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An electrochemically synthesized conducting semi-IPN from polypyrrole and poly(vinyl alcohol)

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The present work reports electrochemical synthesis of a semi-IPN (s-IPN) following electropolymerization of pyrrole from an aqueous medium within a crosslinked network of PVA. This combination resulted in a set of free standing and flexible films having high electrical conductivity and good environmental stability. Primarily three different types of samples were prepared by electropolymerization of pyrrole using a monomeric dopant (styrene sulfonate, SS), a polymeric dopant (poly(styrene sulfonate), PSS) and a crosslinked polymeric matrix (PVA-C). Considering the mechanical strength and flexibility of the resulting films, the PPy-PVA-C s-IPN was found to be the best one. Electropolymerization conditions were optimized by varying the concentrations of monomer and electrolytes and in some cases the solvent. Surface morphology (by SEM), thermal stability (through DSC and TGA) and electrical conductivity at different temperatures were studied and the s-IPN was found to possess improved electrical, thermal and environmental stability as compared to the pure PPy film.

Introduction

An interpenetrating polymer network (IPN) is defined as an intimate combination of two crosslinked polymers (with or without mutual chemical interaction) at least one of which is synthesized and crosslinked in the presence of the other.[1] In other words IPNs are 'polymer alloys' formed from homo-crosslinking of two polymers in close vicinity to each other. If one component of the assembly is crosslinked leaving the other in the linear form then the system is generally termed as 'semi-IPN' (s-IPN). When one polymer of a s-IPN system is synthesized (from monomer) in the presence of the crosslinked form of the other, or one polymer is selectively crosslinked from the homogeneous mixture of the two, then the resulting materials are termed as 'sequential s-IPN'.[2] All these materials generally present single phase systems with synergistic behavior. Over the last two decades considerable attention has been focussed on this topic and lots of IPNs are synthesized from conventional polymers like vinyl polymers, polyacrylates, polyurethanes, thermoplastics, rubber[3–9] and so on. Novel properties of IPNs *viz.* their very high mechanical strength, limited solubility, significant thermal stability, thermosensitivity, volume phase transition[10–12] *etc.* have attracted a great deal of scientific and technological interest. Versatile applications of such materials have also been established *viz.* vibration and noise damping, impact resistance, ion exchange, formation of insoluble coating, fabrication of artificial organs and biological inserts, controlled delivery of solvent, drug and other reactive species[13–16] and so on.

With the progress in the field of inherently conducting polymers (ICP), there is a great deal of scientific and technological interest in synthesizing ICP based IPNs. A suitable combination of interesting optical and electronic properties of ICPs with desirable mechanical and thermal properties of crosslinked polymers should obviously give rise to a series of promising materials with important application potential. Earlier there were two reports from Frisch *et al.*,[17,18] who synthesized electrically conducting s-IPNs from poly(carbonate urethane) (PCU) and crosslinked poly(chloroprene); in this system electrical conductivity of the order of 10^{-4} S cm^{-1} was exhibited by I_2 doped linear PCU chains. However, the perspective of the synthesis of ICP based IPNs is somewhat different from that of conventional IPNs. Conducting polymers are insoluble and infusible in nature and therefore cannot be taken in solution or in melt form; at the same time their rate of chemical polymerization is so high that they cannot be simultaneously polymerized with another monomer to form a single phase polymeric mixture. Therefore 'simultaneous' or 'sequential' techniques generally applied for the preparation of IPN from conventional polymers cannot be applied to ICP based IPNs. Over the last few years there have been a few attempts to synthesize conducting semi-IPNs following modified techniques. In most of these reports a conducting polymer (polypyrrole (PPy) or polyaniline (PAn)) is synthesized chemically or electrochemically within a crosslinked network of a conventional polymer. A series of such IPNs in which crosslinked networks of SIS rubber,[19,20] cellulose,[21,22] PMMA[23] and a few other polymers and copolymers[24,25] are used as the matrix for chemical or electrochemical polymerization of pyrrole and aniline have so far been reported.[19–25] Although these materials were termed as IPN, they are s-IPNs according to the classical definition. On the other hand, Mandal *et al.*[26,27] have suggested that chemical oxidative polymerization of pyrrole or aniline within the films of different polymers *viz.* poly(vinyl acetate) (PVAc), SBA *etc.* results in *in situ* crosslinking of the matrix, so that the composites formed in this way can be referred to as IPN. However, such a conclusion was drawn mainly on the basis of the insolubility of the resulting materials and no strong evidence in support of the crosslinking was presented.

Electropolymerization of an ICP within an insulating polymer film is an extensively applied technique used to produce free-standing conducting films. There are lots of reports describing the synthesis of conducting polymer based composites following electropolymerization techniques. For this purpose, prior to polymerization the working electrode should be coated with a polymer that swells to some extent, to open up channels and allow diffusion of the monomer and electrolyte, but which is not soluble under polymerizing conditions. Conventional polymers with good mechanical properties *viz.* poly(vinyl alcohol), polyamides, polyurethanes, poly(vinyl chloride), Naffion *etc.*[28–31] have been widely utilized to provide

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a suitable matrix for electropolymerization using the appropriate solvent system. Crosslinked polymers, owing to their limited solubility and good mechanical properties are highly desirable in this respect and electropolymerization of a conducting polymer within a crosslinked conventional polymer matrix obviously produces s-IPNs.

PVA is an easily available water soluble polymer having very good transparency and mechanical properties.[32] Owing to the presence of free –OH groups, it is very easy to crosslink this polymer using lower aldehydes *viz.* formaldehyde, glutaraldehyde *etc.* Heating PVA above a certain temperature can also impart some degree of crosslinking to it. Such properties were utilized to synthesize a few crossliked PVA (PVA-C) based conducting semi-IPNs. Earlier Lindsey and Street[33] synthesized PAn–PVA-C composites following the latter technique. In a relevant work Chen and Fang[34] have thoroughly discussed morphological, electrical, thermal and many other physical properties of chemically and electrochemically synthesized PAn–PVA composites. In a recent report de Azevedo *et al.*[35] have cosolvated dedoped PAn with PVA in DMSO followed by crosslinking with glutaraldehyde and subsequent doping of PAn by H_2SO_4. This is a classical example of the formation of a conducting polymer based sequential s-IPN from homogeneous solution. In our earlier publication we reported the synthesis and characterization of a chemically prepared PAn–PVA semi-IPN in which formaldehyde was used as the crosslinker to the PVA component in a stable dispersion of PAn–PVA prepared by the steric stabilization technique.[36,37] In the present work we have electropolymerized pyrrole within the matrix of crosslinked PVA to give PPy–PVA s-IPN. The synthesis technique, characterizations of different physical properties and a few potential applications have been studied and the results are discussed here.

Experimental

Materials

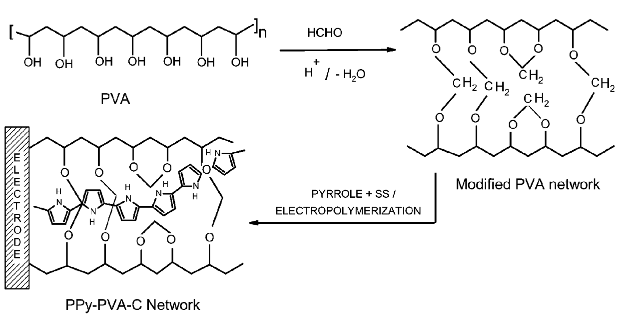
PVA (*M* 72 000) was supplied by Ms. Loba Chemicals (India) and formaldehyde (37–40%, HCHO) was purchased from Sarabhai Chemicals (Baroda, India). Styrene sulfonate (SS) (sodium salt) was used as received (Aldrich, USA) and pyrrole (Sigma, USA) was vacuum distilled before use. A ^{60}Co γ-ray source (dose rate 225 rad min^{-1}) was used for radiation induced polymerization of SS (to PSS). Distilled water and acetonitrile (AN) were used as solvents.

Methods

1. Synthesis. Three types of samples were prepared by electrochemical synthesis; SS doped PPy films (PPy–SS), polymeric dopant PSS doped PPy composite film (PPy–PSS) and PPy–PVA-C semi-IPN. A three-electrode, single compartment electrochemical cell was used for electropolymerization of all the samples. An ITO coated glass electrode (2 × 1 cm^2) (as working electrode), a platinum cathode (as counter electrode) and a saturated calomel reference electrode were used for all syntheses. Electropolymerization was carried out at room temperature (27 °C) under a continuous argon flow. The details of the syntheses of the different samples are given below.

i. PPy–SS. PPy samples were electrochemically deposited on the anode surface by galvanostatic polymerization (current density: 1.5 mA cm^{-2}) of pyrrole for 1 h from aqueous solution containing different concentrations of pyrrole and a fixed concentration of SS.

ii. PPy–PSS. SS was polymerized from a 5% aqueous solution exposed to γ–radiation for 8 h. The resulting polymer (poly(styrene sulfonate)) was precipitated out using methanol as the non-solvent and was dried at 50 °C. The molecular weight of the PSS was of the order of 6 × 10^7 (measured viscometrically). Details of radiation induced polymerization of SS and molecular weight determination have been published elsewhere.[38]



Scheme 1 The synthesis of PPy–PVA-C semi-IPN from PVA and pyrrole.

A weighed amount of PSS was dissolved in water to which pyrrole was added and the well stirred solution was subjected to anodic polymerization for 1 h under conditions identical to those used for the synthesis of PPy–SS. The effect of the nature of the polymerization medium on the resulting samples was studied by changing solvent from a purely aqueous to 1 : 1 and 1 : 2 (v/v) water : AN mixture without changing the other conditions.

iii. PPy–PVA-C s-IPN. The working electrode of the electrochemical cell was first coated with a solution of crosslinked PVA. PVA-C solution was prepared by adding 0.1 mL HCHO to a 5% PVA solution in 1 M HCl on stirring. 0.3 mL of this solution was spread over an ITO coated glass electrode and dried in air. PVA-C modified electrodes were immersed in the cell containing an aqueous solution of pyrrole and SS for 15 min under argon flow and polymerization was carried out at a constant current (1.5 mA cm^{-2}) for 1 h (Scheme 1). By varying the concentrations of the monomer and electrolytes, two sets of samples were prepared.

After each synthesis the film was peeled off the electrode, washed with distilled water and methanol, dried at 50 °C and subjected to different characterizations. Synthesis parameters and physical properties of the samples are listed in Table 1.

2. Characterizations. *i. Scanning electron microscopy (SEM).* The surface morphology of PPy–SS, PPy–PSS and the s-IPN were studied from gold coated films using a Hitachi S-415A electron microscope at 25 kV following a sputter coating technique.

ii. DC electrical conductivity measurements. A standard linear contact four probe technique was used to measure the electrical conductivity of sample films using silver paint for connection. For measurement of the conductivity at higher temperatures samples were fixed within a home made temperature controlled sample holder. A programmable current/voltage generator (Advantest R6142) and a precision digital voltammeter (Solatron S17071) were used for conductivity measurements. The value of each sample was obtained from the average values of few samples.

iii. Thermal studies. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of PVA-C, PPy–SS, PPy–PSS and the s-IPN were carried out in the temperature range 30–600 °C and 30–800 °C in a Mettler TA 4000 system thermal analyzer at a heating rate of 10 K min^{-1} under nitrogen atmosphere. Small closed aluminium pans were

Table 1 Synthesis parameters and physical properties of electrochemically prepared PPy-based composites and semi-IPNs[a]

Sample specification	Polymerization medium	Electrolyte used	Electrolyte concentration	Pyrrole concentration/M	Physical appearance of the films	D.c. conductivity/ S cm^{-1}
PPy–SS-1	Aqueous	SS	0.02 M	0.3	Thin, brittle and coherent films with smooth surface	5.1
PPy–SS-2			0.06 M			8.19
PPy–SS-3			0.10 M			19.16
PPy–PSS-1	Aqueous	PSS	0.4%	0.3	Smooth and coherent films, extremely brittle when dried	Too brittle to measure conductivity
PPy–PSS-2			1.2%			
PPy–PSS-3			2.0%			
PPy–PSS-4	H_2O–AN (1 : 1)	PSS	1.2%	0.3	Thin and brittle films with a rough surface and poor strength	0.90
PPy–PSS-5	H_2O–AN (1 : 2)		1.2%			1.09
PPy–PSS-6	H_2O–AN (1 : 1)		2.0%			1.50
s-IPN-A	Aqueous	SS	0.02 M	0.3	Free-standing and coherent films with very good strength	7.20×10^{-3}
s-IPN-B			0.06 M			21.80×10^{-3}
s-IPN-C			0.10 M			12.80
s-IPN-1	Aqueous	SS	0.10 M	0.06	Free-standing and coherent films with a very smooth surface and good strength	0.53
s-IPN-2				0.12		3.24
s-IPN-3				0.18		5.83
s-IPN-4				0.24		9.80
s-IPN-5				0.30		12.80
s-IPN-6[b]				0.03		18.28

[a] Polymerization temperature 30 °C, solvent 25 mL, current density 1.5 mA cm^{-2}, duration 1 h. Argon flow was maintained during polymerization. [b] Prepared with lower current density (0.5 mA cm^{-2}) and longer duration (3 h)

used and finely cut film samples ~6 mg were used for each measurement. Nitrogen gas flow 5–10 mL min^{-1} (controllable) was maintained during thermal analyses.

Results and discussions

PPy–SS was earlier prepared and characterized in our laboratory;[39] this presented a system with high conductivity but poor mechanical properties. The prime objective of the present work was to improve its properties such as mechanical strength, environmental stability *etc.* of electrochemically synthesized PPy–SS samples without significantly affecting its high conductivity and other important chemical properties. Two approaches were made to achieve this goal: to use a polymeric dopant (PSS) and to polymerize pyrrole–SS within a flexible polymeric network. The former technique resulted in *in situ* composite formation while the latter led to the formation of PPy–PVA semi-IPN. Preliminary observations indicated that the composite PPy–PSS did not produce a system with good mechanical strength and therefore this system was not studied very extensively. On the other hand free standing films of the s-IPN primarily showed good mechanical strength and were therefore studied in more depth in the present context. However, for comparison of properties, a few studies were also done on PPy–SS and PPy–PSS films. Morphological, electrical and thermal properties of all these samples were measured and the results are discussed in detail.

Earlier we studied the modification of PVA by partial crosslinking with HCHO and chemically combined polyaniline with PVA-C.[37] It was noticed that HCHO modified PVA has good mechanical strength and flexibility, and it partially swells but does not dissolve in water. It should be mentioned that a water soluble polymer as well as one with a highly rigid network (which does not allow monomer and electrolyte to pass through) cannot serve as a matrix for electropolymerization in an aqueous medium. Such observations have guided us to select PVA-C as the matrix for electropolymerization of pyrrole resulting in the formation of semi-IPNs. HCHO is known to initiate both (intra-chain) acetalization and (inter-chain) crosslinking of PVA by which only a limited degree of crosslinking can be achieved. The optimum PVA : HCHO ratio was selected from a set of experiments so that the extent of crosslinking is appropriate to impart sufficient swellability to the crosslinked polymer (in contrast to the immediate and large scale gelling induced by glutaraldehyde). The details of the synthesis and properties are discussed separately below.

1. Synthesis and physical appearance of the films of composite and IPN

PSS is a water soluble polymer capable of forming free standing films with good mechanical strength. Previously, there has been a lot of work on the syntheses and characterizations of chemically and electrochemically synthesized PPy–PSS films; spectroscopic and various electrical and electroanalytical characterizations of this material have been reported[40–42] but whether PSS can substantially improve the mechanical strength of PPy was not clearly mentioned. There were, however, a few attempts to combine PSS with PAn using a post-polymerization technique.[43,44] The SS molecules incorporated in the electrochemically grown PAn–SS film in these works were subjected to free radical polymerization (using benzoyl peroxide in CCl_4 as the radical initiator) in order to generate PSS moieties. This process however, did not improve the brittleness of the PAn–SS films significantly. In the present work fully sulfonated PSS was used as the electrolyte during electropolymerization of pyrrole with the aim of combining the mechanical properties of PSS with the electrical conductivity of doped PPy. PPy–PSS films grown from aqueous medium were smooth and coherent when prepared but became extremely brittle on drying. By changing the reaction medium from water to mixed solvents, like 1 : 1 and 1 : 2 (v/v) water–AN, brittleness could be controlled to some extent but the smoothness was seriously hampered. A non-aqueous medium could not be applied owing to the insolubility of the polymer electrolyte. Therefore, the aim of producing materials with good electrical and mechanical properties could not be satisfied with PPy–PSS composites.

On the other hand, electropolymerization of PPy–SS within the PVA-C matrix resulted in the formation of thick, smooth and conducting films having very good mechanical strength. The brittleness of the PPy–SS films was completely removed after the synthesis of the s-IPNs. This presents an electrochemically prepared s-IPN system similar to those reported by Yin *et al.* and others.[19–25] On immersing in water, on drying, on leaving in open air, the s-IPN films did not lose their mechanical strength and therefore the first and foremost objective of the present study was fulfilled. Other important achievements of the work will be clarified later on.

2. Morphology: scanning electron micrograph

The surface morphology of PPy–SS, PPy–PSS and the IPNs are shown in Fig. 1(A–D). The PPy–SS film (A) shows a globular cauliflower-like morphology on the solution side of the film while the electrode side did not show any regular pattern. The PPy film is deposited on the ITO coated glass surface which itself is amorphous; the PPy layer in the vicinity of the ITO attains a morphology similar to the ITO layer and does not thereby show any particular pattern. This observation agrees well with the surface morphology of electrochemically grown PPy and PTh films doped with SS and toluene-*p*-sulfonate (PTS) studied earlier.[39,45] On changing the dopant to its polymeric form (PSS) the cauliflower like morphology of the solution side is changed to a granular morphology (B). This observation very clearly revealed the effect of the nature of the dopant on the morphology of the polymer. For the s-IPN, the solution side (C) reveals cauliflower-like morphology almost similar to that observed for the pure polymer and again the electrode side shows no such pattern. In the s-IPN, the PPy–SS is electrochemically grown within the PVA-C network; according to the previous investigators,[46,47] the first layer of the polymer is deposited on the electrode lifting the insulating coating slightly, followed by the growth of the PPy within the insulating matrix. Therefore, the electrode side of the IPN resembles that of the pure polymer and shows no particular pattern by analogy. As the polymerization proceeds, more and more polymer is grown uniformly throughout the entire matrix and PPy crests grow out of the PVA-C matrix so that the solution side also assumes a morphology similar to PPy–SS. A similar observation was reported previously during electropolymerization of PPy within an insoluble film.[28,45] Therefore SEM images give first hand information about a molecular level combination of the components and rules out the possibility of simple bilayer formation.

3. Electrical conductivity at different temperatures

The composites and IPNs studied in this work were prepared under different experimental conditions. Sample specification and electrical conductivity values of composites, IPNs and pure PPy–SS are listed in Table 1. PPy–SS films are highly conducting and the conductivity somewhat increases on increasing the electrolyte concentration (dopant level) from 0.02 M to 0.1 M. PPy–PSS films grown from mixed solvent are also appreciably conducting; but the same grown from aqueous medium were too brittle to measure its conductivity. In s-IPN films, the electrode sides are highly conducting but the solution sides are almost insulating. This observation is in accordance with that found previously for the PAn–PVA electrochemical composite.[34] As already mentioned, electropolymerization starts on the electrode surface, lifting the PVA-C coating up to a distance of a few nm; therefore the density of PPy is much higher on the electrode side of the IPN giving the electrode side of the film high conductivity. However, with the PVA-C film being sufficiently thick PPy deposition cannot take place on the solution side. In other words, pyrrole monomers always penetrate through the PVA-C film, leaving the upper surface almost intact. After substantial polymerization the matrix fills up and PPy crests even grow out of the supporting matrix; but on the surface the PPy chains are decoupled from each other by insulating interlinks of the PVA-C network resulting in high resistivity of the film. After carrying out the electropolymerization even over a period of 3 h no substantial conductivity of

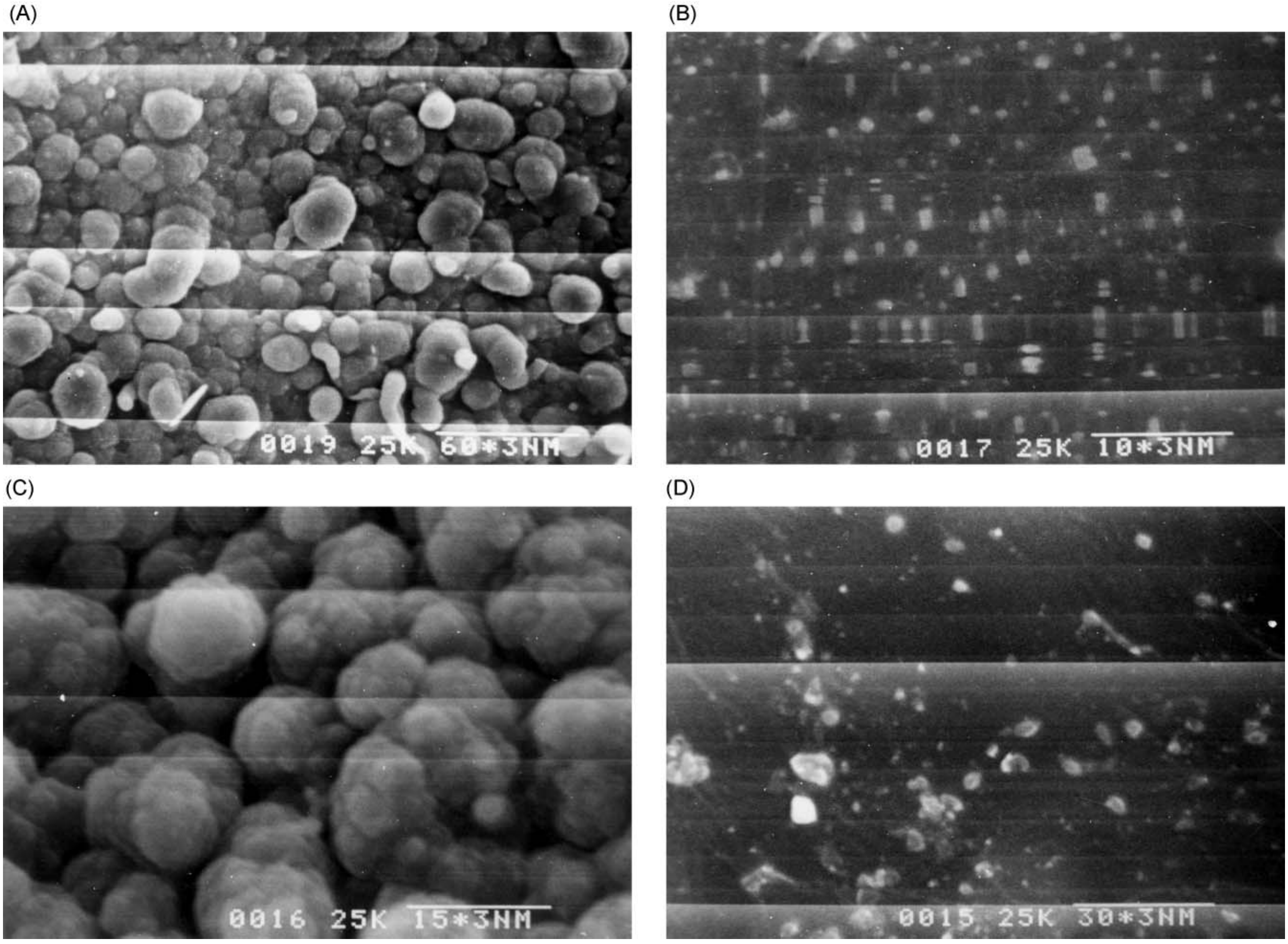


Fig. 1 SEM images of A) PPy–SS-1 (X1000), B) PPy–PSS-5 (X1000), C) s-IPN-5 (X2000) and D) s-IPN-5 (electrode side X1000).

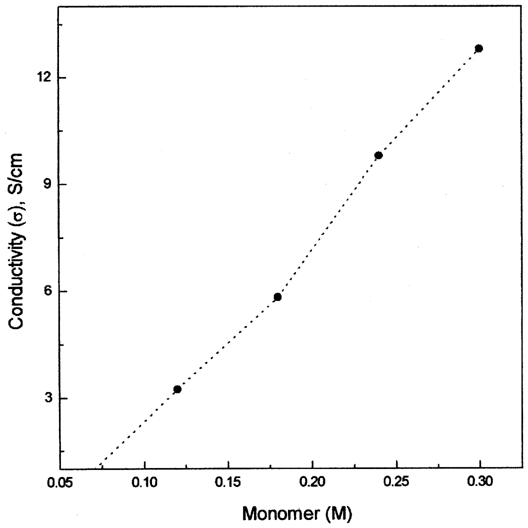


Fig. 2 Variation of the electrical conductivity (σ) of s-IPN samples with concentration of monomer.

the solution side of the film was observed, while some surface roughness was visible.

Increasing the electrolyte concentration from 0.02 to 0.06 M (IPN-A and -B) at a fixed concentration of monomer (0.3 M), room temperature d.c. electrical conductivity of the s-IPNs significantly increases which can be attributed to increasing dopant levels as was also observed earlier. However, by changing the electrolyte concentration to 0.1 M, a jump in the conductivity ($\sim 10^3$ times) was observed (IPN-C), which was in good agreement with earlier results,[39] although in that case the jump was observed at a higher electrolyte concentration (0.3 M). On the other hand, a gradual increase in the monomer concentration at a fixed concentration of electrolyte (0.1 M) resulted in a gradual increase in the conductivity of the samples (Fig. 2) and no jump was observed. This result can be explained as a direct consequence of increasing the conducting fraction in the samples. However, when lower current densities are used in synthesis, films with higher conductivity can be obtained at lower monomer concentration. In the present study only one sample was prepared using a very low pyrrole concentration and lower current density (for a longer time period) which supports this hypothesis. Similar observations have been explained earlier by the previous authors as a consequence of the formation of more ordered samples.[39,48] However a detailed study of these findings is awaited.

Variation of the electrical conductivity of PPy–SS, PPy–PSS and IPN samples as a function of temperature is shown in Fig. 3 and 4. For PPy–SS (Fig. 3) by increasing the temperature, the electrical conductivity rises up to ~100 °C and then falls; the conductivity of the cooling cycle is lower than that of the heating cycle. Similar behavior is also shown by PPy–PSS (Fig. 3), but the lowering of the conductivity was much less pronounced in the cooling cycle. Therefore, the absolute value of conductivity is higher in PPy–SS but the thermal stability of conductivity is better in PPy–PSS as revealed by such large temperature effects. Results of similar heating–cooling cycles applied to a series of s-IPN samples having different PPy fractions and conductivities are shown in Fig. 4A. In these samples the conductivity increases almost up to 120 °C and at the same time the degree of lowering of the conductivity at higher temperature is also less in the cooling cycle. Excellent electrical conductivity and thermal stability was shown by IPN-5 which followed almost a closed cycle without any observable loss of conductivity after heating to 120 °C. The s-IPN sample prepared with minimum monomer feed and the lowest current density (C-6) shows a different thermal profile. It shows a very sharp temperature dependence on conductivity; at 80 °C the value is double that of the room temperature value. In addition, the conductivity of this sample remains almost unchanged within the temperature range 80–120 °C. All these samples revealed overall similar thermal behavior of conductivity and the small differences may be accounted for by the difference in chain length and/or molecular weight of PPy. Therefore these s-IPNs present a series of free standing films in which the electrical conductivity of PPy–SS is almost retained and the thermal stability of the conductivity is significantly improved.

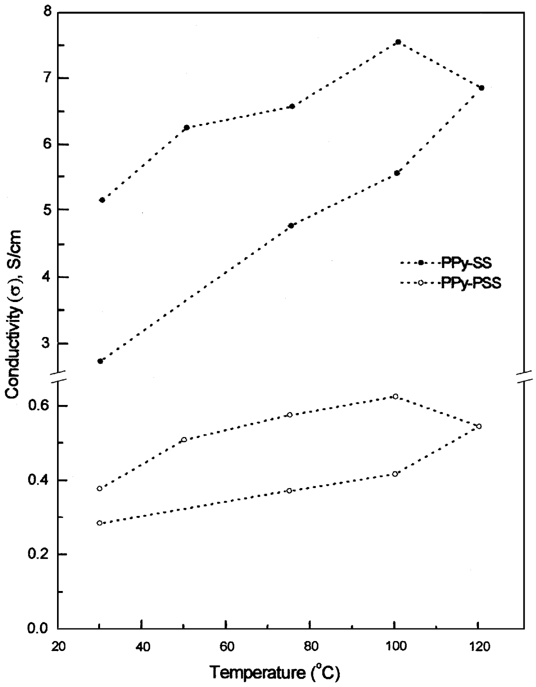


Fig. 3 Effect of the applied heating–cooling cycle on the electrical conductivity (σ) of PPy–SS-1 and PPy–PSS-5.

However, instead of applying the cooling cycle if the sample is subjected to heating at higher temperatures conductivity falls monotonically above 100 °C for PPy–SS and above 120 °C for s-IPN, as shown in Fig. 4B. The presence of conductivity maxima at higher temperatures was earlier reported by different groups of investigators[49,50] and has been interpreted as an effect of α-relaxation.[50] The rate of lowering is gradually diminished which was also observed earlier.[50] On increasing the temperature electron mobility within the materials increases resulting in increased conductivity of the system; at the same time owing to α-relaxation distortion of 'conformons' takes place that disturbs the planarity of the polymer chain hampering delocalization of the π electrons thereby resulting in lowering of the conductivity of the system. During the relaxation period these two contradictory factors compete and the conductivity increases up to a point. If the temperature is further increased the effect of α-relaxation becomes more and more pronounced and the overall conductivity value drops, showing maxima. In fact the appearance of conductivity maxima is considered to be a characteristic of the electronic structure of π-electron systems. If the heating cycle is stopped at 100 °C followed by cooling, an almost closed cycle is obtained indicating that up to a limiting temperature (~100 °C) ring distortion and α-relaxation phenomena only have a temporary effect on the electronic conductivity of the system. Running three consecutive heating–cooling cycles on the same s-IPN sample, it was observed that the conductivity dropped to some extent after each cycle. Similar behavior was observed for PPy–SS samples also although the degree of lowering of the conductivity is larger, as shown in Fig. 4C.

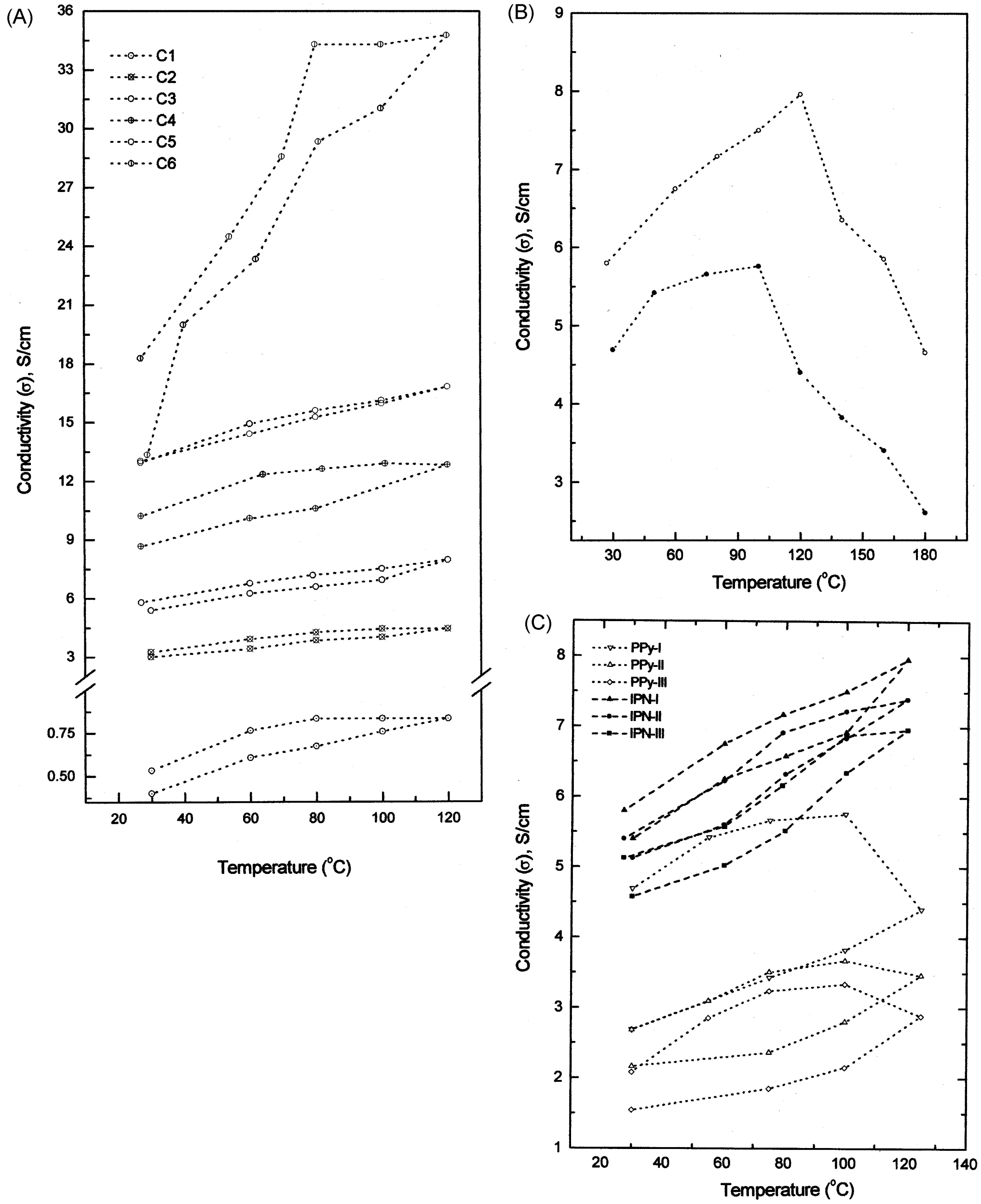


Fig. 4 A) Variation of the electrical conductivity of s-IPN samples (1–6) along the heating–cooling cycle. B) Effect of continuous heating on the electrical conductivity of IPN-3 (open circles) and PPy–SS-1 (solid circles) films. C) Effect of three consecutive heating–cooling cycles on the electrical conductivity of IPN-3 (solid points) and PPy–SS-1 (open points): I, II, III indicate number of cycles.

4. Thermal properties (DSC and TGA)

DSC thermograms of PVA-C, PPy–SS, PPy–PSS and one IPN sample are shown in Fig. 5(A–D). The glass transition (T_g) of PVA generally appears at around 70–80 °C which overlaps with the moisture release endotherm showing a broad peak centered at 90–100 °C. The melting endotherm (T_m) of PVA is at around 200 °C followed by dehydration and crosslinking of the polymer above 300 °C producing polyene structures and volatile products.[36,37,51,52] Ultimately PVA decomposes into carbon and hydrocarbons on heating above 450 °C. On formalization and crosslinking, the thermal profile of PVA is significantly changed (curve A) and its melting endotherm at around 200 °C disappears indicating that PVA-C does not melt at around that temperature. The dehydration (with simultaneous crosslinking) endotherm at around 325 °C is also diminished; because of the blocking of the free -OH groups after crosslinking (inter- and intra-molecular) dehydration cannot occur on a large scale. A small endotherm at around 380–400 °C is observed which may be attributed to melting

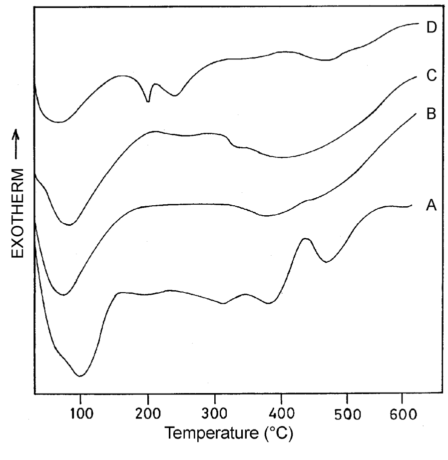


Fig. 5 DSC thermograms of A) PVA-C, B) PPy–SS-1, C) PPy–PSS-5 and D) s-IPN-3.

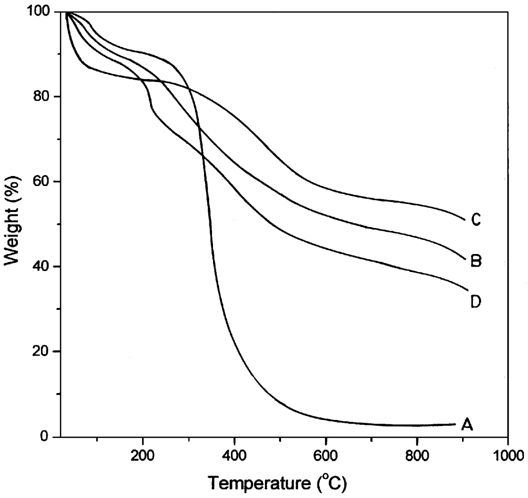


Fig. 6 TGA thermograms of A) PVA-C, B) PPy–SS-1, C) PPy–PSS-5 and D) s-IPN-3.

and/or dehydration of the linear portion of the polymer at this elevated temperature followed by degradation of the polymer above 400 °C. After removal of water at around 100 °C, the endotherm of PPy (curve B) does not show any remarkable thermal profile except for the degradation endotherm at around 350 °C. The thermal profile of PPy is found to remain almost unchanged when PSS is used as a dopant (curve C); the degradation endotherm, however, is found to be expanded over a wide range (300 °C to 600 °C). In the IPN (curve D) the characteristic thermal features of the components (PVA-C and PPy–SS) are not very obvious; two closely spaced endotherms at 200 °C and ~250 °C resemble linear PVA. These peaks may be assigned to the melting and dehydration of the linear part of PVA because PVA-C does not have melting or any other similar transition in this temperature range. Otherwise, immersion of the insulating polymer matrix in water prior to or during polymerization may have caused some physical changes in the matrix resulting in these peaks. The thermal stability of PPy remarkably improved after s-IPN formation; the degradation isotherm of PPy was found to be shifted to higher temperatures and overlapped with that of PVA-C at ~450 °C.

TGA curves of PVA-C, PPy–SS, PPy–PSS and the s-IPN are shown in Fig. 6(A–D). The thermograms of PVA-C (A) is quite simple, showing only two mass loss regions at around 100 °C and 400 °C, owing to moisture release and thermal degradation respectively. PPy–SS (B) shows three mass loss peaks due to moisture release (~100 °C), thermal dedoping (~200 °C) and degradation (350–400 °C). In PSS doped PPy (C) the thermal stability is somewhat improved and 54% residue is left which is significantly higher than 46% for PPy–SS. In the s-IPN (D) characteristic thermal profiles of both the components are present at almost the expected positions; however, the degradation endotherm of PPy was shifted to 400 °C.

5. Application potential and scope for future investigation

The semi-IPN films presented here can successfully combine the electrical conductivity of PPy with the flexibility and mechanical strength of PVA-C. SS-doped PPy films have previously been found to possess high electrical conductivity but poor mechanical strength and environmental stability. After 35 days exposure to ambient conditions its conductivity was lowered by 12%. In the present system the environmental stability of PPy–SS was remarkably improved and after 2 months exposure to ambient conditions, no observable lowering of conductivity was noticed. PPy possesses significant gas sensing capability and there are a lot of publications describing PPy as good ammonia sensing material. The present s-IPNs can retain these important properties of PPy and preliminary results of the ammonia sensing capacity of these films have been published elsewhere[53] and a detailed study in this respect is now in progress. These s-IPNs have shown some response to methanol and ethanol vapours but no response to acetone, methane and liquid petroleum gas. Therefore a detailed study of the concentration dependence and response time of the s-IPN to these gases/vapours should establish them as good sensor materials.

Conducting polymers and their composites that have good electrical conductivity possess an electromagnetic interference (EMI) shielding property which is very important for potential applications of such materials. Previously we observed significant EMI shielding of polyaniline–PVA composites; owing to their comparatively poor electrical conductivity composite sheets/slabs with appreciable thickness (~2.0 mm) were required to show appreciable EMI shielding. Present s-IPN samples possess high conductivity and good mechanical strength such that they are promising EMI shielding materials. Exploring this particular aspect of these samples is worth pursuing.

Conclusions

In this work a series of electrochemically synthesized PPy-PVA-C semi IPN films were prepared which possess high electrical conductivity and good processability and environmental stability. The effect of different synthetic parameters on the electrical conductivity of the samples was studied which revealed that electrolyte concentration has a more pronounced effect compared to monomer concentration. Elaborate studies have shown that the electrical conductivity of polypyrrole remains almost unchanged on IPN formation while other physical properties like thermal and environmental stability, mechanical strength *etc.* were much improved. The crosslinked PVA matrix may have a protective role against thermal and environmental degradation of PPy–SS. In short, these s-IPNs represent conducting polymer based film systems suitable for application in different sophisticated devices.

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