Intrinsically flexible electronic materials for smart device applications

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Intrinsically flexible electronic materials for smart device applications

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A novel method to fabricate chemically linked conducting polymer-biopolymer composites that are intrinsically flexible and conducting for functional electrode applications is presented. Polypyrrole was synthesized *in situ* during the cellulose regeneration process using 1-butyl-3-methylimidazolium chloride ionic liquid as a solvent medium. The obtained polypyrrole-cellulose composite was chemically blended and showed flexible polymer properties while retaining the electronic properties of a conducting polymer. Addition of an ionic liquid such as trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide, enhanced the flexibility of the composite. A functional application of these materials in electrochemically controlled release of a model drug has been demonstrated. This strategy opens up a new design for a wide spectrum of materials for smart electronic device applications wherein the functionality of doping and de-doping of conducting polymers is retained and their processability issue is addressed by exploiting an ionic liquid route.

Introduction

The need for flexible, ultrathin and biocompatible electronic materials for medical implant applications such as electrochemical targeted drug delivery and biosensing have drastically increased over the last decade. Intrinsically conducting polymers (CPs)[1] have been identified to be one of the ideal candidates as functional electrode materials for such applications.[2] CPs are organic polymers which exhibit electrical and optical properties that are usually associated with metals, whilst retaining many of the beneficial mechanical properties of organic polymers. They are often described as 'synthetic metals/smart materials' due to their inherent property to accept a counter ion for charge balance when oxidized and to expel the counter ion when reduced and are used for drug loading and release mechanism in controlled release applications.[3] Despite the fact that these materials are promising candidates for such biomedical purposes, there are a number of disadvantages to CPs; they are intractable, insoluble and not thermoformable which restricts their usage in practical applications. Alternatively CPs can be made flexible by grafting them on flexible materials like paper,[4] fabric[5] *etc*. and also by modifying carbon electrodes using CPs.[6] However grafted polymers suffer with poor adherence to the surface of their host materials and inhomogeneity leading to non-uniform surfaces. Electrochemical synthesis of CPs[7] produce free-standing films that are often thick and brittle and are limited to size restrictions to be deposited in larger sizes. Electrochemical synthesis of CPs using ionic liquids (ILs)[8] has also been explored to improve the flexibility of free standing films and recently there has been a keen interest in using these two materials *viz*. CPs and ILs for electronic device applications.

ILs are perceived as green electrolyte materials[9] and designer solvents[10] possessing superior physicochemical properties to aqueous systems and organic solvents due to their characteristic nature of negligible vapour pressure, wide electrochemical window, non-flammable nature and tunability to achieve desired properties.[11] Chemical synthesis of CPs in ILs has also been reported, but the possibility of generating smooth films was restricted due to the fine dispersion of conducting polymer particles in the ionic liquid matrix.[12] Hereby we are introducing a new class of conducting polymer-biopolymer-ionic liquid composite films generated by using ionic liquid as a solvent medium. Typically conducting polymers are grafted or coated on cellulose or fabric which leads to poor adherent films that lead to peeling off films during the bending and relaxing action or doping/de-doping process. Therefore they may not be suitable for sustainable flexible electronic device applications. However in the current one-pot synthesis method, the polymer composites were prepared *in situ* in an ionic liquid medium generating homogenous films that are chemically blended together. These materials are intrinsically flexible, uniform and have the potential to be tuned with various physicochemical properties; they can also be used in flexible electronic devices such as supercapacitors, actuators, antistatic coatings, and for biomedical applications when designed accordingly by carefully choosing the appropriate components.

The cellulose regeneration process[13] using ionic liquids was exploited to prepare a conducting polymer-biopolymer-ionic liquid composite material using ionic liquids as solvent medium. Fibrous cellulose was chosen as the biopolymer and polypyrrole as the conducting polymer. Cellulose, when regenerated using ILs loses its crystalline nature and transforms into an amorphous material.[14] Extensive literature is available in which the casting of cellulose films after regeneration using various ILs and their properties have been discussed.[15] So far this process has been limited for the processing of natural polymers like cellulose, starch, chitosan, chitin[16] *etc.* and there are no reports to our knowledge for utilizing this method for preparing and processing intrinsically conducting polymer composites.

EXPERIMENTAL

In the present work pyrrole was polymerized *in situ* in the solution of 10 wt% cellulose in 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) ionic liquid at room temperature using ammonium persulfate as an oxidant and benzene sulfonic acid (BSA) as the dopant. The solution turned dark green in two minutes of stirring and transformed to black. Stirring was continued overnight at room temperature to ensure completion of polymerization under nitrogen atmosphere in the Schlenk line. Any water impurities during the reaction had a major influence in the casting of films in later stages. The solution was cast into films of ~300 μm thickness using a coating machine, and washed with water as an antisolvent to remove [C$_4$mim]Cl ionic liquid. Shiny black flexible films were obtained, washed with water several times to remove any residual ammonium persulfate, dried in air followed by drying in a vacuum desiccator at 60 °C overnight and used for various characterization studies. This general experimental strategy as described above is simple but the composite material was prepared altering various parameters/components to optimize and obtain polymer films with desired properties like temperature stability, flexibility, uniformity and electroactivity. The ratio of pyrrole to cellulose (equal wt% in [C$_4$mim]Cl), the addition of an ionic liquid with long alkyl chain such as trihexyl(tetradecyl)phosphonium bis (trifluoromethylsulfonyl)imide ([P$_{66614}$][NTf$_2$], 10 wt%)[17] to act as an IL plasticizer, reaction temperature (90°C), influence of various ionic liquids as solvent medium for cellulose regeneration, effects of various anti-solvents to remove ionic liquids, and the usage various dopants for polypyrrole were all investigated. Table **1** shows the selection of polymer composite materials that were chosen to be presented after optimization of various parameters as stated above. The synthesis procedure for these materials is reported in the supporting information (SI).

Table 1 List of polymers and composites presented in the article and their chemical constituents

Item Number	Sample constituents	Sample Name
1.	Cellulose film	Film 1
2.	Cellulose + polypyrrole undoped film	Film 2
3.	Cellulose + [P$_{66614}$][NTf$_2$] IL plasticizer film	Film 3
4.	Cellulose + polypyrrole + [P$_{66614}$][NTf$_2$] IL plasticizer + benzenesulfonic acid doped film	Film 4
5.	Polypyrrole powder	PPy powder
6.	Fibrous cellulose powder	Cell powder

RESULTS AND DISCUSSION

The composite films were analyzed for their thermal, electrical, mechanical and chemical nature using various solid state characterization techniques. Thermal stabilities of polymer composites were investigated using thermal gravimetric analysis (TGA) and presented in Figures S1 and S2 of SI.
Decomposition temperatures of films 1-4 were between 230 °C and 280 °C whereas the crystalline cellulose had a decomposition temperature of 300 °C comparable to literature (Swatloski et al. 2002). Decrease in the thermal stability of cellulose-polypyrrole composites may be due to the loss of intramolecular hydrogen bonding within cellulose moiety and substituted by interaction with polypyrrole units *via* intermolecular hydrogen bonding.[18] Addition of [P$_{66614}$][NTf$_2$] IL as plasticizer (Films 3 and 4), enabled to enhance the thermal stability of these composite films up to 250 °C whereas in the case of film 1 a slow mass loss was observed until the same temperature which may be accounted to the loss of intermolecular bonded water molecules. However the hydrophobic nature of the IL plasticizer allowed the Films 3 and 4 to be more stable under ~200 °C. In the case of polypyrrole containing films (2 & 4), the degradation of the material after 250 °C was gradual suggesting the decomposition of the polypyrrole[19] backbone up to 500 °C. The thermal stability of these conducting polymer and biopolymer composite materials up to 200 °C covers most of the real world electronic device operational temperatures. Conductivity measured using the four probe conductivity meter was ranging between 1450 μScm^{-1} (doped Film 4) to 40 μScm^{-1} (undoped Film 2). The conductivity of free-standing polypyrrole film normally generated by electrochemical deposition[7] ranges between 1-100 mScm^{-1}. Despite their high conductivity, they are reported to be brittle or not adherent to the working electrode which limits their use as free standing polymer films for electrode applications. In other cases where polypyrrole is impregnated onto flexible materials like paper, they fail the 'Adhesion by Tape Test' (ASTM D3359) which leads to film peeling and indicating non-homogenous materials. In our method, as polypyrrole and cellulose are blended to each other during the preparation process resulted in chemically homogenous films. When tested using 'Adhesion by Tape Test' the composite films don't stick to the tape (Figures S3, SI)

which indicated that polypyrrole was naturally bound to the cellulose matrix and therefore the surface was homogenous.

Figure 1(a-d) shows photographs of polypyrrole powder and film 4 along with their respective scanning electron micrograph (SEM) images. Table 2 provides the elemental compositions of polypyrrole powder and Film 4 analysed by Energy Dispersive X-ray (EDX) spectroscopy. The photographs and SEM/EDX spectra of films 1-3 are provided in Figure S4, S5 and S6 respectively in the SI. Film 1 sputtered with gold had a smooth morphology with no electronically conducting regions; moreover longer exposure (>30 s) caused the film to break under the electron beam which is expected when paper is heated by beam current, moreover as the films were also thin (300 μm) to be stable under ultra-high vacuum in the SEM machine. Film 2 sputtered with gold showed polypyrrole (cauliflower) structures embedded within the smooth cellulose matrix leading to stable homogenous looking films under SEM conditions. Addition of $[P_{66614}][NTf_2]$ IL plasticizer, porosity or roughness of the films (3 & 4) increased and no film breaking was observed. Film 4 showed clear features of both polypyrrole and cellulose; however this film was also stable under high vacuum SEM chamber conditions and enabled to capture images without gold sputtering. This may be attributed to Film 4 being conducting as polypyrrole was present in doped form. Addition of plasticizer also resulted in layered structure as shown in Figure S7 in SI. PPy powder was synthesised as presented in literature[20] showing cauliflower structure[21] but the individual particles were in nano sizes.

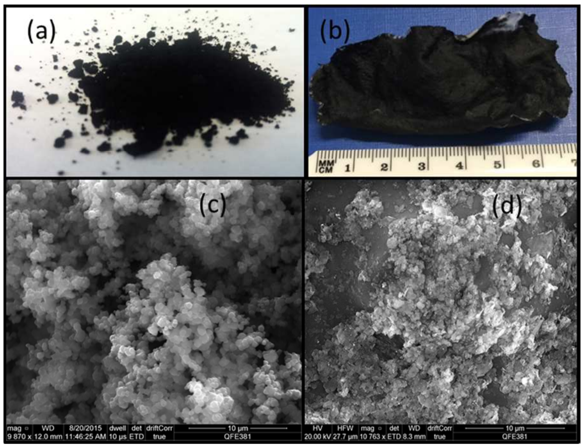

Figure 1 (a) Photograph of PPy powder, (b) photograph of doped polypyrrole-cellulose-$[P_{66614}][NTf_2]$ IL plasticizer Film 4, (c) SEM image of PPy powder, (d) SEM image of film 4.

Table 2 Elemental composition of PPy powder and Film 4 from EDX analysis

Sample name	C %	O %	F %	S %	P %	N %	Cl %
PPy Powder	52.0	22.3	-	6.5	-	17.6	-
Film 4	64.8	19.5	3.0	5.0	3.9	3.4	-

EDX analysis results of various materials listed in Table 1 is presented in Figure S4 – S8 in the SI. Elemental analysis confirmed the presence of elements that constituted the respective composite films, however it was not possible to calculate the exact ratio between polypyrrole and cellulose as the molecular weight of the polymerized pyrrole was difficult to determine. For example Film 1 (Figure S4, SI) being a neat cellulose film showed presence of carbon and oxygen whereas Film 4 (Figure S7) showed the presence of phosphorous from the IL plasticizer, sulfur from IL plasticizer and dopant, fluorine from IL plasticizer, and nitrogen from polypyrrole. Absence of chlorine in Films 1-4 indicate that any residual $[C_4mim]Cl$ remaining in the composite films were below the detection limit of EDX analysis *i.e.* 1 wt%.

Infra-red spectra of cellulose powder, cellulose film and polypyrrole[4] and powder[18] all showed characteristic bands as marked in Figure S10 in the SI. Films 2 and 4 showed C=C stretching from the pyrrole ring at 1590 cm^{-1} and 1577 cm^{-1} respectively whereas polypyrrole powder showed C=C stretching at 1564 cm^{-1}. This blue shift in the cellulose-polypyrrole composites may be accounted to the interaction (hydrogen bonding) between N-H of the pyrrole ring and O-H of cellulose moiety. Characteristic bands for individual components such as cellulose, polypyrrole, benzenesulfonic acid dopant and $[P_{66614}][NTf_2]$ IL plasticizer were all well-defined and present in Film 4.

Conducting polymers such as polypyrrole have poor mechanical integrity and generally are formed as powders or dispersions. This inherent brittle nature of the polymer limits its usage in practical implementation in devices. The mechanical properties of polypyrrole may be improved by templating on cellulose, but are poorly adherent to the cellulose matrix leading to attrition. In our work, as cellulose and polypyrrole are chemically blended homogenously *via*. hydrogen bonding, and therefore they are more stable to attrition. The ultimate tensile strength and Young's modulus of Film 4 increased when compared to Film 2. However Film 3 had better mechanical properties (results in Table S1 and Figure S9 in SI). Basically addition of plasticizer improved the ductility of the regenerated cellulose film (Film 3) and this may be accounted to formation of intermolecular hydrogen bonding between $[P_{66614}][NTf_2]$ IL and cellulose. However addition of polypyrrole further reduced the elongation effect due to additional intermolecular hydrogen bonding thereby reducing intramolecular hydrogen bonding within cellulose matrix or by interacting with the plasticizer. Nevertheless the ultimate tensile strength (8 MPa) and Young's modulus (57 MPa) of film 4 were comparable to regenerated cellulose from ionic liquids.[22] The tunability of the system with various components such as the biopolymer, conducting polymer and ionic liquid will render to optimize conductivity and flexibility by varying the ratio of ionic liquid, monomer, dopant and other polymerization conditions.

Figure 2(a) shows the cyclic voltammogram of Film 4 demonstrating its electroactivity, however cyclic voltammogram (Figure S11, SI) of Film 1 showed resistor behaviour. The film of surface area ~1 cm^2 was directly used as the working electrode. The scan was carried out in the anodic direction first and then reversed to the cathodic direction. A well-defined cathodic peak around -0.7 V *vs*. Pt wire and an anodic shoulder around 0.2 V demonstrating the reduction and oxidation of the polypyrrole backbone comparable to the polymer deposited on Pt electrodes was observed.[23] Presence of benzenesulfonic acid as the dopant rendered the opportunity to test the film for electrochemically controlled release of anionic components into the electrolyte using an electrochemical trigger. Conducting polymers are demonstrated to be good candidates for electrochemical controlled release of drugs.[24] Chronoamperometric studies at a positive potential of 0.5 V *vs*. Pt wire was carried out at an interval of two minutes for 60 minutes and the electrolyte was probed using UV-visible spectroscopy for the increase in the concentration of BSA (Figure 2(b)). On the UV spectra typical benzene peaks were observed ranging between 255 to 275 nm and the increase in these peak heights were accounted to the increase in the amount of benzene sulfonate (BS) anions released by potentiostatic control. Initially any physically adsorbed BS on the polymer composite was released into the aqueous electrolyte. When triggered with 0.5 V for 2 min, the benzene peak height increased considerably demonstrating the controlled release of the model drug under the application of electrochemical potential. After 1 hour the UV peak heights were saturated indicating the release of most of the anionic components from the composite Film 4 into the electrolyte.

These electrochemical studies demonstrated not only the electroactivity of these conducting polymer-biopolymer composite materials but also demonstrated the functionality of these electrode materials capable of doping and de-doping components from the composite matrix on the application of an electrochemical trigger. Various materials *viz*. cellulose, polypyrrole,[24] $[P_{66614}][NTf_2]$ IL and benzenesulfonic acid[25] comprising Film 4 were chosen to be biocompatible from literature to demonstrate an application of these composite materials in drug delivery[26] device applications such as in catheters. Experimental work on detailed inspection of these materials in terms of biocompatibility studies is in progress. Moreover exploitation of these materials in energy storage device application is also under progress in our laboratory.

CONCLUSION

In summary, a novel strategy for producing a new class of electronically active materials comprising of biopolymer-conducting polymer composites that are chemically blended for application in controlled drug release is reported. One-pot synthesis of these composite materials not only renders the opportunity to prepare conductive materials that are intrinsically flexible but also to recycle biomass and make useful electronic materials. The tunable nature of these materials by variable components makes them suitable for applications in smart electrochemical devices such as supercapacitors, actuators and not limited to biomedical applications. Cellulose-polypyrrole composite was prepared, characterized and electroactivity was demonstrated by controlled release of a model drug triggered upon by an electrochemical potential.

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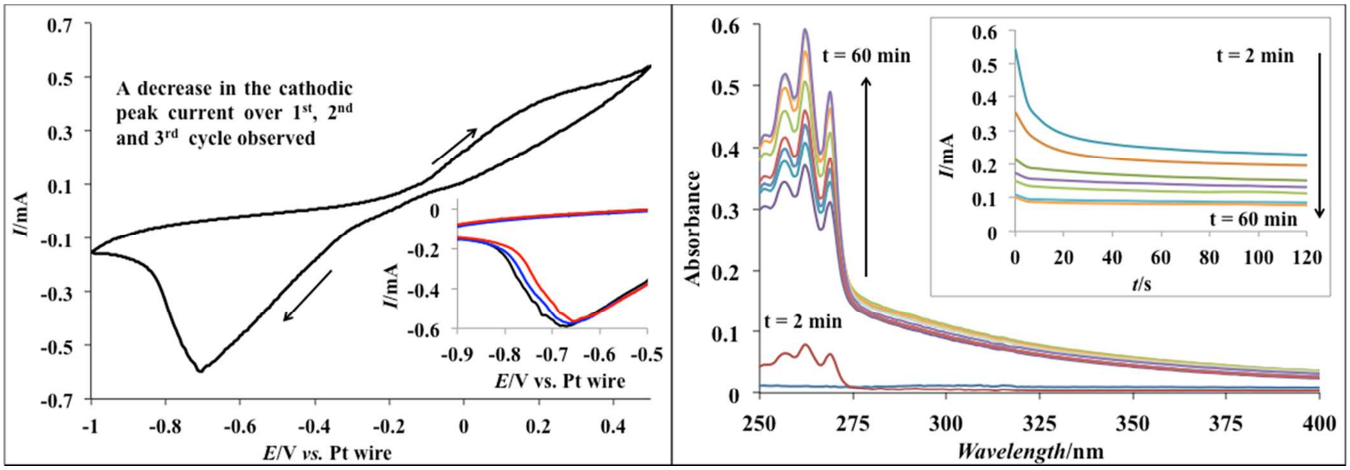

Figure 2 (a) Cyclic voltammogram of Film 4 in 0.1 M of KCl solution in water, arrows indicate scan direction; the inset shows the reduction in the cathodic peak current from cycle 1 to 3 with the release of anions, (b) UV-visible spectra of 0.1 M of KCl electrolyte after various chronoamperometric studies using film 4 over a period of 1 h; inset shows chronoamperometry curves of Film 4 at 0.5 V *vs*. Pt wire over a period of 1 h, arrow shows the increase in time.

Notes and references

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Electronic Supplementary Information (ESI) available: [TGA thermograms of various films 1-4 and cellulose/polypyrrole powder, adhesion tape test photographs of polypyrrole grafted on filter paper and film 4, SEM/EDX/photographs of films 1 -3, IR spectra of various materials presented in Table 1 in the manuscript, mechanical properties of film 2-4]. See DOI: 10.1039/b000000x/

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