ether of bisphenol A cured with bisphenolAdicyanate ester (BADC). For the shape memory effect, a component, viz: phenol-telechelicpoly(tetramethyleneoxide) (PTOH), poly(ε-caprolactone) diol (PCLOH) and poly(propylene) glycol (PPGOH) were synthesized and co-reacted with the epoxy-cyanate ester system. Thus, epoxy-cyanate ester of different switching segments blends of fixed composition (DGEBA/SwS/BADC, molar ratio-1/0.07/0.92) was prepared and evaluated for thermal, mechanical, thermo-mechanical and shape memory properties. This paper outlines the compositional dependency on their shape memory properties.

2. Experimental

2.1 Synthesis of phenol-functional PTMO (PTOH)

PTOH was synthesized by reaction of PTMO (0.1 mol) with PHBA (0.6 mol) in toluene/diglyme solvent in the presence of pTSA catalyst. Same synthesis route are used for PCL and PPG diols. The resultant resin was characterized by fourier transform infrared spectroscopy (FTIR) and size exclusion chromatography (SEC). Estimation of ester value was done by chemical analysis.

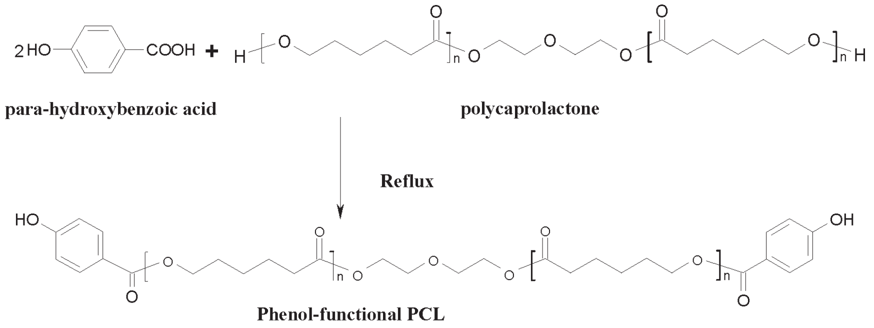
2.2 Preparation of epoxy-PTOH-cyanate ester based thermoset system

The DGEBA/PTOH/BADC blend and catalyst (4 wt% of BADC) were first mixed together, degassed at 80 °C for 30 min and then poured into steel mould. Blends with different switching segments (PCLOH and PPGOH) of DGEBA and BADC were prepared following the same procedure (Table 1). Since the three resins system are difunctional, their molar ratios equal their equivalent ratios.

3. Results and discussion

3.1 Synthesis and characterization of phenol functional of different switching segments

The same synthesis route of PTOH is used for synthesis of PCLOH and PPGOH. The method of synthesis of PCLOH is illustrated in Scheme 1. In the FTIR spectrum, peak at 3419 cm-1 corresponds to vibration of -OH groups and that at 1725 cm-1 to the C=O stretching of the ester group. The peak at 1164 cm-1 corresponds to C-O-C stretching of PCLOH. The polymer is further characterized by ester value estimation. The ester value of PTOH (46 mgKOH/g) conformed nearly to the theoretical value (50 mgKOH/g) and SEC. Same studies are done at PPGOH, it shows 3464 cm-1 corresponds to vibration of OH groups, 1711 cm-1 to the C=O stretching of the ester group and 1107 cm-1 corresponds to C-O-C stretching of PPGOH.



Scheme 1 Synthesis of PCLOH

3.2 Cure characterization of DGEBA/PCLOH/BADC and DGEBA/PPGOH/BADC blends

The cure characterization of DGEBA/PTOH/BADC blend was reported previously. The cure schedule of the PPGOH and PCLOH blends was determined by DSC and FTIR. The DSC profiles of the PPGOH system shows one exothermat low temperature and other at higher temperature (Table 1). The exotherm at 169 °C is attributed to cyanate-epoxy reaction leading to the formation of oxazolidinone groups and that at 203 °C to the polymerisation of cyanate groups. Similar type of reaction is observed in PCLOH system, but the exotherm peaks are at 170 °C and 183 °C.From FTIR completion of cure reaction of the epoxy and –OCN groups of two systems such as PCLOH and PPGOH in the network is confirmed from the absence of peak corresponding to epoxy ring at 916 cm-1 and of –OCN at 2271-2238 cm-1. It was further confirmed from theappearance of triazine peaks at 1363 cm-1 and absorptions of isocyanurate at 1698 and 1459 cm-1. The oxazolidinone rings formed from reaction of BADC and epoxy is observed at 1731 cm-1. Following the above studies, all the compositions were cured under same cure schedules: 100°C - ½ h, 120 °C-1 h, 150 °C-1 h, 180 °C-1 h and 200 °C-3 h. The cyanate ester polymerization in the DGEBA/ BADC occurred at high temperature (240 °C), where asthe blends containing PCLOH and PPGOH showed this exotherm at lower temperature, due to the involvement of the phenolic groups of switching segments in the catalysis of cyanate esterhomopolymersation. It is possible that the phenol groups react with epoxy resin also.

3.3 Flexural properties of different systems

Table 1 compiles the flexural strength of the different switching segments of epoxy-cyanate ester systems. The flexural strength shows slightincreases in the order PPG-20<PCL-20<PTMO-20, this is due same type of reaction are observed in all systems. It is clearly indicated in cure characterization studies. The switching segments provide the epoxy-cyanate ester more flexibility which helps improve its shape memory property.

3.4 Dynamic mechanical thermal properties

Visco-elastic properties of the samples were investigated by DMA in three point bending mode. Fig. 1 and Fig. 2, indicate the storage modulus and loss tangent (tanδ) for different switching segments as a function of temperature. The transition temperature Ttrans is determined from the tanδ peak of the first transition. The modulus ratio Eg/Eris taken as (E'Ttrans-20/E'Ttrans+20). Where, E'Ttrans-20 and E'Ttrans+20standfor the storage modulus at temperature Ttrans-20 and Ttrans+20, respectively. Initially PCL-20 show higher storage modulus than other two systems, but it suddenly drops after 80 °C. Above this temperature PPG-20 shows high modulus than PCL-20 and PTMO-20. When the storage modulus decreases, the Eg/Er ratio (Table 1) increases in the order PPG-20<PCL-20<PTMO-20.The transition temperature shows similar trend of storage modulus in the order PTMO<PCL-20<PPG-20. The high transition temperature of PPG-20 is due to smaller chain length than compared to other two systems and also it contain methyl group, which will restrict the rotation of the polymer chain. In the case of PCL-20 it contains longer aliphatic chain and carbonyl group. Later provide more dipolar interaction of the chain segments. But in PTMO-20, this type of interaction is very less due to ether linkage.

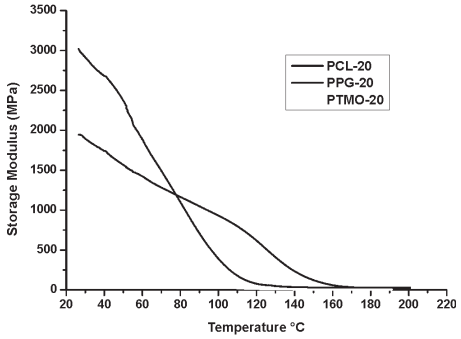


Figure 1Storage modulus as a function of temperature for different systems

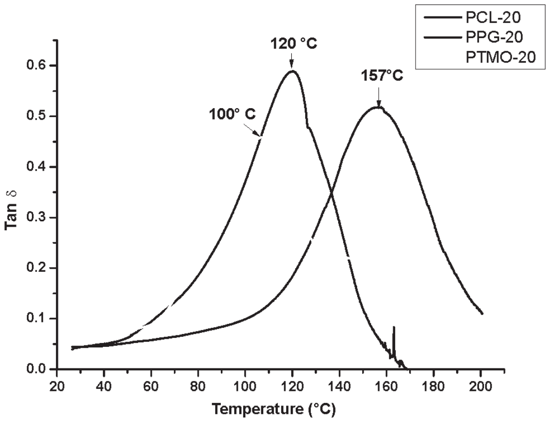


Figure 2Loss tangent as a function of temperature

4. Shape memory properties (Bending test)

The quantitative evaluation of the bending tests of all the systems was conducted at temperatures Ttrans+20 (°C) (Table 1). At Ttrans+20 (°C) the shape recovery increases in the order PPG-20<PCL-20<PTMO-20. The observation conform to the modulus ratio (Eg/Er) [35] which increase in PTOH content and helps the polymer show good shape memory properties than the other two systems. The recovery time decreases proportionally. At high Eg/Erratio, the shape recovery is maximum at minimal recovery time. The highly cross-linked structures have strong restraining force on their segments, which need large free volume and more energy, which also necessarily need higher temperature to accomplish shape recovery. The PTOH system show better shape memory properties than other two systems. All systems are mechanically sturdy and have good thermal stability to be used in composites for developing smart system for diverse application.

Table 1 DSC exotherm peak maximum, Flexural strength, Loss tangent, elastic modulus ratio and shape memory properties of different systems

Sample	Peak max1 (°C)	Peak max 2 (°C)	Flexural strength (MPa)	T_{trans}(°C)	E_g/E_r	% of shape recovery at $T_{trans}+20$ (°C)	Recovery Time (min)	% of shape fixity at $T_{trans}-20$ (°C)
PTMO-20	170	185	100 ± 0.5	100	17	90	2.50	98
PCL-20	170	183	98 ± 0.5	120	11	90	2.55	92
PPG-20	169	203	95 ± 0.5	157	10.4	86	3.10	80

Figure 4 Shape memory properties of PCL-20 and PPG-20 (a) original/permanent shapes, (b) and (c) fixed temporary shapes and (d) recovered shapes.

5. Conclusion

A shape memory thermoset polymer was designed by co-reacting cyanate ester and epoxy with phenol-telechelicof different switching segments. The transition temperature of the blend decreased in the order PPG-20<PCL-20<PTMO-20. The shape recovery increased and the recovery time of the ternary blends depends on the switching segments. All polymer possessed good mechanical properties and thermal stability. The PTOH system showed better shape recovery characteristics than other two systems. The resin suited to process good elastic memory composites as cyanate esters normally promote excellent composite formation. These systems are potentially useful for fabricating smart systems like actuators.

POLYMER SYNTHESIS

PREPARATION AND CHARACTERIZATION OF GELATIN - PULLULAN ALDEHYDE SCAFFOLD FOR TISSUE ENGINEERING

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Introduction

Tissue engineering applies both the principles of engineering and life science. One of the main issues in tissue engineering is to develop a suitable scaffold with appropriate mechanical, physical and biological properties. Natural as well as synthetic polymers were used for the preparation of the scaffold [1]. This work deals with the preparation and characterisation of the scaffold prepared from pullulan aldehyde and gelatin. Pullulan, a natural exopolysaccharide is currently being used in biomedical applications like tissue engineering, gene delivery and drug delivery due to its non toxicity, non carcinogenicity and non immunogenicity. Here pullulan was modified by introducing an aldehyde functionality on it by periodate oxidation [2]. Further the modified pullulan was cross-linked with gelatin to prepare the scaffold. Characterisation studies of the scaffold include FT IR spectroscopy, gelation time, swelling studies and thermal analysis.

Materials and Methods

Synthesis of Pullulan-aldehyde (PuA)

5 g of pullulan was dissolved in 50 mL of distilled water. To this solution, various amount of sodium metaperiodate required for 10%, 20% and 50% oxidation in 20 ml of water was added and stirred for 6 hr in dark at 25°C. This aldehyde solution was purified by dialysis for 3 days using a dialyzing tubing of MWCO 3500. The absence of periodate in the dialysate was checked by adding 1 mL of 1% solution of sodium nitrate to 1 mL of the dialysate. After the complete removal of periodate (no turbidity with silver nitrate), the dialysate was frozen and lyophilized. Oxidized pullulan was obtained in high yield of 85%.

Hydrogel Preparation

Gelatin -Pullulan aldehyde hydrogel (GPuA) was prepared from 20% solution of pullulanaldehyde in 0.1M borax and 10% and 15% solution of gelatin by Schiff's base reaction. Gelling time was determined for different composition of pullulan aldehyde and gelatin. Hydrogel was washed and lyophilized to get the scaffold.

Characterisation of Scaffold

Pullulan aldehyde was characterized by FT-IR spectroscopy. The aldehyde content in PuA was determined by titrimetric method. Prepared scaffold was characterized by gelation studies, swelling studies, thermal analysis and FT- IR spectroscopy. The cross-linking density of the scaffold was determined by TNBS assay.

Results and Discussion

The vicinal diols in the pullulan was cleaved by sodium metaperiodate into dialdehyde. In the present work pullulan with different degree of oxidation was prepared by varying the amount of periodate. The aldehyde content in the 10% and 20% oxidized PuA was determined using hydroxylamine hydrochloride. It is found that PuA-1(10% oxidized) PuA-2(20% oxidized) contains 3.146×10-3 moles/g and 5.43×10-3 moles/g of aldehyde groups respectively.Gelatin-pullan aldehyde hydrogel (GPuA) was prepared based on the Schiff's base cross-linking reaction. Schiff's base is formed by the cross-linking of aldehyde groups in PuA and free amino groups of lysine or hydroxylamine side groups of gelatin. In the present work, cross-linking and hydrogel formation was carried out using 20 % solution of PuA in 0.1 M borax with aqueous solution of gelatin of different concentrations.

From Table 1 it is clear that gelation time depends upon the percentage of oxidation of PuA and concentration of gelatin. Gelation time decreased with increase in percentage oxidation as well as increase in gelatin concentration. This is due to the increased availability of functional groups for cross-linking reaction with increase in percentage oxidation and increase in concentration of gelatin.

Table 1. Gelation studies of Gelatin-Pulluan aldehyde scaffold

Percentage of oxidation	Concentration of PuA (%)	Medium	Concentration of gelatin (%)	Gelling time (S)
10	20	borax	10	43±2
10	20	borax	15	67±2
20	20	borax	10	30±2
20	20	borax	15	21±2
50	20	borax	10	20±2
50	20	borax	15	12±2

Infrared spectrum of Pu, Pu-1 (10% oxidized), Pu-2 (20% oxidized), Pu-3 (50% oxidized) and GPuA showed proof for the cross-linking between aldehyde group of PuA and amino group of gelatin. Thermal stability was analysed by TGA.

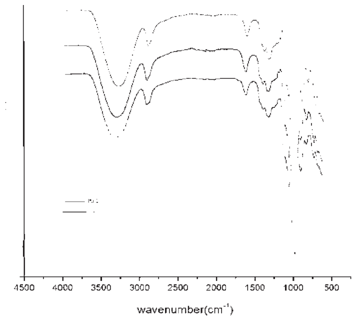

Fig 1. FT IR spectrum ofPullulan, pullu1(10%oxidised), pullu 2(20%oxidised), and Pullu 3(50% oxidized)

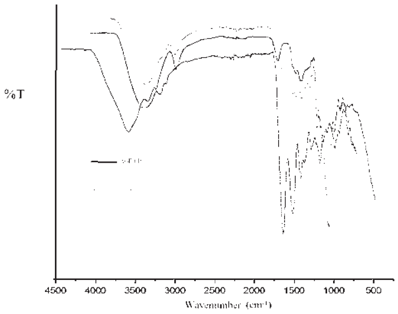

Fig 2. FT IR spectrum of pullu1(10%oxidised), gelatin and GPuA.

TNBS assay was used to determine the degree of cross-linking . To study the swelling of scaffold prepared from 10% oxidized pullulan aldehyde and gelatin, 5mL of PBS was added on the top of weighed scaffolds, kept in a vial. Scaffolds were stored at room temperature and weighed at regular intervals. After weighing, fresh PBS was added to the hydrogels. The swelling ratio is expressed as

$$Qm = (Ws - Wd)/Wd$$

Where Ws and Wd are the weight of the swollen and dry scaffold [3].

Degree of swelling of the hydrogel was also determined. It is defined as the reciprocal of the volume fraction of the polymer in the hydrogel (v2) [4].

$$Q = v2-1 = [(1/ \rho p)[(Qm/ \rho s) + 1/ \rho p]-1]-1$$

Conclusion

The polysaccharide pullulan was oxidized using periodate to generate aldehyde functionality that would enter into crosslinking with amino groups of protein, gelatin and forms hydrogel. Hydrogel was lyophilized to get the scaffold. This new class of scaffold was characterised by swelling studies, gelation studies, and FT IR spectroscopic analysis. Cell culture studies will be carried out to assess the suitability of the scaffolds to be used as matrices for tissue engineering.

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ACRYLIC POLYMERS CROSSLINKED BY CLICK CHEMISTRY – SYNTHESIS AND CURE CHARATERSTICS

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Click chemistry is a fast emerging field in the design of molecules with diverse characteristics. The copper catalysed alkyne-azide 1,3- cyclo addition (CuAAC), popularly known as Huisgen 1, 3-dipolar cycloaddition is considered as an ideal Click reaction because of its high efficiency, stereo specificity, high yield and absence of by products. The reaction is widely being explored for the preparation of dendrimers, nanoparticles, hydrogels, adhesives and a variety of copolymers with varying degrees of functionalization.

In the present work, we report the synthesis of pendant azide and alkyne functionalized acrylate polymers by conventional free radical polymerization technique followed by chemical transformation and their subsequent curing via click chemistry to form triazole networks. The cure characteristics were studied by thermal and rheological methods and the related activation parameters were evaluated. Figure 1 shows the crosslinking of click groups- functionalized acrylic polymers.

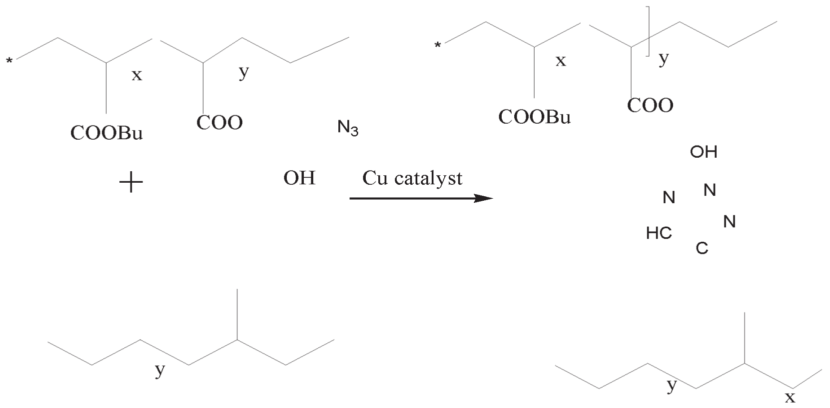

Figure 1: Crosslinking of azide- and alkyne- functionalized acrylic polymers via click reaction

Azide functional copolymer was synthesized by the reaction of pendant epoxy groups of a butyl acrylate-glycidyl methacrylate copolymer with NaN3. The propargyl functional polymer was realized by the reaction of the pendant -COOH group of a butylacrylate-acrylic acid copolymer with propargyl bromide. The copolymers were characterized by FTIR, NMR, Elemental analysis, functional group analysis (acid value and epoxy value) and GPC. The click functionalized copolymers were then crosslinked by the Huisgen 1, 3-dipolar cycloaddition.

The copper- mediated azide- alkyne coupling reaction of the copolymers (blended in stoichiometric ratio) was carried out by blending the two polymers in presence of 0.1% of cuprous Iodide as catalyst at 60°C. FTIR spectrum showed absorptions at 2100 cm-1 (ascribed to the –N3 group) and at 3267 cm-1 (due to propargyl group) in the respective copolymers, as shown in Figure 2 (A&B). These peaks vanished completely after curing by the 1,3-cycloaddition, indicating completion of the click reaction (Figure 2-C). The band at 3139cm-1 and 1698 cm-1 corresponds to the stretching vibration of ν(C-H) in the triazole ring (=C-H) and C=C in triazole ring respectively.

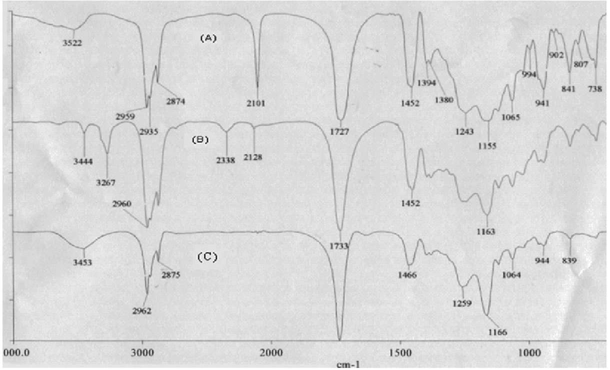

Figure 2: IR spectra of (A) Azide functionalized copolymer (B) propargyl functionalized copolymer (C) Cured polymer

The curing reaction of azide- and alkyne- functionalized acrylic copolymers, was monitored using differential scanning calorimetry (DSC) and rheometry. Figure 3 shows the dynamic DSC scan of the system under catalyzed and uncatalyzed conditions. Cure initiation is observed at around 40°C for the catalyzed system whereas for the uncatalyzed system, cure initiated by around 120°C. The second exotherm in catalysed case is due to the decomposition of unreacted azide group. In the case of uncatalysed system, curing is accompanied by dissociation of azide.

Kinetic parameters (activation energy and pre exponential factor) were determined using the Ozawa method, by performing the DSC of the systems at different heating rates. Activation energy for reaction of the stoichiometric blend was calculated as fraction of catalyst concentration. The activation energy decreases with catalyst concentration and follows the relation, EA=EA0-K[C].

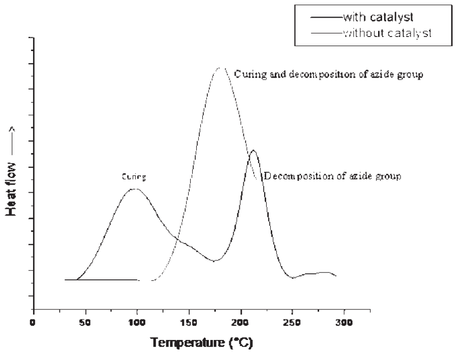

Figure 3: Comparative DSC scan of click systems with and without catalyst

The cured polymer was characterized by TGA for their thermal stability. The triazole decomposition was observed at 240°C. The polymers are suited for application as film adhesive that cures through click chemistry.

CONCLUSION

Azide- and propargyl- functional acrylate copolymers were synthesized and characterized. The click reaction of Azide-alkyne functional acrylate copolymers was successfully conducted using copper iodide catalyst. Influence of the catalyst on the cure reaction was monitored. Kinetics of the cure reaction was evaluated by DSC and rheometry. The activation energy confirmed by ozawa method shows strong dependency on catalyst concentration. The relationship of EA on catalyst concentration was established*. The polymer with film forming characteristics and curable at low temperature can be efficiently used as film adhesive.

** Kinetic parameters were used for isothermal cure prediction*

ALLYL PHENOL FORMALDEHYDE- BISMALEIMIDE RESIN: SOME ASPECTS OF SYNTHESIS, CURING AND COMPOSITE PROPERTIES

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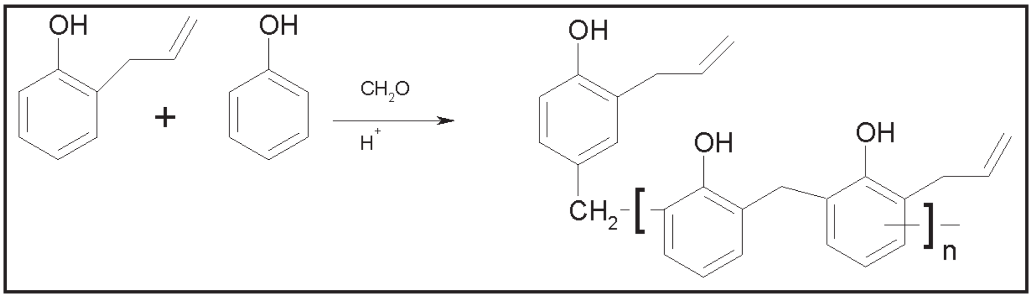
1.0 Introduction

Bismaleimides (BMI) are of interest as matrix resins for use in structural composites. Though the system possesses high glass-transition temperature and high modulus, their structural feature render them inherently brittle.To improve the performance and reduce the brittleness of BMIs, blending and structural modification are often explored. Structural modification of BMI through incorporation of allyl group is expected to be very effective. The present work deals with the synthesis and characterization of two-component allyl phenol formaldehyde –BMI alder ene resin systems and processing of carbon fibre reinforced composites based on them. Allylnovolac (AN) was co-reacted with 2, 2'-bis [4-(4-maleimido phenoxy) phenyl] propane (BMIP) in varying proportions. The cure characterization of the blends was done by FT-IR spectroscopy, DSC and Rheometry. Corresponding Carbon fibre reinforced composites were also prepared and their mechanical and thermo mechanical properties were evaluated.

2.0 Experimental

2.1 Synthesis of AllylNovolac (AN)

Allylnovolac, incorporating 50% of allyl phenol was synthesized and characterized (mol.wt: ~500-600, PDI ~1.7). The extent of allylation was confirmed by NMR spectroscopy. Typical synthesis of AllylNovolac is shown in Scheme 1.



Scheme 1: Synthesis of allylnovolac

2.2 Curing and processing of composites

In the present study, BMIP was reactively blended with allyl –functional novolac by melt mixing in varying proportions. The cure reaction was monitored by FTIR, Rheometry and DSC. Rheological evaluation under isothermal conditions at 150°C reveals that gelation of the system initiates at around 120 minutes and curing gets completed in about 6 hrs, as shown in Figure 1(a). DSC thermogram [Figure 1 (b)] of all the blends showed an endotherm around 100-130oC which is attributed to the melting of the AN and BMI components. The system cured through a sequence of reactions as reported and evidenced from DSC. Thus, the thermograms showed broad cure exotherms at 75° C, representing the Ene reaction and a second exotherm at around 180°C corresponding to the Diels-Alder reaction.

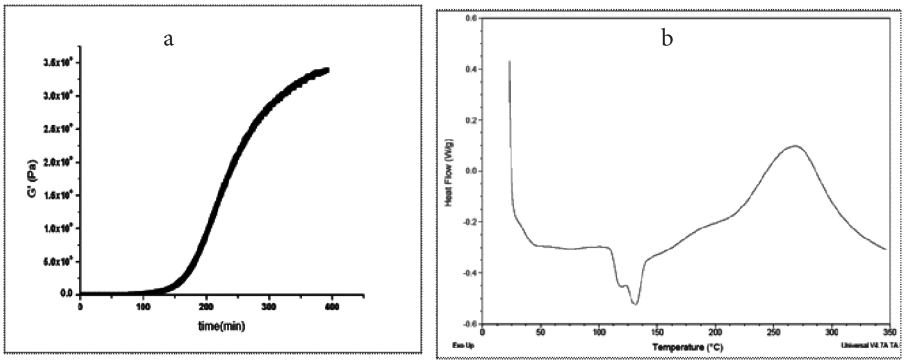
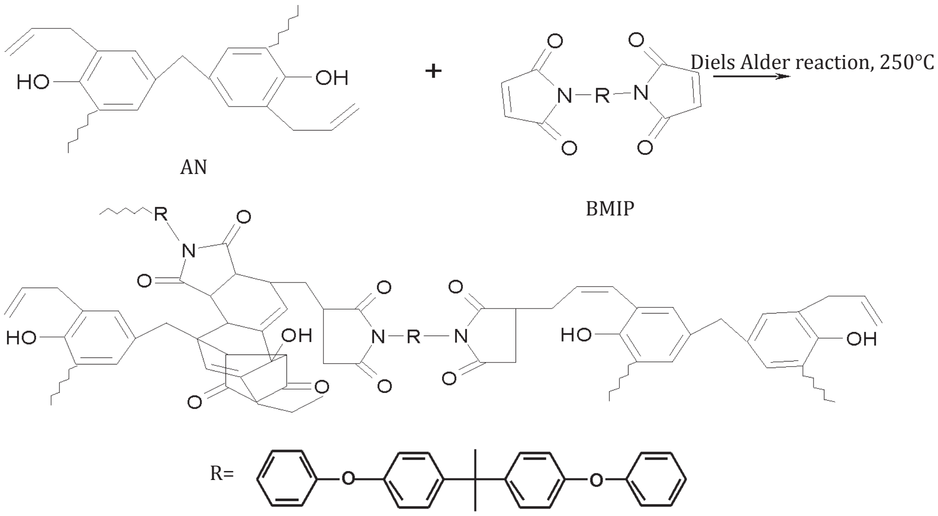


Figure 1: (a) Isothermal rheogram of BMIP -AN (1:1) blend at 150°C (b) Typical dynamic DSC scan of the blend

The typical alder ene cure pattern of the of BMIP-AN blend is represented in Scheme 2.



Initial decomposition temperature (Ti) of BMIP-AN cured blends increased with increase in the maleimide content. The change in Ti and Char yield (Ycat 800° C) with varying maleimide content is represented in Figure 2.

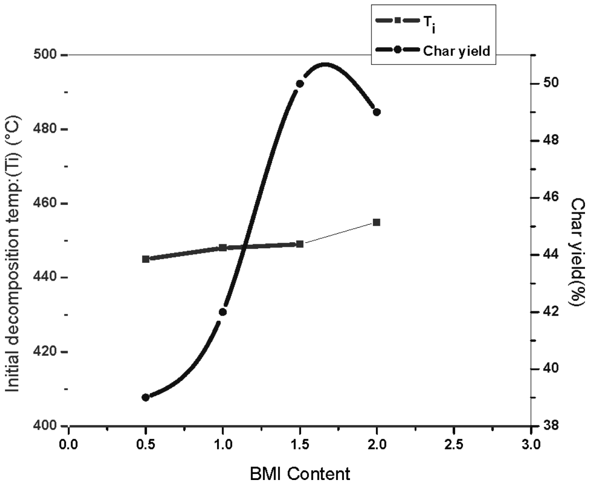


Figure 2: Thermal decomposition characteristic of BMIP-AN resin system

Alder ene polymer composites, reinforced with carbon fabric were prepared using the blends with fiber to resin ratio of 60:40 by weight. DMA of the cured composites exhibited a single transition, indicating the existence of single phase. The Tg of the cured composite showed no significant dependanceupto 1:1 stoichiometry of BMIP: AN, and thereafter, a significant change was observed (Tg shifted from 278 °C to 287 °C) as shown In Figure 3 with a proportionate increase in modulus.

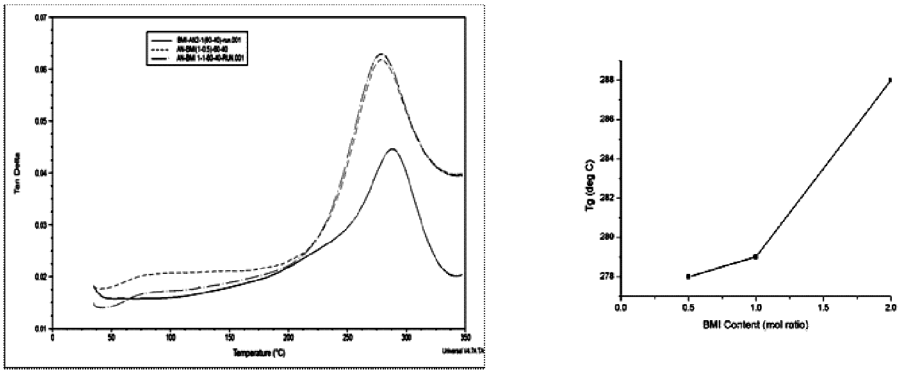


Figure 3: Influence of BMIP content on the Tan δ and Tg of BMIP-AN composite

Mechanical properties such as flexural strength and Impact strength of the cured composites were evaluated, which shows that, as the maleimide content increases, flexural strength increases gradually (80% improvement for the mole ratio of BMIP from 0.5to 2). However, though the impact strength increases up to 1:1.5 composition of the blend, it declines beyond this composition due to excessive crosslinking, leading to matrix embrittlement. The mechanical property of the composites with respect to the varying BMIP content is represented in Figure 4.

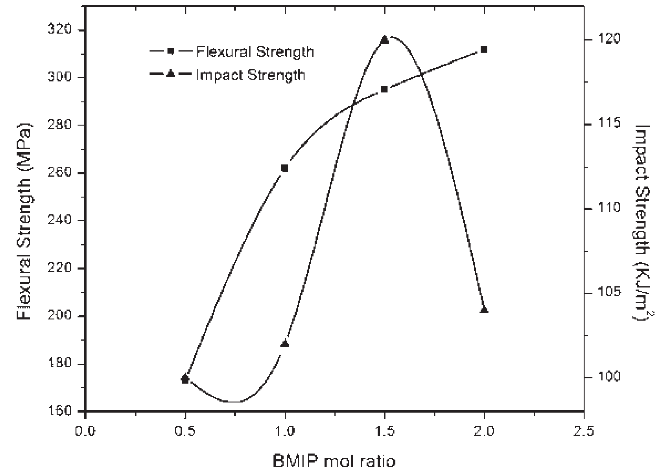


Figure 4: Variation in mechanical properties of the composites with BMIP content

Reasonably good adhesion of the resin to the fibre surface was observed in the morphological analysis by SEM.

3.0 Conclusion

Allylnovolac was reactively blended with BMIP in different molar ratios and characterized. The systems cured through a sequence of reactions including the Ene reaction followed by Diels Alder reaction. It was observed from the rheological evaluation that, gelation of the blend at

150°C initiates in about 120 minutes and gets completed in 6 hrs. DMA of the cured composite showed existence of a single phase. As the maleimide content increases, flexural strength of the composites increased. However, impact strength increases to a certain level and then decreases with higher BMI content attributed to the network structure. Morphological evaluation showed reasonably good adhesion of the resin to the fibre surface. The Tg of these systems was in the range of 278-287 °C. Thermal stability and anaerobic char yield increased with increasing bismaleimide content in the blend.

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PHENOLIC –EPOXY TRIAZOLE ELASTOMERIC NETWORK THROUGH CLICK CHEMISTRY, SYNTHESIS AND CHARACTERISATION

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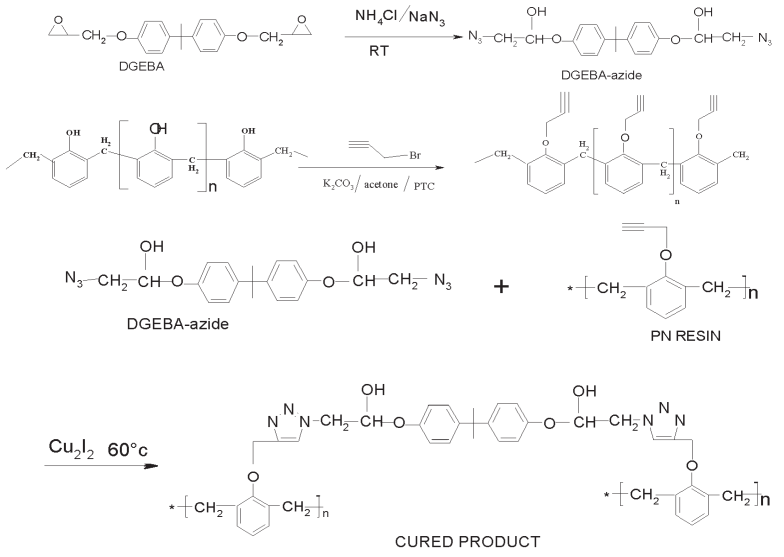
Introduction

Novolac-cured epoxy resins are widely accepted as tough, moisture resistant systems for use as adhesive and microelectronic application. These are synthesized by reaction of novolac with epoxy resin at high temperature. Due to the ether linkage such polymers possess thermophysical properties inferior to those of either phenolic or epoxy resin. Their curing often warrants use of basic or acidic catalysts and curing is a long process.

Here we report an alternate route for synthesis of phenolic epoxy resin. We have explored the possibility of exploiting the click chemistry based on 1, 3-cycloaddition reaction of azides with propargyl group. The copper catalyzed reaction occurs at lower temperature with the incorporation of rigid triazole groups that can possibly alter the characteristics of conventional epoxy phenolic matrix. The phenolic novolac was transformed to the propargyl ether derivative and the epoxy to the hydroxy ethyl azide derivative and both were cured together by the Huisgen reaction.

Synthesis of azide and propargyl systems

Propargylatednovolac resin was synthesized by reaction of novolac resin with propargyl bromide and characterized. DGEBA is converted to the azide derivative by appropriate synthesis strategy. The azide-alkyne cycloadditionreactions leading to triazole networks were conducted at 60°C in the presence of cuprous iodide catalyst. The reaction scheme is depicted in scheme 1.



Scheme 1. Curing of DGEBA-N3 and PN resin via 'click chemistry'

Cure reaction was monitored using FTIR and DSC. FTIR spectrum confirmed the cure as indicated by the diminished absorption at 2100cm-1 of the azido group corresponding to the azide peak with simultaneous appearance of peaks at 1607cm-1 and 3180cm-1 corresponding to the triazole networks.

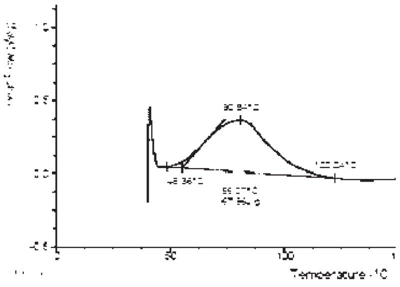


Figure1. DSC of Curing mixture

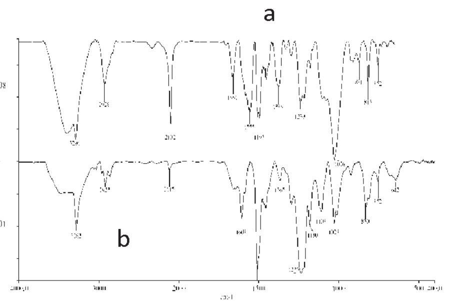


Figure 2 FTIR before (a) and after (b) curing

Kinetics of the reaction was monitored using Osawa method and activation parameters were calculated.

Sheets of the PN-DGEBA-N3 systems were cast and cured. The thermal, mechanical and thermo mechanical properties of the cured slabs were evaluated. Cured PN-DGEBA-N3 slabs blended in 1:1 stoichiometry resulted in elastomeric triazole networks which exhibited tensile strength of 4.5MPa, tensile modulus of 15MPa and elongation of 75%. Syntactic foam composites, reinforced with silica fibre and filled with glass microballoonswere also processed using different compositions of propargylated phenolic resin and DGEBA-N3 and their mechanical and thermo mechanical properties were evaluated. Compressive strength around 8MPa and impact strength of 0.9KJ/m2 was observed. An improvement of around 10% was observed in the impact strength of the foam composites, compared to the phenolic resin- based syntactic foam composites.

Morphology of the cured systems was evaluated and mechanical properties were correlated to the composition and morphology.

Conclusion

Phenolic resin modified with propargylgroups were cured via Huisgen 1,3-dipolar cycloadditionwith DGEBA-N3 at moderate temperature. The system cures at 60°C, resulting in phenolic –epoxy elastomeric triazole networks. Syntactic foam composites of the system exhibited enhanced impact resistance and comparable mechanical properties with their phenolic resin- based counterparts.

ELASTOMERS, HIGH PERFORMANCE POLYMERS

Optimization of Polyaniline [PANI] – Natural Rubber [NR] based blends using Design of Experiments [DoE]

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INTRODUCTION

Polyaniline (PANI) is an intrinsically conducting polymer that combines high conductivity, ease of processibility and low density. It is quite thermally stable, but may lose conductivity at high temperatures due to loss of dopant. The main limitations are low solubility in organic solvents and poor plasticity of resulting films. Thus, there is a need of design of new material either through chemical synthesis from monomer or polymer precursor or by blending PANI with some other polymer or compounding with additives. Blending is a simple, fast effective and economical method and also provides a high performance to cost ratio.Natural rubber [NR] compounds are known for high extensibility, strength, excellent abrasion resistance, high resilience, etc. A few drawbacks are low compression set, low ozone resistance and inadequate electrical properties. In this paper we investigate the mechanical and electrical properties of PANI-NR blends. Various formulations of these blends have been evaluated using Design of Experiments [DoE] technique.

Design of Experiments (DoE) is a statistical technique for establishing relation between a set of variables of a process and its output. It provides maximum information with minimum experimentation. In this study, aface centred composite design [FCCD] with three factors [viz. PANI content, carbon black loading and Sulfur/Accelerator (S/A) ratio] and three levels [+1, 0, -1] was used. The FCC Design consists of all combinations of the factors at three levels, six centre points and star points at the face of the cube portion of the design. Accordingly 18 experiments were carried out.

EXPERIMENTAL ANALYSIS

Rubber compounding was done on a two-roll mill, optimum cure time was obtained from rheograms and samples were molded at 150°C, 200 MPa pressure. Characterization studies were carried out on the molded sheets; they included mechanical properties, electrical properties, Shore ‘A’ hardness and Scanning Electron Microscopy (SEM) examination.

RESULTS AND DISCUSSION

The data obtained from the characterization studies were subjected to regression analysis which provided mathematical equations for predicting the properties of NR-PANI blends. Thefollowing second-order polynomial equation was used

$$y = \beta_0 + \beta_i x_i + \beta_{ii} x_i^2 + \beta_{ij} x_i x_j$$

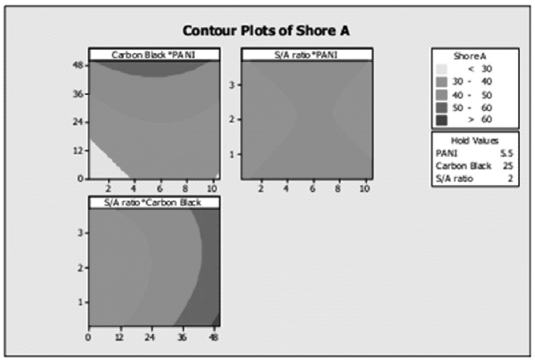
Where y is the response, and xiand xjare the coded independent variables. Whennormalizedcentred representations (coded levels) are used to represent factor levels, β0,βi, βii, and βarethe mean values of responses, linear, quadratic, and interaction constant coefficients, respectively.Each coefficient (except interactions) estimates the change in the mean response per unit increasein x when all other factors are held constant. Minitab software was used for generating the regression model.

For each response (Shore A hardness, conductance, loss coefficient, dielectric constant), the analysis comprised the following parts:

Adequacy of regression model: This is established by examining the values of R-sq and R-sq (Adj). As per statistical principles, when these two values are within 5-10% of each other, and each is close to 100%, the model is deemed to have adequately captured the underlying relationship between the response and the experimental factors.

Prediction equation: As per the analysis, the prediction equation was determined. Values were substituted in the prediction equation and the resulting value of response was compared with the experimental value obtained previously.

Minitab was also used to generate contour plots for each property of interest. Contour plots were generated from the equations obtained in the regressionanalysis before adjusting the coefficients. The two-dimensionalcontour diagram is a series of curves ofconstant response for different combinations of factorlevels. Such diagrams illustratethe change in properties when two or more variables change together and allowpredictions to be made for combinations notactually run in the experiment.The figure below represents a typical contour plot for Shore ‘A’ hardness.



These contour plots were overlaid to provide the feasible set of combinations of variables meeting a set of specifications. The specifications may be chosen to cater to such applications as Electromagnetic Interference (EMI) Shielding and Anti-static devices.

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MoldFlow Analysis of an injection moulded nylon 66 gear

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INTRODUCTION

In recent years polymers have replaced several metallic components used in automobiles and have contributed to increased fuel efficiency, speed, variety of models, etc. These polymeric components are produced by such processing techniques like injection moulding, extrusion, thermoforming, etc. [1-3] Mould Flow Analysis software has been used to simulate the conditions present during the moulding process and provide the processing window for selecting the best process parameters. In this paper, we present results of process parameter optimization for a gear component based on nylon 6,6.

MOLD FLOW ANALYSIS [4]

This is implemented using Moldflow Plastics Insight, a complete suite of plastics injection molding process simulation tools to predict and eliminate potential manufacturing problems and optimize part design, mold design, and the injection molding process. This analysis consists of several steps. The component drawing made in ProE is imported into the Mold Flow Software. It is necessary to select the type of meshing needed for the component. In meshing, the component is divided into several nodes or triangular elements to estimate stresses /strains based on finite elemental analysis [FEA]. Dual Domain mesh type was selected since it allows one to perform detailed analyses on thin-wall, surface meshed models. The surface mesh analysis works by simulating the flow of the melt on both the top and bottom parts of the mold cavity. Consistency between the results on the opposite sides is maintained by using “connectors”: elements with zero flow and heat resistance

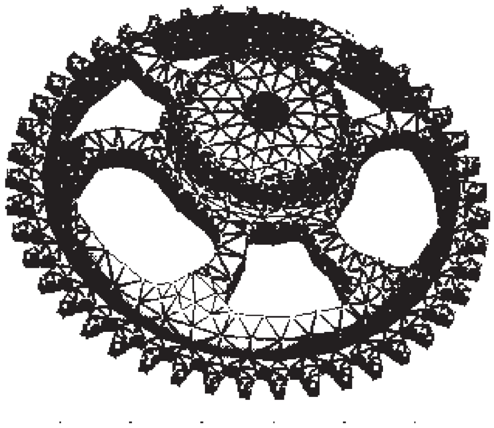

Figure 1 Mesh Generation for NYLON Gear

The connectors are inserted automatically at locations determined according to the geometrical features of the model as shown in Figure 1.

MESH CORRECTION

The meshed model showed certain errors during meshing due to fillets and corners of various sizes. Mesh corrections were done based on aspect ratio, overlapping of elements, mesh orientation and free edges. The mesh statistics before and after correction are shown in tab1e 1.

Table 1 Meshing parameters for nylon 66 gear

Parameter	Before correction	After correction
Entity Counts		
Surface triangles	3416	3366
Nodes	1696	1671
Mesh Area	94.852 cm^2	94.758 cm^2
Edge Details		
Free Edges	0	0
Manifold Edges	5124	5049
Non-Manifold Edges	0	0
Intersection Details		
Elements Intersection	15	0
Fully Overlapping Elements	0	0
Duplicate Beams	0	0
Surface triangle aspect ratio		
Minimum Aspect Ratio	1.159	1.159
Maximum Aspect Ratio	46.080	10.150
Average Aspect Ratio	2.802	2.470
Match Percentage		
Match Percentage	78.10%	78.70%
Reciprocal Percentage	75.00%	76.60%

As shown in the table, the aspect ratio has been reduced to an acceptable level [< 6.0] after mesh correction.

MOLDING WINDOW ANALYSIS

The Molding Window Analysis is used to quickly provide recommendations for the values of injection time, mold temperature and melt temperature to use as preliminary inputs for further analyses. It uses the part geometry, the material, the selected injection location and specified process ranges and limits. The process settings obtained for the nylon gear were: mould temperature : 109^o C, melt temperature : 303^o C and injection time : 0.38 s.

QUALITY PLOT

The Quality plot provides an indication of how the overall quality of the part will vary as the input variables [viz. mold temperature, melt temperature, and injection time] vary. This quality measure is derived from the results obtained for minimum flow front temperature, injection pressure, maximum cooling time, maximum shear rate, and maximum shear stress under a given set of molding conditions. Better values for these individual quality criteria produce an overall better quality measure result [see figure 3]. From the analysis it is found that the quality measure increases with reduction in injection pressure, maximum cooling time, maximum shear rate, maximum shear stress and will increase with increase in minimum flow front temperature.

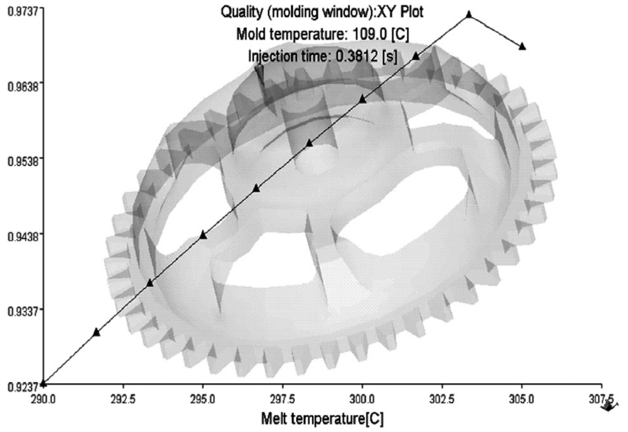

Figure 2 Quality as a function of melt temperature for nylon gear

GATE LOCATION ANALYSIS

The Gate Location analysis can be used to identify the best place to inject the material. The optimum injection location creates balanced flow, allowing the extremities of the mold to fill at the same time and pressure. It looks for the best location, based on flow resistance, thickness and molding feasibility. In the figure 3 the regions are shaded according to their suitability as gate location. From the figure we find the centre portion of the gear to be most suitable for the gate locations.

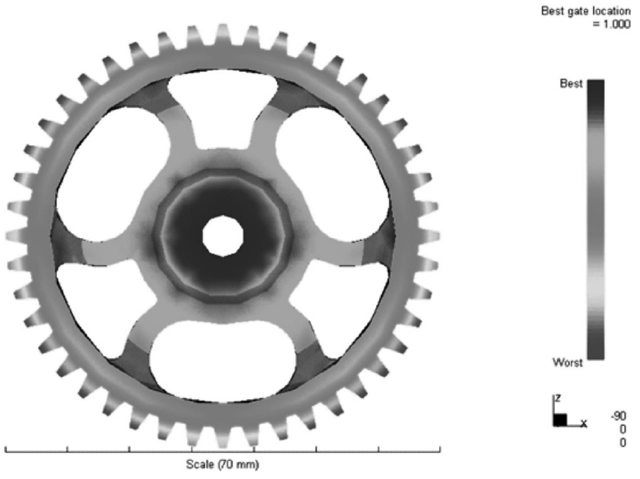

Figure 3 Gate Location Analysis for Nylon Gear

CONCLUSION

Mould Flow Analysis was carried out for a nylon 66 gear. The various steps included mesh generation and correction, generation of quality plots, Moulding Window Analysis and gate location analysis. Based on Mold Flow analysis the process parameter obtained were:

mould temperature : 109^o C

melt temperature : 303^o C

injection time : 0.38 s

gate location : centre of the gear

These process parameters combined with the preferred gate locations provide with gears with acceptable quality.

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Melt-Polymerization and Foaming of Sucrose and Boric Acid for the Preparation of Oxidation Resistant Carbon Foams

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Carbon foams are new generation materials that are prepared with tailor made electrical and thermal conductivities and with a range of densities. They find major applications in the area of thermal management such as high temperature thermal protection materials, ablative materials, heat exchangers, radiators and host structures for phase change materials. They are also used as electromagnetic interference shielding materials, electrode materials in batteries and catalyst support. In addition, carbon foams are used as fire resistant core materials for light weight sandwich composite structures. Carbon foams are prepared by foaming and carbonization of synthetic organic polymers such as phenol-formaldehyde, furfural resin,polybenzoxazine and poly arylacetylene. Mesophase pitch is a very good alternative for synthetic polymers for preparation of carbon foams. The carbon foams produced from mesophase pitch have superior properties compared to that prepared from synthetic organic polymers. However, the petroleum and coal that are the sources of mesophase pitch are depleting.

Recently, preparation of carbon foams from bio-molecules of plant origin such as tannin and sucrose is getting importance due to the renewable nature of the raw materials and green nature of the processes. Among the bio-molecules, sucrose is a widely available agricultural product having 42.1 wt.% carbon. Recently, we have reported a preparation of low density carbon foams from molten sucrose using an aluminium nitrate blowing agent. The process produces carbon foams with density in the range of 0.05 to 0.08 g/cc. However, the carbon foams produced have poor mechanical strength. Moreover, the alumina produced from the aluminium nitrate blowing agent has a negative impact on the oxidation resistance of carbon foams. It is well known that doping with boron improve the oxidation resistance of carbon based materials. In the present work melt-polymerization and foaming of sucrose and boric acid followed by carbonization is used for the preparation of boron doped carbon foams.

250 g sucrose was melted in a borosilicate glass reaction kettle. Finely powdered boric acid was added to the molten sucrose with continuous stirring with a mechanical stirrer. Stirring was continued for another 2 minutes after the addition of boric acid. The amount of boric acid used was in the range of 2 to 8 wt. % of the sucrose. The homogenous melts thus obtained were transferred to a 1. 5 liter borosilicate glass trays and heated in an air oven at 120 ^{o}C for 48 hours for foaming and setting. The solid organic foams obtained were first dehydrated at 250 ^{o}C in air atmosphere and then carbonized by heating in an inert atmosphere up to 900 ^{o}C.   The solid organic foams were characterized by infrared spectroscopy and thermogravimetric analysis. The boron doped carbon foams were characterized by density measurement, compressive strength measurements and scanning electron microscopy. Oxidation resistance of the boron doped carbon foam samples were evaluated and compared with that of phenolic resin derived carbon foams and carbon foams prepared from molten sucrose using aluminium nitrate blowing agent.

Sucrose on heating above its melting point undergoes condensation through the –OH groups and form products such as $C_{24}H_{36}O_{18}$, $C_{36}H_{50}O_{25}$ and $C_{125}H_{188}O_{80}$. The boric acid in presence of poly hydroxyl compounds acts as a strong acid that facilitate the condensation between –OH groups in sucrose. Moreover, boric acid acts as cross-link between the sucrose condensation products. The cross-linking is evidenced from increase in viscosity of the melt with increase in boric acid concentration and presence of peak corresponding to B-O-C linkage in the IR spectrum of the solid organic foams. The sucrose-boric acid melt undergoes slow foaming and setting when heated at 120 ^{o}C. The bubbles generated in the melt due to the water vapour produced as a result of the –OH to –OH condensations are stabilized by the high viscosity of the melt. The foam volume increases with increase in boric acid concentration. The foaming time and setting time decreases with increase in boric acid concentration. Density of the boron doped carbon foams obtained (0.1 to 0.2 g /cc) is higher than the density of the carbon foams prepared using aluminium nitrate blowing agent. The boron doped carbon foams produced have cellular structure with uniform cell size. The compressive strength of the boron doped carbon foams are found higher than that of the carbon foams prepared using aluminiun nitrate blowing agent.

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Polymer-Grafted-Magnetite/Nanocellulose Superabsorbent Composites for the Selective Separation and Recovery of Immunoglobulin from Aqueous Solutions

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1. Introduction

Immunoglobulin (γ-globulin) is a large Y-shaped protein used by the immune system to identify and neutralize foreign objects such as bacteria and viruses, and hence its recovery is inevitable in biomedical applications. In this study, a novel hydrogel, poly(methacrylic acid–co–vinyl sulfonic acid)–grafted-magnetite/nanocellulose composite (P(MAA-co-VSA)-g-MNCC) was synthesized by graft copolymerization technique. The hydrogel was well-characterized using TG, XRD, SEM and FTIR techniques. The antibody, Immunoglobulin (IgG) was immobilized onto P(MAA-co-VSA)-g-MNCC, under different optimized conditions. The present study was proposed to utilize the cation exchange capacity of the carboxyl and sulfonyl groups from the adsorbent surface to recover IgG from aqueous solutions. Studies on separation of IgG from mixture of proteins were carried out to ensure its better applicability in the biotechnological and biomedical fields.

2. Experimental

2.1. Preparation of P(MAA-co-VSA)-g-MNCC

The general procedure adopted for the preparation of P(MAA-co-VSA)-g-MNCC consists of three steps.

Step 1. Extraction of nanocellulose (NC) from saw dust

In the present work, cellulose was first extracted by acid-alkali treatment of saw dust (collected from Local saw mill, Trivandrum) and subsequent bleaching using 5.0 % hydrogen peroxide (Mulinari and Da Silva, 2008). The bleached cellulose (5.0 g) was added to 250 mL distilled water and 140 mL conc. H2SO4 wasdropped to itwithout cause heating. After complete addition, the mixture was heated at 50 oC for 2 h. The hot reaction mixture was quenched using crushed ice and the obtained white colloidal nanocellulose (NC) was centrifuged and freeze-dried.

Step 2. Preparation of magnetite nanocellulose composite (MNCC)

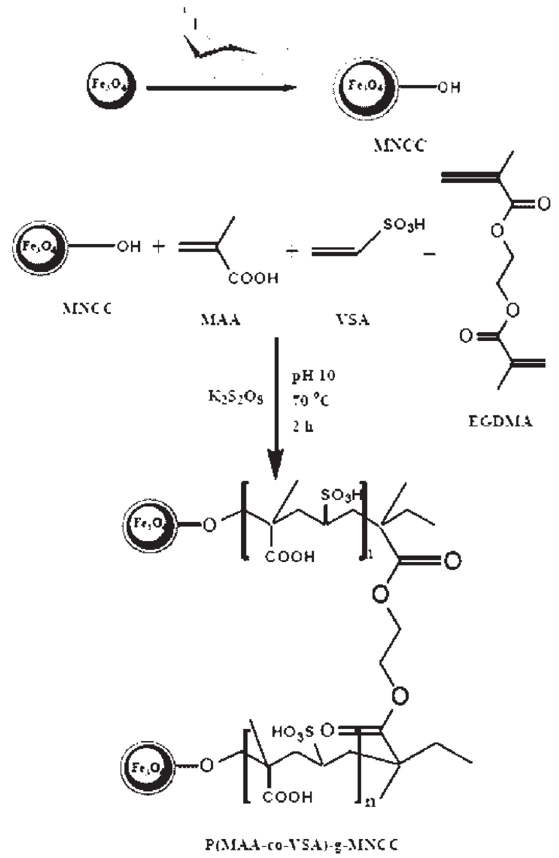
The MNCC was prepared by co-precipitating Fe(II) and Fe(III) ions in aqueous solution containing NC with ammonia. Briefly, about 1.5 g of NC was added to 200 mL distilled water and stirred for 10 min. To the mixture, 1.49 g FeCl3·6H2O and 0.765 g FeSO4·7H2O were added to form a source of iron, and heated at 60 ºC. Chemical precipitation was achieved by adding 8.0 M ammonia solution drop wise with vigorous stirring and a constant pH of 10, upon which an orange color suspension obtained was changed to a black precipitate. After incubation for 4 h at 60 ºC the mixture was cooled to room temperature with stirring, and the resulting MNCC particles were separated magnetically. The product thus obtained was washed several times with distilled water, finally with ethanol and dried.

Step 3. Preparation of P(MAA-co-VSA)-g-MNCC

The general procedure adopted for the preparation of P(MAA-co-VSA)-g-MNCC is illustrated in Scheme 1. Typically, about 0.5 g of MNCC was stirred well with 100 mL distilled water (60 ⍰C, 20 min). K2S2O8 (0.004 M, 0.92 g) was added and kept at 60 ºC for 10 min. After cooling the suspension to 40 ºC, a mixture of MAA (0.1 M, 8.5 mL), VSA (0.1 M, 7.8 mL) and EGDMA (0.015 M, 2.83 mL) were added. The pH was adjusted by NaOH to 10. The temperature was risen to 70 ºC and maintained for 2 h to complete the reaction. The obtained product was filtered and washed repeatedly with distilled water and ethanol to remove excess chemicals and then dried in vacuum at 70 ºC. The dried sample was then grounded and sieved to obtain -80 +230 mesh size particles (average diameter of 0.096 mm) and used throughout the studies.

3. Results and Conclusions

A cellulose-based hydrogel, P(MAA-co-VSA)-g-MNCC was synthesized by graft copolymerization of MAA and VSA onto MNCC, in the presence of EGDMA as cross linking agent and K2S2O8 as free radical initiator. The amount of sulfonyl and carboxyl functional groups in P(MAA-co-VSA)-g-MNCC was estimated to be 1.92 and 1.36 meq/g, respectively, was an evidence for proper grafting of PMAA and PVSA onto MNCC. The zero point charge of cellulose and P(MAA-co-VSA)-g-MNCC was observed at pH 5.5 and 3.6, respectively. The adsorbent was well-characterized by means of TG, XRD, SEM and FTIR techniques. TG curves show an enhanced thermal stability of P(MAA-co-VSA)-g-MNCC with respect to Cellulose and can be used at high temperature conditions. The average crystallite size of NC and MNCC calculated from XRD pattern was 25.0 and 23.8 nm, respectively. Swelling capacity of P(MAA-co-VSA)-g-MNCC was found to be increased with increase in pH and temperature. The efficiency of P(MAA-co-VSA)-g-MNCC in the recovery of IgG was tested by batch adsorption technique. The optimum pH for maximum adsorption was found to be 6.8 with the adsorption percentage of 98.4 % (12.3 mg/g) and 96.8 % (24.2 mg/g) for an initial IgG concentration of 25 and 50 mg/L, respectively. Electrostatic interaction has played an important role in the adsorption process of IgG onto P(MAA-co-VSA)-g-MNCC. Equilibrium was achieved within 3 h. IgG adsorption on P(MAA-co-VSA)-g-MNCC follows a pseudo-second-order kinetic model, which is based on ion-exchange mechanism followed by complexation. The adsorption isotherm results were well-fitted into Sips and Langmuir isotherm models, which confirm monolayer coverage process at higher concentrations. The maximum adsorption capacity according to Langmuir model was found to be 203.78 mg/g at 30 oC. The adsorption capacity towards IgG was found to increase with increase in temperature from 10 to 40 oC, indicating endothermic nature of adsorption. Gibbs free energy possesses negative values for all interactions, indicating the spontaneous nature of adsorption. The positive values of ΔH0 and ΔS0 indicate the endothermic nature of adsorption and increased randomness at the solid-liquid interface, respectively. Adsorption capacity was found to be increased with increase in salt concentration. Satisfactory results were obtained from the attempts for the selective separation of IgG from mixture of proteins. The adsorbed IgG was effectively regenerated using 0.1 M KSCN. The present investigation shows that P(MAA-co-VSA)-g-MNCC can be used as an effective adsorbent for the selective separation and recovery of IgG molecules from aqueous solutions.



Scheme 1. Proposed reaction mechanism for synthesis of P(MAA-co-VSA)-g-MNCC.

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Influence of Thermal History and Host Structure on the Structural Changes of syndiotactic polystyrene during the Guest Exchange with n-Alkanes

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Introduction:

Syndiotactic polystyrene (sPS) has been attracting a lot of attention from both sides of science and industry because of its characteristic behavior in crystallization, phase transition and the related change in physical properties. SPS forms complexes with various kinds of organic compounds and these complexes are further classified into clathrates and intercalates. Guest exchange phenomena using sPS clathrates attracted the attention of researchers as this process is a simple route for the preparation of the composite materials in a molecular level with a variety of functional molecules such as dye, fluorescent, photo-reactive, paramagnetic, optical active molecules and so on. Incorporating the larger molecules into the cavity of the δ form by guest exchange phenomenon has expanded the range of guest molecules for the sPS clathrates. Many authors including us studied the incorporation of a variety of guest molecules into the cavity of sPS by guest exchange process which includes linear and flexible molecules like n-alkanes, planar aromatic molecules like xylene and naphthalene, cyclic molecules like crown ethers, macromolecules like polyethylene glycol dimethyl ether (PEGDME) and so on. In particular, guest exchange process with n-alkanes attracted lot of interest from the structural point of view of both host and guest.

In the present paper we systematically investigated the effect of host structure on the structural changes of syndiotactic polystyrene (sPS) during the guest exchange process with a series of n-alkanes mainly by wide-angle X-ray diffraction (WAXD) and Fourier transform infrared spectroscopy (FTIR). It should be emphasized here that for the first time we have utilized sPS/toluene δ clathrate samples for the detailed investigation of the structural changes during the guest exchange with a series of n-alkanes.

Experimental Section

sPS sample purchased from Idemitsu petrochemicals, Japan. Amorphous glassy sample prepared by quenching the molten sample into liquid nitrogen or ice. The α form samples were prepared by heating the amorphous sample overnight at 1900C. The γ form samples were prepared by dipping the amorphous samples in acetone for 24 hours.Amorphous, α form and γ form samples were dipped in chloroform for 12 hours and toluene for 2 days at room temperature in order to obtain the sPS/chloroform and sPS/toluene complexes, respectively.

Results and Discussion

The solvent exchange process was performed by dipping the sPS/chloroform complex or sPS/toluene complex in a series of n-alkanes (n-octane to n-decane) for 32 days at room temperature. The X-ray diffraction measurements were performed on various samples after the guest exchange process to understand the structural changes. Figure 1 shows the powder X-ray diffraction patterns of various samples at different time intervals after guest exchange. When sPS/chloroform complex prepared from the amorphous sample is used for the guest exchange with n-alkanes, it is observed that the monoclinic δchl sample transformed in to the mixture of the δform and the ε form after the guest exchange process as shown in Figure 1. On the other hand, the α form samples dipped in chloroform transformed in to the triclinic δform alone after the guest exchange with n-alkanes, where the n-alkanes took bent like structures within the cavities of the δform. Here the δform transformed from monoclinic to triclinic, similar to the observation made by Tarallo et al. In the case of the γ form samples dipped in chloroform transformed to the ε form alone after the guest exchange with n-alkanes. Unlike the previous case, here the n-alkanes organize parallel to the molecular chain axis of sPS, which results the formation of the ε form where the cavities are in the channel shape.

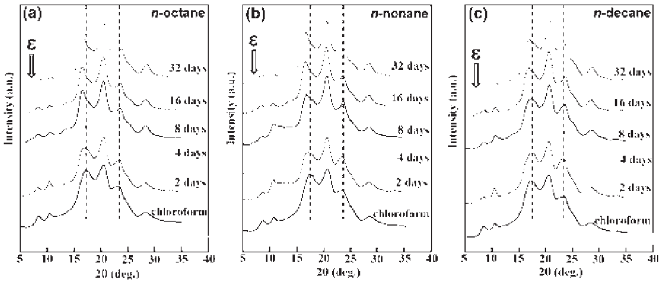

Figure 1: Powder X-ray diffraction patterns for various sPS/n-alkane samples after the solvent exchange from chloroform to n-alkanes at different time intervals. SPS/chloroform pattern is also given at the bottom for the purpose of comparison.

We also used toluene as a guest molecule to prepare the sPS/toluene complex and thus prepared samples were used for the guest exchange with n-alkanes in the second part of this work. Here we found that irrespective of the thermal history of the starting sample and host structure, the δ triclinic structure was obtained after the guest exchange process with n-alkanes.

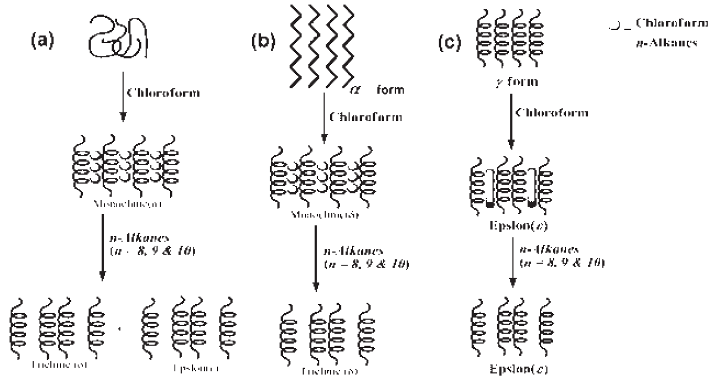

Figure 2: Schematic representation of the chain-packing model during the guest exchange process starting with the amorphous, alpha and gamma samples after treatment with chloroform.

In this way we found that the starting morphology of the sample influences both the guest and host structures after the guest exchange process. We also studied the influence of starting δchl crystallinity on the guest exchange process and found that the crystallinity of the starting sample also plays an important role on the structural phase transitions.

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STUDIES ON THE CURING KINETICS OF CYANATE ESTER-EPOXY SYSTEM USING ISOTHERMAL CURING STUDIES

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Interpenetrating network system of co-cured cyanate ester (CE) with epoxy resin possess excellent dimensional stability, resistance to irradiation, low dielectric constant, unique physico-chemical, electrical, thermal properties and excellent adhesion property for the fabrication of insulation systems for fusion relevant prototype magnetic winding packs as well as in space craft structures. In the case of thermosetting composites, the chemical reactions taking place during the cure process which will affect resin morphology, which in turn determines the other properties of the cured system. For this reason, the relationships between processing, morphology, and properties of a wide range of thermosetting systems have been deeply investigated. Resin transfer molding (RTM) is one of the low-cost manufacturing processes used for these advanced composites. A good way to assure high quality and low manufacturing cost of the products is to create mathematical models of the different parts of the curing process of the system.This can give a deep understanding of curing mechanisms and cure kinetics which is the key for obtaining an optimal cure. In this work, curing properties and rheological behavior of CE-epoxy resin were studied and process parameters computed using a dual-Arrhenius viscosity model and engineering models. Studies revealed that, it can provide a basis for parameter optimization and simulation of the manufacturing processes and properties of CE-epoxy composites of different formulations.

Studies on the cure-kinetic and chemo-rheological characterization of thermosetting epoxy-cyanate ester blend system is important since the chemical, thermal, mechanical and rheological properties of the final product are strongly affected by the curing and manufacturing process Effects of temperature and molar composition of the blend system on the visco-elastic property was studied by conducting temperature dependent rheological behavior the epoxy-cyanate blend system under oscillatory/ rotatory mode using modulated compact rheometer. Studies suggested that the viscosity or flowability can be tuned by composition of the blend system and temperature of the system.

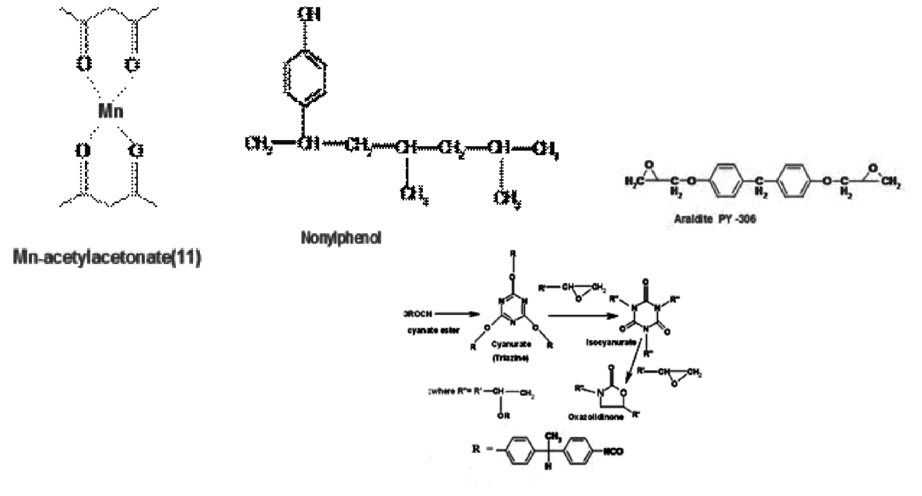

Figure .1. Chemical structure of Arocy L-10, Araldite PY-306, Mn-acetylacetonate and Nonylpheno and the reaction scheme for copolymerization of cyanate and epoxy

The primary objective of this paper is focused on the evaluation of cure-kinetic parameters of CE-epoxy blend systems through isothermal curing studies using differential scanning calorimeter. Here, we have studied the CE-epoxy blend system in presence of manganese acetyl acetonate in nonylphenol as catalyst and co-catalysts, respectively. Effect of curing temperature, compositional variation of CE:epoxy blends and presence of catalyst on the conversion, order, rate constants and kinetic parameters are studied and evaluated. The evaluated cure kinetic parameters could be used in comprehending the curing processes towards achieving the tailor made optimum properties. Homopolymerisation of cyanate ester to triazine is the main conversion taking place in the chemical controlled regime which is leading to onset of gelation. Then triazine combines with epoxy to form oxazoline and oxazolidinone in the diffusion controlled region

It has been observed that the curing process occurring in the diffusion controlled region is very complex and dependent on many factors like curing temperature, compositional variation of epoxy/CE, catalysts etc. Curing process conducted in presence of catalyst shows high value of α onset and α max on comparing with systems conducted in the absence of catalysts. As the curing temperature increases, the α onset and α max and order of the reaction also varied positively. The rate of conversion is fast in the chemical control regime and is very slow in the diffusion control regime due to vitrification effect after α onset. The increased epoxy content in the blend system increases the α onset and α max . Results revealed that the reaction order ‘n’ may not be a constant through out the curing process. A conversion variable ‘n ‘ kinetic model can be used for these thermosetting systems which follow n th order kinetic model. The cure –kinetic parameters and fitting parameters evaluated can be used for predicting the cure process for achieving the insulative blend systems with tailor made properties.

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Optimization of Polyaniline – Natural Rubber based blends using Design of Experiments

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ABSTRACT

Electrically conducting polymer composites are explored largely due to the combined properties of the conventional polymers like ease of processability, low density, environmental stability and corrosion resistance with electrical properties of conducting polymers.They have attracted a great deal of attention for their potential applications in various fields such as electromagnetic interference shielding, antistatic coatings, chemical sensors, transducers, and corrosion protection coatings. EMI shielding essentially depends on the conductivity, dielectric constant and magnetic property of the materials for various applications. Polyaniline (PANI) is an intrinsically conducting polymer that combines high conductivity, environmentally stable and having unique conductive mechanism and conductivity can be tuned from most electrically insulative state to conductive state by appropriate doping. But the problem with these materials is its high cost and low processability. To make EMI shielding products viable, composites have been fabricated by blending them with compatible and mechanically sound conventional polymers.Thus, there is a need of design of new material either through chemical synthesis from polymer precursor or by blending PANI with some other polymer or compounding with additives. Blending is a simple, fast effective and economical method and also provides a high performance to cost ratio.

Natural rubber [NR] compounds are known for high extensibility, strength, excellent abrasion resistance, high resilience, etc. But the problem with these materials is its cost and low processability A few drawbacks are low compression set, low ozone resistance and inadequate electrical properties. In this work, we have investigated various formulations of these blends to make EMI shielding products viable, composites have been fabricated by blending them with compatible and mechanically sound conventional polymers like nitrile rubberand have been evaluated using Design of Experiments [DoE] technique.Design of Experiments (DoE) is a statistical technique for establishing relation between a set of variables of a process and its output. It provides maximum information with minimum experimentation. In this study, a face centred composite design with three factors [viz. PANI content, carbon black loading and sulfur/accelerator (S/A) ratio] and three levels [+1, 0, -1] was used. The FCC design consists of all combinations of the factors at three levels, six centre points and star points at the face of the cube portion of the design. Accordingly 18 experiments were carried out. Rubber compounding was done on a two-roll mill, optimum cure time was obtained from rheograms and samples were molded at 150 °C, 200 MPa pressure. Characterization studies were carried out on the molded sheets; they included mechanical properties, electrical properties, Shore 'A' hardness and scanning electron microscopy.

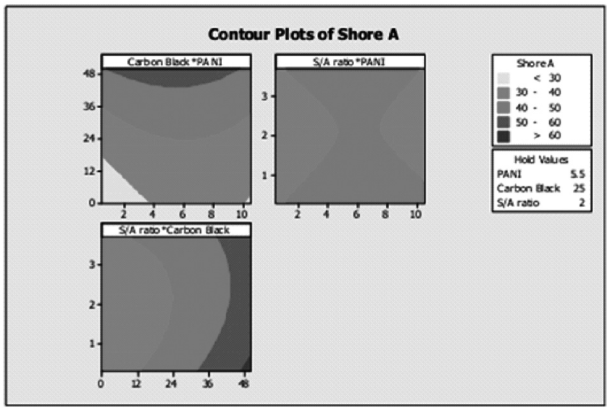
The data obtained from the characterization studies were subjected to regression analysis which provided mathematical equations for predicting the properties of NR-PANI blends. The following second-order polynomial equation was used

$$y = \beta_0 + \beta_i x_i + \beta_{ii} x_i^2 + \beta_{ij} x_i x_j$$

Where y is the response, and xi and xj are the coded independent variables. When normalized centred representations (coded levels) are used to represent factor levels, β0, βi, βii, and βare the mean values of responses, linear, quadratic, and interaction constant coefficients, respectively. Each coefficient (except interactions) estimates the change in the mean response per unit increasein x when all other factors are held constant. Minitab software was used for generating the regression model.

For each response (Shore A hardness, conductance, loss coefficient, dielectric constant), the analysis comprised the following parts: Adequacy of regression model: This is established by examining the values of R-sq and R-sq (Adj). As per statistical principles, when these two values are within 5-10% of each other, and each is close to 100%, the model is deemed to have adequately captured the underlying relationship between the response and the experimental factors.Prediction equation: As per the analysis, the prediction equation was determined. Values were substituted in the prediction equation and the resulting value of response was compared with the experimental value obtained previously.

Minitab was also used to generate contour plots for each property of interest. Contour plots were generated from the equations obtained in the regression analysis before adjusting the coefficients. The two-dimensional contour diagram is a series of curves of constant response for different combinations of factor levels. Such diagrams illustrate the change in properties when two or more variables change together and allow predictions to be made for combinations not actually run in the experiment. The figure 1 below represents a typical contour plot for Shore 'A' hardness.



These contour plots were overlaid to provide the feasible set of combinations of variables meeting a set of specifications. The specifications may be chosen to cater to such applications as electromagnetic interference (EMI) shielding and anti-static devices.

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Studies on the beneficial properties of Sol-gel Ceramic Nano Hybrid Fillers for Advanced Epoxy Polymers Electrical Insulators

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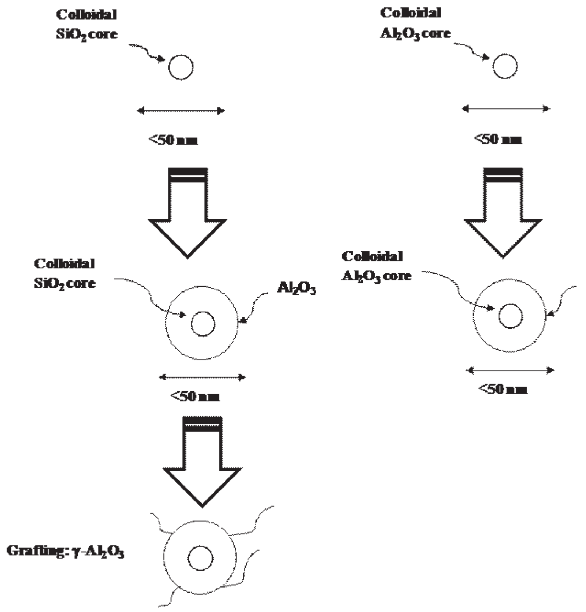
Epoxy polymers have been considered as Future Electrical Insulators due to their excellent low dielectric nature, low temperature processing, high mechanical strength and easy availability at cheaper cost. However, a drawback noticed in epoxy polymer for any insulator application is its poor thermal conducting property. Composite approach is earlier suggested as promising technique to obtain enhanced thermal conductivity. Addition of thermally conducting ceramic phases such as AlN, Al2O3, BeO, and carbon allotropes like CNTs, Graphite as fillers into epoxy polymer matrix was reported and demonstrated for high thermal conductivity. Unfortunately the improvement of thermal conductivity is observed at the expense of mechanical strength degradation and increased dielectric constant, electrical conductivity which is undesirable.

Use of surface modified, core-shell type nano composite hybrid fillers can produce high performance, advanced epoxy insulators. Hence in this work sol gel assisted ceramic-polymer nano hybrid fillers have been designed and introduced into epoxy resins to make ceramic-polymer nanocomposites.

In a typical work, Epoxy resin was procured from Huntsman Company and micron and nano size silica and alumina particles procured from Aldrich. The micro, nano and micro/nano blends taken in the ration of 10-80 wt% were incorporated into epoxy resin and cured using the hardener mixed in the ratio of 110:80. A routine solution mixing, casting and elevated temperature curing was followed to prepare the samples. Hybrid nanofillers were processed through sol gel technique in which silica and alumina layers were made on the surface of nano/nano and nano/micro ceramic fillers. In addition to that a different surface functional groups were also attached by chemical treatment.

The beneficial properties of hybrid nano fillers compared to single phase alumina, silica micro/nano fillers were studied with respect to rheology, thermal stability, glass transition and dielectric properties. The schematic representation of the different steps involved n the work is shown in Fig. 1.

The efficiency of sol gel nano ceramic hybrid fillers has been systematically analyzed and reported.



CURE STUDIES OF BISPHENOL PHTHALONITRILE-BISPROPARGYL ETHER BLENDS

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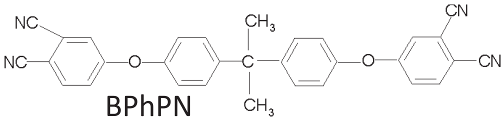
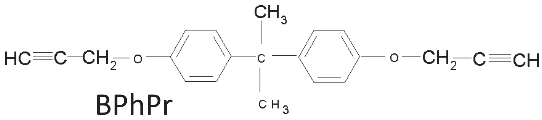
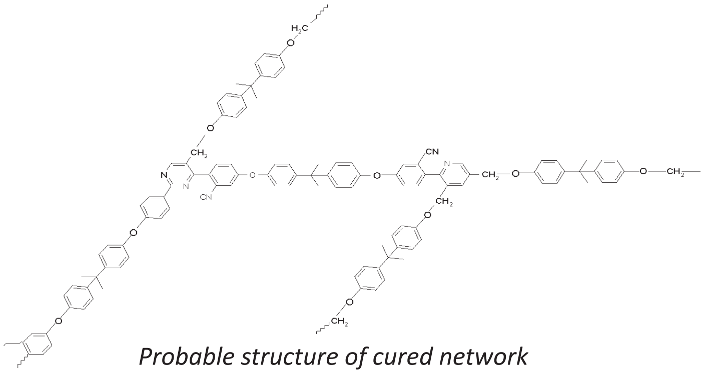
Phthalonitrile polymers offer an attractive combination of properties including outstanding thermo-oxidative stability, excellent mechanical properties, low water absorptivity and superior flame resistance. However, the phthalonitrile polymer systems demand curing at elevated temperatures for long durations to ensure their complete polymerization leading to the above highly desirable features. The introduction of addition curable groups such as propargyl could reduce the cure temperature to a reasonable level without sacrificing the thermal and mechanical properties considerably. The present study investigates the influence of propargyl groups on the cure behavior of phthalonitriles using bisphenol phthalonitrile (BPhPN) and bispropargyl ether (BPhPr).

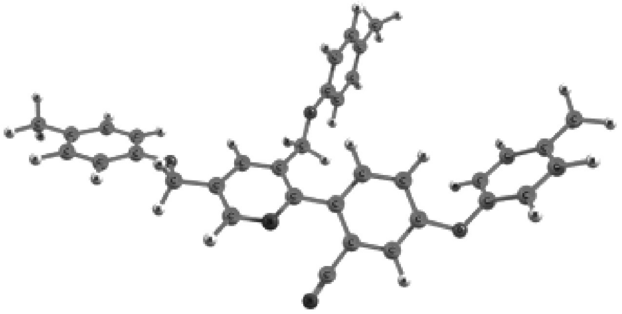

BPhPN


BPhPr

The bisphenol phthalonitrile-bispropargyl ether of bisphenol A blends (BPhAPN-Pr) were formulated with 1:1, 1:1.5, 1:3 and 1:5.7 molar ratios of bispropargylated ether of bisphenol A and bisphenol phthalonitrile monomers, respectively. The cured network of phthalonitrile-propargyl ether blend consists of pyridine, pyrazine and pyrimidine- based structures, the composition of which is determined by that of the blend


Probable structure of cured network

The cure mechanism operating in phthalonitrile – propargyl ether blends was studied theoretically using B3LYP/6-31G** level of density functional theory (DFT). Model compounds, phthalonitrile ether of p-hydroxy toluene and propargyl ether of p-hydroxy toluene were selected for the theoretical studies. Among the probable cure products, pyridine derivative was found to be the most stable one (2:1 blend ratio of propargyl to phthalonitrile) with heat of reaction of -120 kcal/mol.



Optimized structure of Pyridine derivative

DSC scans of the blends showed two well resolved endothermic transitions corresponding to the melting of monomers and a merged exotherm with two maxima around 270°C and 310°C which can be attributed to the co-curing of phthalonitrile groups with the propargyl moieties, as shown in Figure 1. When the molar ratio of phthalonitrile monomer was increased from 1 to 5.7 with respect to propargyl ether, the ultimate cure temperature shifted from 344°C to 392°C, drawing more nitrile functions into the cured networks.

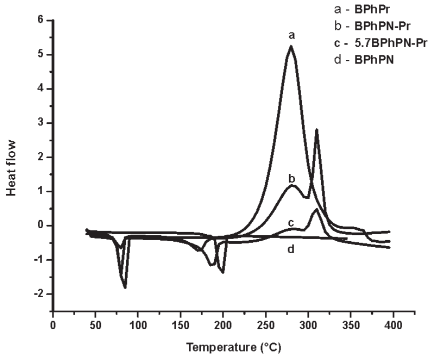


Figure 1: Curing of individual components and different BPhPN-Pr blend compositions

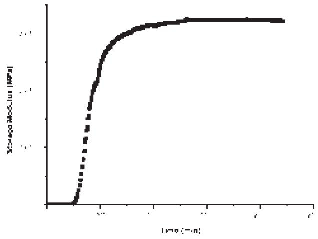


Figure 2: Rheological curve of 5.7BPhPN-Pr blend at 280°C

The kinetic parameters of cure reaction were determined by Ozawa and Kissinger methods. Activation energy for the reaction was calculated to be around 135 kcal/mol for 1st step and 90 kcal/mol for the second step

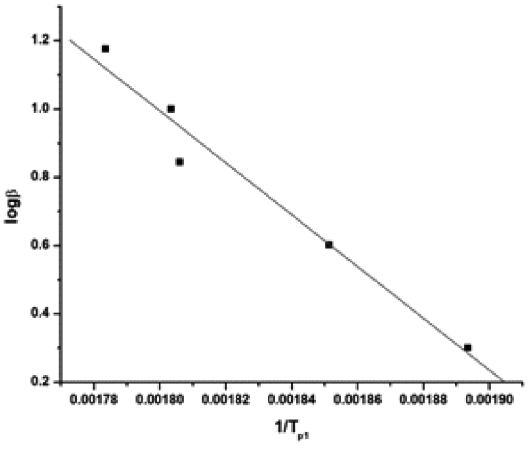


Figure 3: Typical Ozawa plot for BPhPN-Pr blend

TGA showed a proportionate increase in thermal stability of the cured resin with the increase in phthalonitrile content of blend. The peak decomposition temperature was shifted from 440°C to 465°C. But the char content at 900°C was greater for 1:1 bispropargylated ether–bisphenol phthalonitrile blend (51%) whereas all other compositions gave residue around 35%.

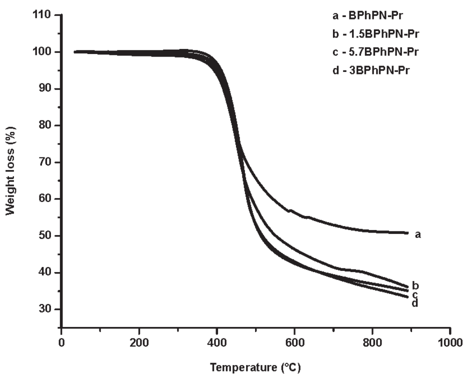


Figure 4: TGA curves of phthalonitrile-propargyl blends

Conclusion

Influence of propargyl groups on the cure behavior of phthalonitrile functions was investigated using bisphenol phthalonitrile (BPhPN) and bispropargyl ether (BPhPr) of bisphenol A. Co curing of phthalonitrile and propargyl functions were established by DSC and the probable products in the cured network structure were theoretically predicted. Cure activation parameters, were calculated for both stages of the reaction by Ozawa and Kissinger methods. Thermal stability of the blends increased with increase in phthalonitrile content.

Studies on the Cardanol based Bioplastic with its excellent Properties

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Biomass-based plastics (bioplastics), made using renewable plant resources as raw materials, have been attracting increased attention for use in environmentally sensitive applications in the face of petroleum resource depletion and global warming caused by the increase in carbon dioxide. Representative bioplastics currently used in mass production are polylactic acid (PLA) and chemically modified starch derivatives which are mainly used in general products including textiles and tableware. Efforts have been made to improve the durability of PLA, particularly its strength and heat resistance and it is now being used in durable products such as electronic devices, automobile parts, and medical goods. These bioplastics use starch as the main resource, which is produced from plants that are generally edible. However, fears of future food shortages are driving an effort to use plant resources that are not edible. Furthermore, there should already be a stable supply of the resources to prevent having to increase their production and thereby further affect the environment. Therefore, biomass-based byproducts currently generated in large amounts are the optimal candidate resources. We focused on plant resource that satisfies these conditions: cardanol, a unique structured organic compound derived from cashew nut shell generated in large amounts as a byproduct.

Cardanol (CD) is a main organic ingredient (about 30wt %) in cashew nut shell. Cashew nut is an agricultural renewable resource, and cashew trees (Anacardium occidentale L.) are widely planted in tropical countries such as India and Vietnam. A large amount of the shell is a non-edible byproduct. CD is a phenol derivative consisting of unsaturated hydrocarbons as a flexible long side chain part (carbon number: 15) and phenol as a rigid aromatic part with a reactive hydroxide group. It is superior to common phenol derivatives in terms of many practical characteristics such as water resistance, flexibility, and friction when used as a major component in thermosetting plastics such as phenol resins and epoxy resins. These resins are mainly used in surface coatings, insulating materials, adhesives, friction materials, etc. In the present investigation, we have derived modified cardanol to produce a durable biomass-based thermoplastic. We used hydrogenated CD, in which the unsaturated bonds in the alkyl side chain were changed to saturated ones by adding hydrogen to prevent cross-linking among CD molecules during modification. We found that the modified CD resulted in a bioplastic with good thermoplasticity and high durability properties such as high water resistance, high tenacity and high heat resistance.

Self Assembly of Triblock copolymer in Epoxy Resin: Strategy for the Development of High Performance Materials

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The block copolymers have the ability to self-assemble into different nanoscale structures [1]. The micro and nanostructured thermosetting blends of epoxy resin are prepared by using amphiphilic block copolymers with one of the block is miscible with epoxy resin [2-5]. The aim of the study has to investigate the effect of addition of poly(styrene-block-butadiene-block-styrene) (SBS) triblock copolymers in the modification of epoxy matrix and how the epoxidation on polybutadiene in SBS will influence the network structure of the epoxy precursors. We have studied in detail the morphologic analysis, mechanical properties and cure kinetics of epoxy modified block copolymer blends. The epoxidation reaction was carried out by H2O2 in the presence of an in-situ prepared catalyst system in water/dichloroethane biphasic system [2].The different epoxidation degree was obtained by varying the time and temperature of epoxidation. Due to the immiscibility of styrene and butadiene units in epoxy matrix, the macroscopic phase separated blends with heterogeneous morphology was observed. Further studies with epoxidised SBS showed a good compatibility of epoxidised butadiene domains in epoxy resin and a progressive increase in miscibility is observed as the epoxidation degree increases. Morphological analysis by TEM and optical microscopy is an evidence for the transition from macro to nanophase morphologies. The results confirmed that the nanophase separated polystyrene domains are arranged in the epoxy matrix containing both epoxidised and nonepoxidised polybutadiene units. The impact and fracture toughness values of epoxy blends of epoxidised SBS are increases with epoxidation degree and the composition.

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Effect of copper nanoparticles on the cure kinetics of an epoxy/ cycloaliphatic amine system

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The effects of copper nanoparticles on the cure kinetics of DGEBA-based epoxy resin / aliphatic amine system were studied. Cure kinetics studies were carried out by performing dynamic and isothermal differential scanning calorimetric (DSC) experiments. The dynamic DSC experiments were carried out at four different heating rates. Dynamic kinetic modeling was performed using Kissinger and Ozawa approaches. Since these methods are based exclusively on the maximum rate of cure, which occurs approximately at the beginning of the cure reaction, the activation energy calculated using these methods is valid only for the initial stage of the cure. A plausible reaction mechanism which involves the effect of the nanoparticle as an accelerator of the cure reaction was proposed. The Isothermal DSC scans were carried out at three different temperatures. The experimental data showed an autocatalytic behavior of the reaction, and the isothermal modeling was carried out by Kamal autocatalytic model. The results showed a very good agreement within the whole conversion range for the unfilled and all the filled systems.

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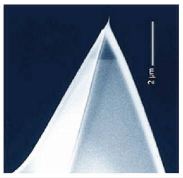
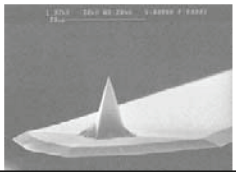
Nanosensors", Switzerland NANOSENSORS™ www.nanosensors.com Leading supplier of silicon probes. Offer a comprehensive range of fully characterized, high quality probes that fit all well-known commercial AFM's / SPM's.	 

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About the Seminar……

Polymers are the most versatile material in the modern world. Ever since its first production in 1909, the importance of polymers in man's life is on the increase with tremendous impact on industries and consumers throughout the world. Polymers are now used in nearly all manufactured products: from household items such as packaging, cosmetics, building materials, hosiery, clocks, radios, toys, flooring, food containers, bags, electric plugs, garden hoses, bodies and parts of automobile, boats etcright to airplane, rockets and space vehicles. The space research, medicine and microelectronics are the best beneficiaries of advances in this field. The volume of synthetic polymers produced is greater than the volume of steel. Furthermore, polymer consumption of developed and developing countries increase roughly in proportion to their gross national products. In terms of areas of research, since the mid-1980s, there has been a significant broadening of research areas and polymer science and technology is now interacting with many other modern scientific and technological disciplines. Polymer research has taken a digression towards supramolecular assembly, polymer-nano and polymer-inorganic composites, smart, shape memory and self-healing polymers etc that give a *grand espoir* for the future. The 21st century is the Age of Polymers.

As the importance of polymer science and technology is expected to grow even further, it is essential that the young polymer scientists keep themselves abreast of the new developments. It is in this backdrop that SPSI thought it appropriate to organize a one-day seminar on Recent Advances in Polymer Science and Technology. The seminar focuses on introducing the latest advances in the field of polymer science and technology and material science to students and young researchers by eminent scientists in this field. It also encourages contributed papers from student researchers to be presented in the conference. In the seminar, the students and young researchers get a unique opportunity to expose their work and to interact with fellow researchers and eminent scientists of the country.

The Society for Polymer Science India

SPSI is one of the premier professional scientific bodies of the country with its headquarters a Pune and regional chapters spread all over the country. It has been instituted with the intention of promoting advancement in the field of Polymer Science and Technology. It also serves as a forum for interaction among the polymer scientists, engineers and technologists in the R&D laboratories, universities and industries across the country. Its objectives include promoting science education and inculcating research interests among students. The Thiruvananthapuram chapter also strives to help disseminate ideas and facilitate communication among the fellow members by organizing regular meetings, seminars, invited lectures and workshops on contemporary topics in Polymer Science. Frequently, the Chapter conducts workshops on specified areas for the benefit of the student community. The subjects of such workshops include Latex Technology, Smart Materials, Advances in Polymer Science and Technology etc. A newsletter 'Polymer News' published quarterly by the Chapter serves as the voice of the polymer fraternity. This Chapter has established close collaboration with several other professional bodies in the city and has jointly conducted many seminars. The Chapter has instituted a best PhD award with the intention of promoting research and encouraging scholars in the field of Polymer Science and Technology.

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