Title of the PhD thesis: Development and Applicational Studies of Copolymer(S) and Blend(s) of some Conducting polymers

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ABSTRACT

Conducting polymers have become one of the most promising fields of research and development since the discovery of intrinsically conducting polymers by Alan J. Heeger, Hideki Shirakawa and Alan G. MacDiarmid in 1977, for which they were awarded the Nobel Prize in Chemistry, in the year 2000. These polymers have tremendous applications in different fields, especially in the electronics industry. However, the major concern in this area is the lack of processibility of these polymers. Lately, the rapidly expanding field of nano conducting polymer composites is generating many exciting new materials with novel properties. It is therefore, of immense significance to explore whether nanostructures of conducting polymers can lead to better performance in these already established areas, and whether reliable and scalable synthetic methods can be developed for the synthesis of conducting polymer nanostructures in order to provide the necessary materials base for both research and applications. The main objective of the present work is the quest of processibility of these conducting polymers, blends, composites and interpenetrating networks (IPNs) at micro as well as nanoscale .This thesis has been organized into 6 Chapters:

CHAPTER - 1: embodies the general introduction of some conducting polymers, their mechanism of conduction, method of synthesis , doping, processibility, drawbacks and methods to over come their processibility, formulation of composites ,blends,

interpenetrating networks and copolymers, conduction theory in composites and blends, advent of nanotechnology, literature survey on recent studies of conducting polymer based on blends,composites,copolymers as well as nano-scale synthesis and current applicational studies of conducting polymers.

CHAPTER – 2 deals with the formation of micro composites of polypyrrole with poly(methylmethacrylate) (PMMA),micro blend formation of polyaniline with coconut oil based poly(esteramide-urethane) (CPEAU) and interpenetrating network formation of polypyrrole with coconut oil based poly(esteramide-urethane) (CPEAU). The blends/composites/IPNS were further characterized by FT-IR, DSC, TGA, XRD and SEM..

CONCLUSION:

The physico-mechanical characteristics of the films of the PMMA/PPy blends were found to deteriorate with the increased ratio of ferric chloride in the blend, causing decrease in the conductivity. Conductivity values were found to be similar when molar ratios of Py:$FeCl_3$ were taken as 1:1 and 1:2 at the same loading of pyrrole in the blend.The blends lost their elasticity and flexibility on heating and turned into rigid and brittle material showing no glass transition temperature indicating crosslinking between the two polymers on heating. We have therefore called these blends as "pseudothermoset".

Micro blends of ClO_4^- doped polyaniline with coconut oil based poly (esteramide urethane) (CPEAU) were prepared by solution blending technique using different ratios of polyaniline(2wt%, 4wt% and 8wt%). Conductivity was found to be in the range 2.5 X 10^{-5}- 5.7 X 10^{-4} S cm^{-1} .The composite was found to show weak interactions between PANI and CPEAU at 8wt% loading through hydrogen bonding.

The micro IPNs of polypyrrole with CPEAU were prepared by dipping the $FeCl_3$ impregnated films of the latter in aqueous pyrrole solution for different time periods. CPEAU-Ppy IPN films were found to be flexible and stiff when they were prepared by soaking in $FeCl_3$ upto four hours. Water uptake in the $FeCl_3$ impregnated CPEAU films increased with the increase in the impregnation time, and reached 5 wt% for a maximum of four hours in impregnated films. Conductivity of the IPN films was found to be in the semi-conducting range $2.1 \times 10^{-4} Scm^{-1}$- $6.8 \times 10^{-6} Scm^{-1}$.

CHAPTER – 3 includes the synthesis and characterization of nano-scale poly(1-naphthylamine) (PNA), nanocomposites with polyvinyl alcohol(PVA), nano blends with poly(vinylchloride) and nano-IPNs with linseed oil based polyurethane amide. They were characterized by FT-IR and UV-visible spectroscopies, TEM ,stress strain studies ,electrical conductivity measurements as well as moisture absorption studies under controlled humidity.

CONCLUSION:

The particle size of PNA in PVA was found to be in the range 5nm to 75nm. All the composites showed good conductivity falling between $5 \times 10^{-1} S/cm$-$5.7 \times 10^{-3} S/cm$ .The percolation threshold was observed for 4-PNA/PVA composite ($5 \times 10^{-1} S/cm$).The stress-strain characteristics of 10-PNA/PVA matched with low density polyethylene (LDPE).In all the composites saturation in the absorption of moisture under controlled humidity (65%) at $20^0 C$ was observed ,lowest moisture absorption was found for 10-PNA/PVA nancocomposite and the highest for 2-PNA/PVA nanocomposites

The PNA/PVC composites showed good conductivity in the whole range of their compositions .Percolation threshold was observed at 4wt % loading of PNA.

The combination of the electrically conducting poly(1-naphtylamine) (PNA) with the linseed oil based polyurethanes amide (LPUA) was accomplished through different

weight loadings (0.5-2.5 wt%) of the conducting polymer.The particle size of the nanocomposite was determined by TEM and was found to be in the range 17-27 nm. Intermolecular hydrogen bonding between the two polymers as well as formation of urea linkages was confirmed by FT-IR .Electrical conductivity of the nanostructured conducting composites at 2.5wt% loading was found to be comparable to the reported PANI/PU at 30wt% loading of PANI which shows their remarkably superior properties and potential for application in anti-static as well as corrosion protective coatings.

CHAPTER – 4 incorporates the studies on the effect of oxidant on the properties of nano-scale poly(1-naphthylamine) is reported for the first time in CSA micellar medium using benzoyl peroxide,ammonium persulphate and potassium dichromate as oxidants.The nanopolymers were characterized by FT-IR,UV-visible,DSC,TGA ,XRD ,DLS as well as SEM techniques.

CONCLUSION:

FT-IR spectral investigations revealed the polymerization of 1-naphthylamine through N-C(5) linkages.The UV studies revealed the differences in the chain conformation of the polymers and their polaronic states. The nanosize of the conducting polymers was analyzed by DLS and SEM. DLS analysis showed that the particle size of the polymer prepared using the three oxidants varied between 115nm-117nm.SEM showed that particle size of the three polymers on a higher side from 100nm-312 nm.XRD as well as DSC analyses confirmed partial crystallinity of these polymers. Conductivity was found to be in the range of 10^{-3} to 10^{-2} S/cm which could be correlated to the conformation of the polymeric chains and delocalization of polarons. Polymerization of PNA was confirmed by FT-IR as well as UV visible spectra.

The in-situ intercalative polymerization of PNA within MMT layers was confirmed by FT-IR,XRD, conductivity; SEM as well as TEM studies.XRD revealed intercalated as

well as exfoliated structures of PNA/MMT nanocomposites which were compared with the reported polyaniline-MMT nanocomposites.The increase in the concentration of PNA in the interlayer galleries of MMT led to destruction of the layered clay structure resulting in exfoliation of the nanocomposite.Conductivity of the nanocomposites was found to be in the range of 10^{-3} to 10^{-2} Scm^{-1} which was found to be higher than the ones reported for PANI-clay nanocomposites

CHAPTER- 5 This chapter includes the synthesis, characterization and evaluation of nano-scale copolymers of poly(1-naphthylamine) with aniline and o-toluidine.Nanopolymers of poly(1-napththylamine) with aniline and o-toluidine were synthesized via template synthesis and were characterized for their spectra,thermal,morphological and conductivity studies.

CONCLUSION:

Spectral studies revealed the copolymer formation while the thermal stability was found to be unaffected by copolymerization. TEM shows the average particles size of poly(1-naphthylamine) to be 30nm while incase of copolymers it was found to be 130-150nm.Conductivity of the nanocopolymers was found to be in the semi-conducting range.

CHAPTER- 6 focuses on the application potential of the synthesized conducting polymeric composites/blends/IPNS and copolymers as corrosion protective and anti-microbial materials.Coconut oil based conducting blend coatings of polyaniline and poly (urethane ester amide) were prepared by loading different ratios (2wt%, 4wt% and 8wt%) of polyaniline in poly(urethane esteramide) and linseed oil based conducting nanocomposite coating material of poly(1-naphthylamine) (PNA) and poly (urethane amide)(LPUA) were prepared on steel substrate by loading different ratios (0.5wt%,1wt%,1.5,2.0wt%and 2.5wt%) of poly(1-naphthylamine) in poly(urethane

amide).The coatings investigated for their physico-chemical, thermal, morphological, conductivity and anti-corrosive coating characteristics. The anti-microbial activity of PNA, PNA-PVA, PNA/PVC, PNA-co-PANI, PNA-co-POT and PNA/MMT were also investigated which show different behavior against E.coli and S.aureus

CONCLUSION:

The corrosion protective performance of the coatings of the PANI/CPEAU blends were found to be far superior than that of plane poly(esteramide-urethane) (CPEAU) and were found to show enhanced corrosion owing to the formation of a dense non porous protective coating on the steel substrate. Conductivity of the blends was found to be in the range 2.5 X 10^{-5}- 5.7 X 10^{-4} S cm^{-1}An increase in the thermal stability of the coatings of the blend was noticed in the aged samples accompanied by a decrease in their conductivity which was attributed to the crosslinking effect while corrosion protective performance remained almost unaffected even after 2 years of aging.

Linseed oil based conducting nanocomposite coating material of poly(1-naphthylamine) (PNA) and poly (urethane amide)(LPUA) were prepared on steel substrate by loading different ratios (0.5wt%,1wt%,1.5,2.0wt%and 2.5wt%) of poly(1-naphthylamine) in poly(urethane amide).Open circuit potential (OCP) of the nanocomposite coated stainless steel in different corrosive media showed a significant shift in the corrosion potential towards more positive values.

The anti-microbial activity of PNA, PNA-PVA, PNA/PVC, PNA-co-PANI, PNA-co-POT and PNA/MMT were also investigated which show different behavior against E.coli and S.aureus.While PNA shows higher activity (8 mm)against standard (6 mm) for E.coli,it exhibited comparable activity (5mm) to the standard in case of S.aureus. PNA-co-POT and PNA-co-PANI showed zone of inhibition (5mm) comparable to the standard drug (6 mm) in E.coli ,the former has better activity (8 mm) than the standard

value (6 mm) for S.aureus.In PNA/MMT-I,PNA/MMT-II and PNA/MMT-III mild or

no activity was observed against E.coli however, good activity was shown against

S.aureus comparable to the standard drug.

List of Publications

1. .*"Development of novel conducting composites of Linseed oil based polyurethane amide with nanostructured poly(1-naphthylamine)"*
   S.M.Ashraf, Sharif Ahmad and **Uffana Riaz**
   Polymer International   **[2007]**

2. *"Miscibility Studies of Linseed Oil Epoxy with   Poly(vinyl alcohol)"*
   H.O. Sharma, Manawwer Alam, **Ufana Riaz**, Sharif Ahmad and S. M. Ashraf
   J Macromol Sci Part-A Pure & Appl Chem (2007)   **[In Press]**

3. *"High Performance Corrosion protective DGEBA/Polypyrrole coatings"*
   Ufana Riaz S.M.Ashraf and Sharif Ahmad
   Prog.Org.Coat. 59,138-145   **[2007]**

4. *"Effect of Ferro fluid concentration on electrical and magnetic properties of Fe_3O_4/PANI nanocomposites"*
   Javed Alam, **Ufana Riaz** , Sharif Ahmad
   Journal of Magnetism and Magnetic Materials 314,93-99   **[2007]**

5. *"Miscibility studies of polyester amides of linseed oil and dehydrated castor oil with poly vinyl alcohol"*.
   M.Ashraf,Sharif Ahmad,**Ufana Riaz**, Manawwer Alam and H.O.Sharma
   International Journal of Polymer Materials,56,1-15   **[2007]**

6. *"Miscibility behavior of polyester amides of Linseed oil and Dehydrated castor   oil epoxy with poly(methacrylic acid)"*
   S.M.Ashraf,Sharif Ahmad,Ufana Riaz ,Manawwer Alam and H.O.Sharma
   Journal of Applied Polymer Science,103,1367-1374   **[2006]**

7. *"Development of conducting composite of polyaniline-poly(esteramide urethane) from a sustainable resource"*
   S.M.Ashraf, Sharif Ahmad, Yukti Malik and **Ufana Riaz**
   Journal of Macromolecular Science, Part A Pure & Applied Chemistry
   43(4-5),679-687   **[2006]**

8. *"Studies on miscibility of dehydrated castor oil epoxy (DCOE) with poly (methylmethacrylate)"*
   S.M.Ashraf, Sharif Ahmad, **Ufana Riaz** and H.O.Sharma
   Journal of Applied Polymer Science,100(4),3094-3100   **[2006]**

9. *"Miscibility Studies on Linseed oil Epoxy Blend with Poly(methacrylic acid)"*

S.M.Ashraf, Sharif Ahmad, **Ufana Riaz**, Manawwer Alam and H.O.Sharma
Journal of Applied Polymer Science,
99(5) ,2512-2519   **[2005]**

10. *"Compatibility Studies on Dehydrated Castor oil Epoxy Blend with*
    Poly(methacrylic acid)"
    S.M.Ashraf, Sharif Ahmad, **Ufana Riaz**, Manawwer Alam and H.O.Sharma
    Journal of Macromolecular Science Part A Pure & Applied Chemistry
    46,1409-1421   **[2005]**

11. *"Corrosion studies of polyaniline/coconut oil polyesteramide urethane*
    coatings"
    Sharif Ahmad, S.M.Ashraf, **Ufana Riaz**
    Polymers for Advanced Technologies16(7), 541-548   **[2005]**

12. *"Conducting Semi-interpenetrating polymer network of polypyrrole with*
    poly(esteramide urethane) synthesized from a sustainable resource."
    S.M.Ashraf, Sharif Ahmad, **Ufana Riaz** and Ritica Dua
    Journal of Macromolecular Science, Part A Pure & Applied Chemistry
    42,521-533   **[2005]**

13. .*"Pseudothermoset Blends of Poly (methylmethacrylate) and*
    Polypyrrole"Morphological,Thermal,and Conductivity Studies"
    S.M.Ashraf,Sharif Ahmad and Ufana Riaz
    Journal of Applied Polymer Science,93 ,82-91,   **[2004]**