

Structural and Thermal Studies of Biscitraconimide/Poly(etherimide)/Polyaniline Nanocomposites

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Abstract— Biscitraconimide (MBMI)/Polyetherimide (PEI)/CSA doped PANI nanocomposite films were successfully prepared by in-situ polymerization method. The obtained nanocomposites possess higher thermal stability than neat MBMI/PEI semi-IPN matrix. With increasing wt% of CSA doped PANI nanoparticles, the decomposition temperature of MBMI/PEI semi-IPN increased. Structural studies were done by Fourier Transform Infrared (FTIR) Spectroscopy.

Index Terms— Nanocomposites, Semi-IPN, Scanning Electron Microscope

I. INTRODUCTION

Nano Polyaniline (PANI) can be applied in different areas such as electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electrorheological, chemical, membrane, sensors, EMI Shielding and so on because of its some special properties such as conductivity, increase of viscosity in solution when under an electric field, change in electrical conductivity or color when exposed to acidic, basic and some neutral vapors or liquids, easy variation of oxidation states, very high capacitance values, volume changes at different oxidation states, and its ability to emit color under various excitations, etc [1-7].

The main problem associated with the effective utilization of PANI is its infusibility and poor solubility in all available solvents [8, 9]. However, the solubility of PANI can be improved through doping with a suitable dopant or modifying the starting monomer [10, 11]. There is ample scope for modifying the processability of PANI through the selection of a suitable dopant and suitable level of doping and also by controlling its structure during synthesis [10, 12]. Another avenue for the successful utilization of PANI is through blending it with a commercially available polymer that has good processability and mechanical properties. Polymer composites containing PANI, where it is used as conducting filler, have received much attention because of the combination of improved processability and fairly good mechanical properties coupled with good conductivity. Consequently, there is a wider scope for the practical applications of such composites [13, 14].

Among the polymers, polyimides (PI) possess reliable high temperature stability, good mechanical strength and excellent

chemical resistance. In recent years, the preparation of polyimide composite materials has been extensively studied due to the dramatic improvements over their pure state in the thermal stability, mechanical properties and other functional features by introducing only small fraction of inorganic fillers [15]

But a single polymeric material suitable as a matrix for the fabrication of composites that has both toughness and good compressive modulus has not been found. Polymeric matrix resins that have good compressive modulus generally possess high cross-link density which imparts brittleness. On the other hand, tough resins have poor processability because of their very high melt viscosity at the processing temperature. Thus to overcome the above disadvantages the concept of semi-interpenetrating polymeric networks (semi-IPNs) has been developed to obtain macromolecular systems which combine the high temperature properties of thermoplastic polymers and processability of thermosetting polymers. Semi-IPNs are composed of two chemically different polymers, one is crosslinked and other is linear.

Therefore, different compositions of semi-IPN polyimide system were prepared through solution blending using biscitraconimide (MBMI) and polyetherimide (PEI) as previously reported [16]. Since PEI (Figure 1) is an excellent engineering thermoplastic having good mechanical properties as well as high glass transition temperature (T_g) and thermo-oxidative stability. Whereas phosphorous containing biscitraconimide resin was prepared by reacting citraconic anhydride (CA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and bis(3-amino propyl)phenyl phosphine (BAPPP). One important advantage of phosphorous containing polyimide is that, these resins show good flame resistant properties. The synergistic fire retarding properties of phosphorous and nitrogen containing functionalities are well documented in literature [17]. Moreover incorporation of flexible chain segment helps to overcome brittleness and enhance ductility as well as toughness [18]. Among them 20:80 MBMI: PEI composition was chosen for composite fabrication due to its flexible film forming ability with maximum thermoset fraction coupled with good optical transparency and flame retardant property.

Only few researchers have studied the synthesis and characterization of polyimide/PANI nanocomposites. So far, to

the best of our knowledge, preparation of polyimide semi-IPN based nanocomposites has not been found. Thus in the present study polyimide semi-IPN based nanocomposites films were prepared by using PEI/biscitraconamic acid precursor solution and Camphor Sulphonic Acid (CSA) doped PANI nanoparticles via in-situ polymerization method. Here biscitraconamic acid was used as a precursor of biscitraconimide (MBMI). The semi-IPN nanocomposites films were examined for their spectral and thermal properties.

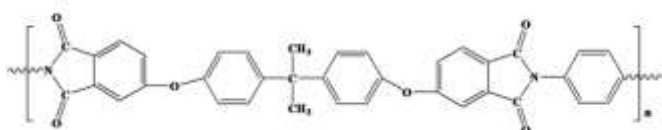


Figure 1: Chemical structure of PEI.

II. EXPERIMENTAL

A. Materials

Aniline and Camphor sulphonic acid were supplied by Aldrich. Aniline was dried over Zinc dust before use. Sodium Lauryl sulphate (SLS) (S.D. Fine Chem. Limited, Mumbai) was used as received. Polyetherimide (Ultem® 1000) was supplied by General Electric Plastics, USA in pellet form and was dried for 8 h in an oven at 150°C before use to remove moisture, if any. Bis(3-aminopropyl)phenyl phosphine (Alfa Aesar) and citraconic anhydride (Aldrich) was used as received. 3,3',4,4'-benzophenone tetracarboxylic dianhydride supplied by Aldrich was recrystallized from acetic anhydride before use. N,N-dimethylacetamide (DMAc) from Merck was purified by distillation over phosphorous pentoxide under reduced pressure and stored over 4Å molecular sieves.

B. Measurements

The infrared spectra were recorded on Perkin Elmer FTIR spectrophotometer (Model RX1) using KBr pellets in the range 4000-400 cm⁻¹. Glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC), Model DSC Q 200, TA instruments; USA at a heating rate of 10°C/min under nitrogen atmosphere at a flow rate of 50ml/min. Degradation temperatures were recorded by Hi-Res TGA 2950 thermogravimetric Analyzer (TA instruments), at a heating rate of 10°C/min under nitrogen atmosphere. About 7±2 mg of sample was heated at 10°C/min from room temperature to 1000°C in a dynamic nitrogen atmosphere (flow rate 60ml/min).

C. Synthesis of CSA doped PANI Nanoparticles

In the present work 50% camphor sulphonic acid doped nano PANI (Figure 2) was synthesized by emulsion polymerization technique. For its synthesis 500 mL of 0.1 M HCl was taken in a three necked round bottom flask fitted with mechanical stirrer was used as an aqueous phase in micellar solution. Nitrogen was purged for 10-15 min to remove dissolved oxygen. Then 0.07 moles of sodium lauryl sulphate (SLS) was added to the aqueous phase and stirred for 1 hr in

order to get homogeneous micellar solution. Then, 0.1 mole of aniline was added drop wise and the reaction mixture was further stirred for 1 hr. Thereafter 10 mL 0.1M HCl including ammonium peroxodisulphate (APS, 0.05 moles) were added drop wise into reaction mixture. After an induction period of about 30 minutes, the homogeneous colorless mixture turned emeraldine green and after another 2-3 minutes it became dark green. To this solution 0.05 moles camphor sulphonic acid was added and polymerization was carried out for 24 h at 20 °C. At the end of this stage the reaction mixture turned dark green. Then excess amount of methanol was added into the reaction mixture to precipitate the nanoparticles and to stop the reaction. The precipitate was collected with Millipore filtration assembly and washed two times each with methanol, acetone and deionized water to remove unreacted chemicals, aniline oligomers and SLS. The obtained PANI was dried in vacuum oven at 40 °C for 48 h.

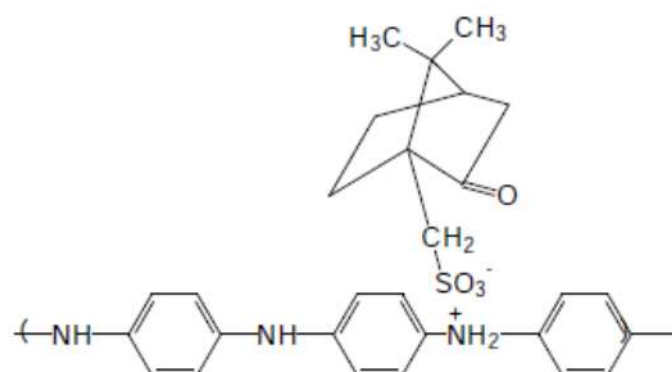


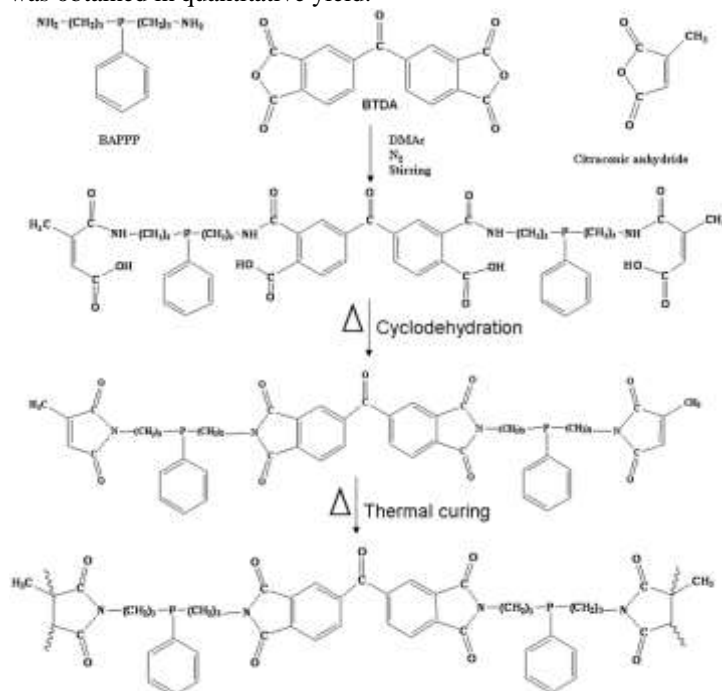
Figure 2: General structure of CSA doped PANI

D. Synthesis of Biscitraconamic acid

Biscitraconamic acid (CA/BAPPP/BTDA), the chemical structure of which is shown in Scheme 1, was prepared in two steps. Step one concern reaction of diamine and dianhydride (BAPPP/BTDA). Step two deals with the addition of citraconic anhydride with BAPPP/BTDA according to the following procedure.

A 500 ml three neck round bottom flask equipped with a nitrogen inlet, a stirrer bar and a guard tube was charged with 41.67 mmol of diamine (BAPPP) and 150 ml of freshly distilled DMAc. The solution was stirred until the diamine dissolved completely. 20.84 mmol of dianhydride (BTDA) was added in fractions to this solution under effective stirring. The reaction mixture was stirred for 8h at room temperature. A solution of 41.67 mmol of citraconic anhydride (CA) in 50 ml DMAc was added to the same solution over a period of 15 minutes. After 10 minutes the colour of the reaction changes from white to yellow, room temperature stirring for 8h was further continued to ensure complete reaction. DMAc was distilled under reduced pressure (10mm of Hg) at 90°C, the solid material obtained was biscitraconamic acid (MW 922 gm/mole). After that dry benzene was added to biscitraconamic acid and further distilled. This process was repeated twice in

order to remove moisture completely. Biscitraconamic acid was obtained in quantitative yield.



Scheme 1: Schematic of crosslinked biscitraconimide synthesis route.

E. Synthesis of PEI/MBMI semi-IPN/ CSA Doped PANI Nanocomposite films

CSA doped PANI nanoparticles (1 wt%) was added into DMAc solvent and ultrasonicated for 4h. For preparing semi-IPN system, 1.085 ml (217mg), 20 wt% solution of biscitraconamic acid (equivalent to 200 mg of biscitraconimide, mol. wt. 850) in DMAc was mixed with 4 ml (800 mg) 20 wt% solution of PEI in same solvent. The mixture was stirred for 1h at room temperature to give a clear brown solution, which contained 20% by weight of solid. The weight ratio of biscitraconimide and PEI was 20 to 80 and this composition was designated as PM. Then the above CSA doped PANI suspension was added to PEI/biscitraconamic acid solution and the reaction mixture was ultrasonicated for another 4h at room temperature in order to ensure fine dispersion of CSA doped PANI nanoparticles in PEI/MBMI semi-IPN matrix. Then the reaction mixture was poured on clean and dry glass plate and thermal imidization was carried out in an oven at 100 and 150°C for 2h at each temperature then 200, 250 and 300°C for 1h at each temperature. Other compositions of nanocomposites were prepared in similar manner by adding the above components in the required ratios and their formulations are given in Table 1.

Table 1: Sample Codes for MBMI/PEI semi-IPN and MBMI/PEI/CSA doped PANI nanocomposites.

Sample Code	PEI (wt %)	MBMI (wt %)	CSA doped PANI Nanoparticles (wt %)
MP	80	20	-
MPPN1	80	20	1
MPPN3	80	20	3
MPPN5	80	20	5

III. RESULT AND DISCUSSION:

A. FT-Infrared Spectroscopy

The FTIR spectra of CSA doped PANI, MBMI/PEI Semi-IPN and their nanocomposite (5 wt% PANI) are shown in Figure 3. The FTIR absorption spectrum of CSA doped PANI (Figure 3 (a)) demonstrates the band at 3438 cm⁻¹ is due to the N-H stretching. The peak corresponding to vibration stretching of N-quinoid ring is at 1462 cm⁻¹ for CSA doped PANI. Vibration stretching of N-benzenoid ring can be seen at 1586 cm⁻¹. The band at 1119 cm⁻¹ is typical of the protonated state of PANI. The absorption at 787 cm⁻¹ is characteristic of 1, 4 di-substituted phenyl ring [19]. The spectrum of MBMI/PEI semi-IPN (Figure 3 (b)) shows characteristic imide group absorptions at 1778 and 1720 cm⁻¹ (asymmetrical and symmetrical stretching of imide carbonyl bond), 1380 and 735 cm⁻¹ (C-N stretching and bending) [20].

Similar absorption bands are also observed in MBMI/PEI/CSA doped PANI nanocomposite as shown in Figure 3(c). These results clearly confirmed the complete imidization of amic acid into imide in nanocomposites. The characteristic absorption peaks due to both MBMI/PEI semi-IPN and CSA doped PANI are observed in nanocomposites. The peak positions of the absorption bands for each component remain almost unchanged in nanocomposites when compared with the IR spectra of CSA doped PANI and MBMI/PEI semi-IPN. The results revealed successful incorporation of CSA doped PANI in MBMI/PEI semi-IPN matrix.

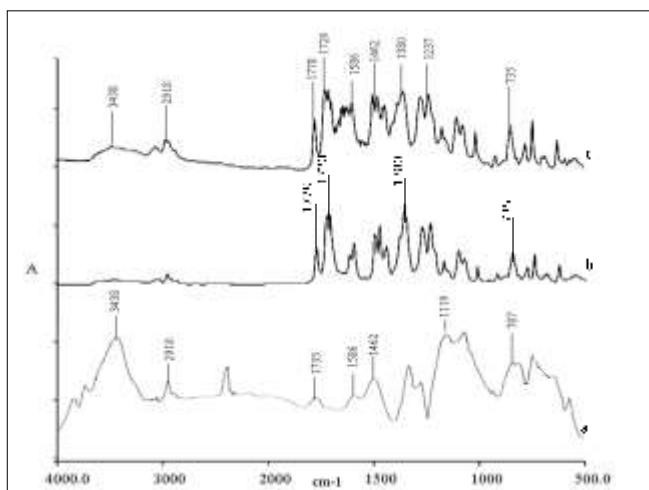


Figure 3: FTIR spectra of (a) CSA doped PANI nanoparticles (b) MBMI/PEI semi-IPN (c) MBMI/PEI/CSA doped PANI nanocomposite (MPPN5)

B. Thermal studies

Thermal studies of nanocomposites were carried out by TGA and DSC.

Thermo gravimetric Analysis (TGA)

To investigate the effect of CSA doped PANI nanoparticles incorporation on the thermal stability of MBMI/PEI semi-IPN matrix, TGA was performed. TGA measurements were conducted at a heating rate of 10°C/min under nitrogen atmosphere. Figure 4 shows the TGA thermographs for semi-IPN and nanocomposites. The onset degradation temperature of MBMI/PEI semi-IPN was found to be 435°C which increases to 437, 439 and 443°C with incorporation of 1, 3 and 5 wt% of CSA doped PANI nanoparticles, respectively (Table 2). This reveals that the presence of nano PANI enhances the thermal stability of MBMI/PEI matrix as reported in many nanocomposites [21-24]. Furthermore, even the char yield also slightly improves in the nanocomposites (Table 2).

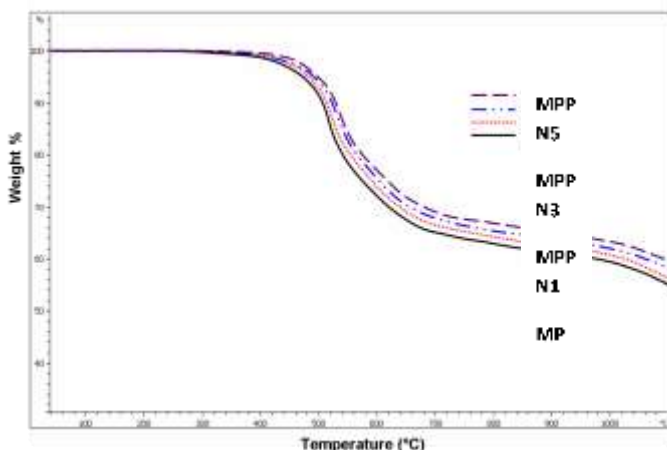


Figure 4: TGA thermographs of (a) MP (b) MPPN1 (c) MPPN3 (d) MPPN5

Differential Scanning Calorimetry (DSC)

Thermal behavior of MBMI/PEI/CSA doped PANI nanocomposites were evaluated by DSC. DSC measurements were conducted at a heating rate of 10°C/min under nitrogen atmosphere. Samples were dried at 150°C for 5h in an oven before DSC measurements. The Tg values of MBMI/PEI/CSA doped PANI nanocomposites are shown in Figure 5 from which it is clear that the Tg shows up shift with increase in the wt% of PANI. The Tg of MBMI/PEI semi-IPN was 209°C which increases to 210, 213 and 215°C with incorporation of 1, 3 and 5 wt% of PANI nanoparticles, respectively (Table 2). It may be due to the ionic groups present on the surface of PANI nanoparticles, which interact and modify the intermolecular forces, thus hindering segmental mobility of the polymer segments. This increases the Tg of the nanocomposites [25-26].

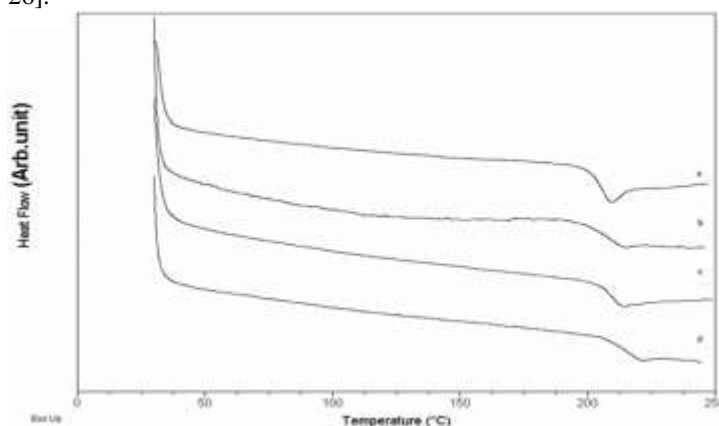


Figure 5: DSC curves of (a) MBMI/PEI semi-IPN (b) MPPN1 (c) MPPN3 (d) MPPN5

Table 2: Thermal data of MBMI/PEI semi-IPN system and various compositions of MBMI/PEI/CSA doped PANI nanocomposites measured at a heating rate of 10°C/min in N2 medium.

Sample designation	TGA				DSC
	T _{onset} ^b (°C)	T _{max} ^c (°C)	T _{endset} ^d (°C)	Y _c ^e at 800°C (%)	T _g ^a (°C)
MP	435	513	646	64	209
MPPN1	437	515	648	65	210
MPPN3	439	516	650	66	213
MPPN5	443	519	653	67	215

- aGlass transition temperature.
- bTemperature of onset of decomposition.
- cTemperature of maximum rate of weight loss.
- dTemperature of endset of decomposition.
- eChar yield at 800°C under nitrogen.

IV. CONCLUSIONS

MBMI/PEI/CSA doped PANI nanocomposite films were successfully prepared by in-situ polymerization method. The

FTIR results revealed successful incorporation of CSA doped PANI in MBMI/PEI semi-IPN matrix. The obtained nanocomposites possess higher thermal stability than neat MBMI/PEI semi-IPN matrix. With increasing wt% of CSA doped PANI nanoparticles, the decomposition temperature of MBMI/PEI semi-IPN increased.

Acknowledgements

The authors thank Director, DMSRDE, Kanpur, India for providing laboratory facilities and his kind support to carry out this work successfully.

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