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Zein-Polyaniline Blends—a Route to Electrically Conductive Biopolymer

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Preparation of zein-methanesulfonic acid doped polyaniline (PANI) conductive blends using different approaches is described. Zein-PANI films from homogeneous solutions of the components in 1-methyl-2-pyrrolidinone were made by casting method. In another approach, in situ polymerisation of aniline in the presence of zein or corn gluten meal (CGM) was performed. It was carried out in heterogeneous conditions onto the suspension of zein or CGM and also homogeneously with zein and aniline dissolved in aqueous alcohol. The electrical conductivity of the zein-PANI products was measured. They were also characterised by Fourier Transform Infra Red Spectroscopy, Dynamic Mechanical Thermal Analysis*, Gel Permeation Chromatography, X-ray Photoelectron Spectroscopy, Elemental analysis and Scanning Electron Microscopy.*

Keywords Biopolymer; electrical conductivity; in situ polymerisation; polyaniline; zein

Introduction

Polyaniline (PANI) is a frequently used conducting polymer in combination with different inorganic fillers [1,2] or as a polymer blend [3]. There are only a few publications dealing with PANI blended with biopolymers, such as cellulose [4–6], starch [7,8], chitosan [9] and acacia gum [10]. PANI based materials offers a number of applications, such as in electronic devices, rechargeable batteries, sensors, switchable membranes, anticorrosive coatings, etc. Moreover, combining PANI with a biopolymer can improve PANI properties, like poor mechanical strength of the films formed from pure PANI [9]. Zein (the prolamin fraction of corn, *Zea mais*) is one of the promising biopolymers that can be used in a combination with PANI. It is a mixture of different polypeptides soluble in aqueous alcohols, where about 80% is α-zein. The second major fraction is β-zein. Some minor fractions were also referred, such as γ-zein, zein-2, C-zein, D-zein etc. Zein molecules consist of about 20 amino acids, including nonpolar amino acids (leucine, proline, alanine), $-$OH containing amino acids (serine, threonine and tyrosine), $-$S containing amino acids (methionine and cysteine), basic amino acids (lysine, arginine and histidine) and acidic amino acids, $-$COOH containing (glutamic and aspartic acids). The last two amino acids in commercially available zein exist in the form of their amides (glutamine and asparagine), which represent about 30% of the amino acid composition in zein molecule being the most promising sites for interactions

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between zein and PANI molecules. Zein fractions (α-, β- and other) have different amount of individual amino acids and therefore slightly different solubility. Zein by itself is a widely applied substance with a number of useful properties, such as hydrophobicity, processibility, capability to be mixed with anti-microbial, antioxidative substances and even with some drugs to be delivered in humans. The main application of zein is the preparation of zein-base coating for cosmetics, electronic devices, paper, edible coatings for food products, etc. It is also applied to make zein-based textile fibers, anticariogenic chewing gum, surgical closure of body organs and blood vessels, wound dressing [11]. When it is processed with plant- and animal-derived plasticisers, due to the brittleness of pure zein, it produces rigid and flexible sheets showing high ductility and tensile strength compared to other biopolymers. They are applied to manufacture packaging and other materials where biodegradability is required [12].

In the present work, zein-methanesulfonic acid doped PANI blends were investigated with the aim of adding functionality to zein, thus utilising the natural biopolymer to provide an abundant, readily processable, biodegradable 'carrier' for the relatively non-processable conducting polymer, and on the other hand to achieve electrical conductivity of a non-conductive natural biopolymer. A commercially available and cheap product, corn gluten meal (CGM), which typically contains about 60% of zein and is a raw material source for zein, was also attempted for the same procedure.

Experimental

Materials

Zein (Lot No. 8479H) was supplied by MP Biomedicals, Inc. CGM ("Avongold") was supplied by Penford (New Zealand). Aniline, ammonium persulfate (APS), methanol, 1-methyl-2-pyrrolidinone (NMP), methanesulfonic acid (MSA) and triethylamine (TEA) were all analytical grade reagents and were used as supplied by Sigma-Aldrich.

Measurements

Fourier Transform Infra Red (*FTIR*) spectra were taken in the solid state of analysed samples using a Thermo Electron NICOLET 8700 FT-IR spectrometer using both ATR using Germanium (Ge) crystal and KBr pellets for powder samples. The signals were processed by means of "OMNIC" software.

The *GPC* system consisted of a Waters 515 HPLC pump, a Degassex DG-4400 on-line degasser connected to a series of three GPC columns (a Waters Styrogel HR6 column and two Polymer Labs PolyPore columns) with a PolyPore guard and 0.5 μm in-line filter. The eluent was NMP and the flow rate was 0.3 mL/min. Sample concentrations were 2 mg/mL and injection volume was 200 μL. The detector used was a Waters 2410 Differential Refractometer. Both the columns and RI detector were maintained at 35°C. Data acquisition and processing were performed using the ASTRA 4 software (Wyatt Technologies Corporation). The Polymerlabs EasyCal PS-1 set of ten Polystyrene standards were dissolved in the same eluent at 2 mg/mL and used for the Calibration curve under the same conditions. The chromatographic traces were resolved using band resolution, with the peak fitting function of the Origin software using the Gaussian function.

The *XPS* data were collected on a Kratos Axis UltraDLD equipped with a hemispherical electron energy analyser. Spectra were excited using monochromatic Al Kα X-rays

(1486.69 eV) with the X-ray source operating at 150 W. Survey scans (0–1300 eV) were collected with a 160 eV pass energy, whilst core level scans were collected with a pass energy of 20 eV. The analysis chamber was at pressures in the 10^{-9} torr range throughout the data collection. Data analysis was performed using CasaXPS software.

Dynamic Mechanical Thermal Analysis (*DMTA*) was performed using a Rheometric Scientific Mark IV analyser at the oscillatory frequency 1 HZ and the rate of temperature increase 3°C min^{-1}.

Scanning Electron Microscopic (*SEM*) study was carried out using Philips XL30S FEG.

Electrical conductivity was measured by means of Jandel RM2 instrument (four-point probe measurement technique) at room temperature.

Preparation of the Blends

Approach 1: Zein-PANI blends from their homogeneous solutions in NMP. In a typical synthesis of MSA doped PANI, 1.5 g (16.1 mmol) of aniline was dissolved in 60 ml of 1 M aqueous MSA. 4.11 g (18.0 mmol) of APS was added dropwise under constant stirring, followed by additional stirring for 5 h. The reaction was carried out at 20°C–25°C. The resulting PANI precipitate was filtered, washed with 100 ml of water, vacuum dried at 40°C for 24 h. and used for the preparation of the zein-PANI films and also for the PANI (Blank) in the Approach 2 [13].

A solution of 4 g of zein in 40 ml of NMP was divided it four portions by 10 ml. Then a solution of 1 g of PANI doped with MSA in a mixture of 20 ml of NMP and 2 ml of triethylamine (TEA) was prepared. For each 10 ml of zein solution, 1 ml, 2 ml, 4 ml and 6 ml of PANI solution in NMP-TEA were added correspondently. It gives PANI contents 5%, 10%, 20% and 30%. Zein-PANI blend films were made by casting the solution mixtures in aluminium containers, and allowing the solvent to evaporate at 70°C.

Approach 2.1: In situ polymerisation of aniline onto zein or CGM in heterogeneous conditions. 0.5 g (5.4 mmol) of aniline was dissolved in 20 ml of 1 M aqueous MSA. 0.5 g of zein (CGM) was dispersed in the aniline solution with continuous magnetic stirring, and 1.37 g (6.0 mmol) of APS, dissolved in 10 ml of water, was added dropwise over a period of about 30 min at 20°C. The resulting mixture was continuously stirred for 5 h at 20°C–25°C. The product was filtered in vacuum, washed with 100 ml of water and vacuum dried for 24 h at 40°C.

Approach 2.2: In situ polymerisation of aniline in homogeneous conditions

2.2.1 0.5 g of zein was dissolved in the mixture of 20 ml of methanol and 5 ml of water while stirred magnetically. Then 1.92 g of MSA and 0.5 g (5.4 mmol) of aniline were dissolved in there. To this solution 1.37 g (6.0 mmol) of APS dissolved in the mixture of 20 ml of methanol and 5 ml of water, containing also 1.92 g of MSA, was added dropwise. Therefore, APS (oxidant) was added to aniline (monomer). The resulting mixture was continuously stirred for 15 h at 20°C–25°C, then centrifuged for 20 min (3000 rpm). The precipitate was separated by decanting the supernatant and vacuum dried for 24 h at 40°C.

2.2.2 0.5 g of zein and 1.37 g (6 mmol) of APS were dissolved in the mixture of methanol and 5 ml of water while stirred magnetically. Then 1.92 g of MSA was also dissolved in there. To this solution 0.5 g (5 mmol) of aniline dissolved in the mixture of 20 ml of methanol and 5 ml of water, containing also 1.92 g of MSA, was added dropwise. Therefore, aniline (monomer) was added to APS (oxidant). The resulting mixture was

continuously stirred for 15 h at 20°C–25°C, then centrifuged for 20 min (3000 rpm). The precipitate was separated by decanting the supernatant and vacuum dried for 24 h at 40°C.

The primary difference between the Approaches 2.2.1 and 2.2.2 is the sequence of addition of the reactants (monomer and oxidant).

Treatment of the supernatants from 2.2.1 and 2.2.2. Each supernatant was put in a beaker and then 50 ml of water were added. In few hours the mixture was separated by centrifugation. Some additional precipitate was collected and vacuum dried at 40°C for 46 h.

Results and Discussion

Approach 1: Zein-PANI blends from their homogeneous solutions in NMP. All doped forms of PANI (conductive) are practically insoluble substances. However, dissolution of the doped PANI in NMP can be achieved adding a small amount of TEA [14] or another amine, e.g. diethylamine, ethylenediamine. On the contrary, many solvents for zein were mentioned [15–17], but NMP has never been reported among them, according to our knowledge. We have been found it as a good solvent for zein as well, which allows to get upto 10% concentration at room temperature and to be used as a common solvent for both PANI and zein.

Electrical conductivity (σ) of PANI doped with MSA was measured by the four-point probe method at 20°C–25°C showed conductivity $(3 \pm 0.1) \times 10^{-1}$ S cm^{-1}. The conductivity of the films containing PANI at 5% and 10% in the zein-PANI blends was too low to detect. Zein-PANI blends containing 20% or 30% of PANI were electrically conductive having $(2.7 \pm 0.3) \times 10^{-7}$ S cm^{-1} and $(2.4 \pm 0.3) \times 10^{-6}$ S cm^{-1} respectively. The PANI present in the blend could be partially dedoped due to the acid-base reaction with TEA, making it soluble in NMP. This conversion causes low conductivity of films prepared from zein and PANI. An attempt to re-dope these films with 1 M aqueous MSA for 24 h did not provide any significant improvement of electrical conductivity.

FTIR spectroscopic studies of a representative zein-PANI (20%) blend and its individual components were shown in Fig. 1. The characteristic peaks at 1653 cm^{-1} (Amide I),

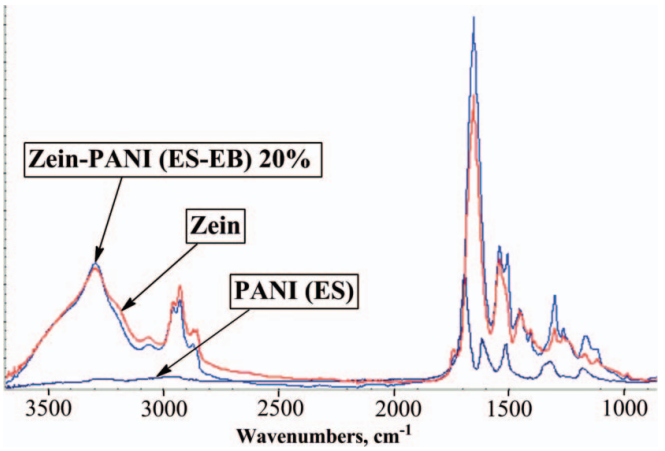

Figure 1. FTIR spectra of zein, PANI and zein-PANI film.

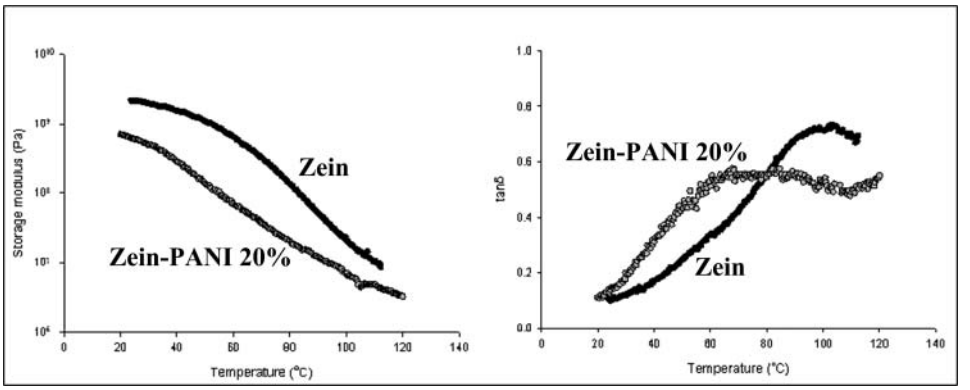

Figure 2. DMTA of zein and zein-PANI 20% film.

1540 cm^{-1} (Amide II), 2929 cm^{-1} (stretching vibrations from CH_3, CH_2 and CH groups) and a wide peak at 3296 cm^{-1} due to NH stretching vibrations were observed for zein [18]. Typical IR peak positions for PANI i.e., stretching of quinoid (N—Q—N) and benzenoid (N—B—N) double bonds were found at 1567 cm^{-1} and 1455 cm^{-1} respectively [3]. In the case of zein-PANI blend, the weak quinoid signal from PANI was masked by the strong amide I peak from zein. However, the benzenoid signal from PANI was clearly visible, but shifted to 1505 cm^{-1} that indicates partial dedoping of the PANI [3] or even be a sign of a zein-PANI interaction, e.g. hydrogen bonding as well as ionic interaction between the dopant ion and the nitrogen containing or other polar moieties in zein molecules, which corroborates the findings from electrical conductivity studies.

The same zein-PANI (20%) blend film was compared with a film made from pure zein by *DMTA* studies (Fig. 2). Incorporation of PANI in zein reduced the storage modulus values of the blend and shifted T_g towards lower temperature, suggesting plasticization effect of PANI on zein.

The *SEM* images (Fig. 3) demonstrated that PANI in granular form was well dispersed in the zein matrix that was an advantage of preparing films from homogeneous solutions. However, the individual PANI particles were separated from each other at submicron level as a result did not form continuous conducting network. Hence, the partial de-doping effect from TEA on PANI as well as the inadequate network path formation caused low conductivity in these films.

Approach 2.1: In situ polymerisation of aniline onto zein or CGM in heterogeneous conditions. In situ polymerisation of aniline onto zein or CGM was carried out by a conventional method [13] applying MSA as a dopant. Blank experiments, such as MSA and APS treatment of zein and preparation of a MSA doped PANI were also performed for comparison purpose.

Electrical conductivity measurements showed that both the zein-PANI and CGM-PANI composites were electrically conductive. They have about 1/2 of conductivity of pure PANI doped with MSA prepared at the same conditions: PANI $(3.1 \pm 0.1) \times 10^{-1}$ S cm^{-1}; zein-PANI $(1.2 \pm 0.2) \times 10^{-1}$ S cm^{-1}; CGM-PANI $(1.4 \pm 0.1) \times 10^{-1}$ S cm^{-1}. This approach showed an improved conductivity of the zein-PANI product as compared to the previous approach. The reason for such an improvement is a higher amount of the conductive emeraldine salt form of PANI present in these blends.

FTIR spectroscopy of these zein-PANI or CGM-PANI products using both ATR(Ge) and transmission method by KBr pellets revealed only the presence of PANI that could be

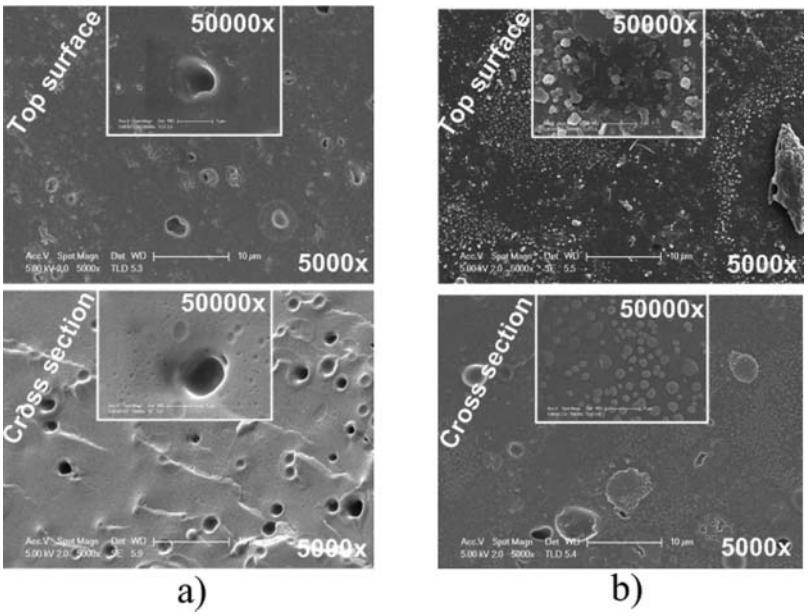

Figure 3. SEM images of: (a) zein; (b) zein-PANI 20% film.

due to the formation of PANI coating on zein surface. As a result the characteristic peaks for zein were undetectable.

The individual components of the *in situ* polymerised product in the system were detected by *GPC* (Fig. 4). The chromatographic traces were multicomponent as they were broad with shoulders due to the eluted peaks overlapping. The major deconvoluted peaks for zein appeared at elution volume 19.37 ml and 20.39 ml, and those for PANI at 17.77 ml, 19.31 ml, 21.00 ml and 24.29 ml. In case of the zein-PANI product, the peaks at 18.81 ml and 19.90 ml resemble those of zein whereas the peaks at 21.45 ml and 23.95 ml are similar to pure PANI. The 17.77 ml and 19.37 ml peaks for PANI could be overlapped by zein peaks. Relative changes in peak intensities and the shifting of all four peaks in the final product suggest possible interaction between zein and PANI.

Elemental analysis data of the blank samples and the zein-PANI or CGM-PANI products are shown in Table 1. The value of the C:N atom ratio allows to evaluate the relative amount of individual components present in the product. For example, the C:N ratio was higher for PANI (6.22:1) as compared to zein (4.21:1). In case of the zein-PANI product,

Table 1. Elemental analysis results for Approach 2.1

SAMPLE	C, %	H, %	N, %	S, %	C:N, atom ratio
PANI (Blank)	58.84	4.98	11.03	5.54	6.22:1
Zein (Blank)	51.05	7.51	14.15	<0.3	4.21:1
Zein-PANI	54.01	6.10	12.25	3.27	5.14:1
CGM (Blank)	50.00	7.57	10.79	1.25	5.40:1
CGM-PANI	54.70	6.26	10.86	2.95	5.88:1

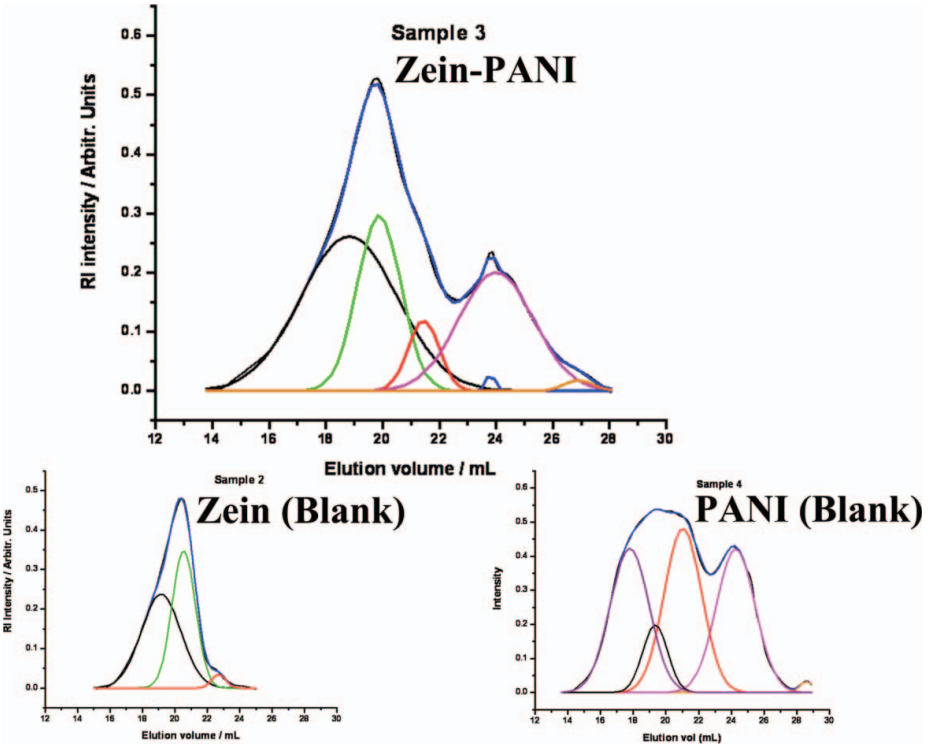

Figure 4. GPC of zein, PANI and zein-PANI product (Approach 2.1).

the C:N ratio was 5.14:1, which indicates 54% of zein and 46% of PANI in it. Similarly, CGM-PANI product contained 42% of CGM and 58% of PANI, i.e. similar to the initial mass ratio of the reactants (aniline monomer:zein or CGM:: 50:50).

Zein-PANI product and the blank zein and PANI were compared by *XPS* studies. The binding energy scale was calibrated by using the C(1s) signal from saturated hydrocarbon at 285.0 eV for zein and 284.6 eV for both PANI and zein-PANI product as an internal standard. Deconvoluted spectra of C(1s) are shown in Fig. 5. Four components were found in zein (Fig. 5A) at 284.9 eV (63.9 Atom%) for C—C (component 1), 286.0 eV (10.5 At%) for C—N (2), 286.8 eV (6.5 At%) for C—O (3) and 288.4 eV (19.1 At%) for C=O (4). Three components for PANI (Fig. 5B) appeared at 284.5 eV (52.1 At%) for C—C (1), 285.7 eV (36.0 At%) for C—N (2) and 287.0 eV (11.9 At%) for C—S from MSA (3). Also three components for zein-PANI product (Fig. 5C) were observed at 284.8 eV (64.0 At%) for C—C (1), 285.9 eV (27.2 At%) for C—N (2) and 287.8 eV (7.8 At%) for C—S (3).The absence of C=O peak and the occurrence of C—S peak in zein-PANI product suggests the presence of PANI coating on the outer surface in it. A decreased At% of the carbon connected to nitrogen (Fig. 5C, component 2) can appear due to hydrogen bonding or covalent bonding between zein and PANI, in particular NH_2 and OH groups in zein molecules. These types of interactions were reported for chitosan [19,20] and polysaccharide [10] in their combination with PANI. The N(1s) peaks were also seen in all the samples. In zein sample this element had the peak maximum at 399.8 eV (N1s of amide moiety [21]), while in the PANI and zein-PANI had it at 399.1 eV.

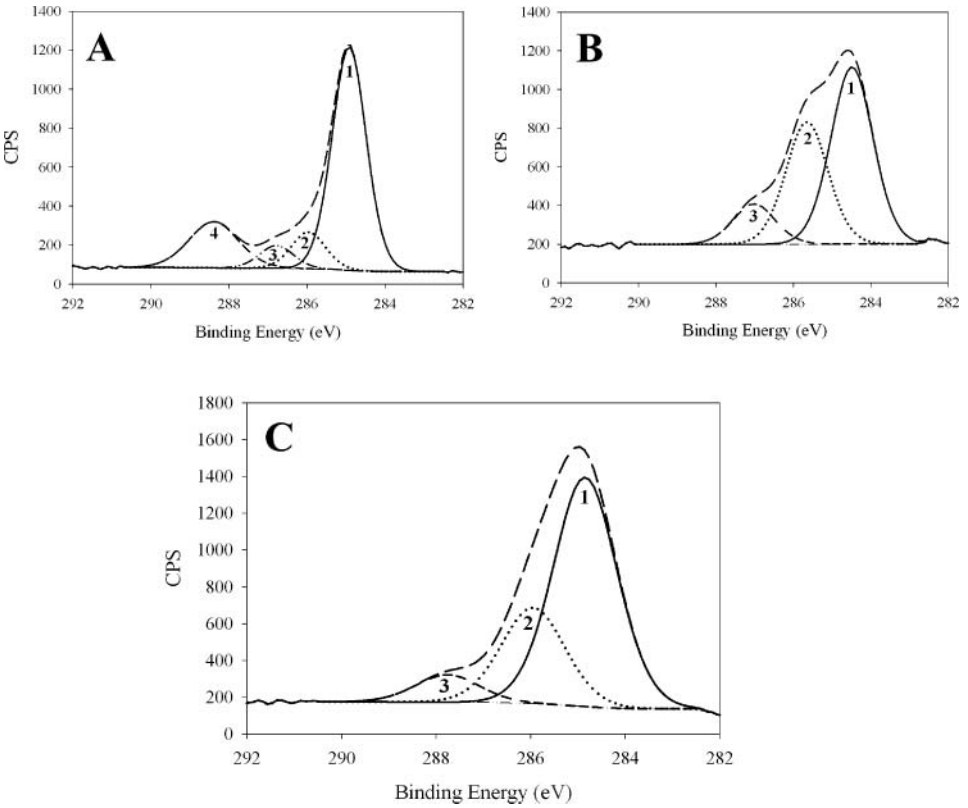

Figure 5. XPS C 1s deconvoluted spectra of (A) zein (Blank), (B) PANI (Blank) and (C) zein-PANI product (from the Approach 2.1).

Morphological studies of zein, PANI and zein-PANI product by *SEM* were shown in Fig. 6. Pure zein as received showed porous structured morphology. However, such structured morphology was absent while zein was treated with MSA and APS in a blank experiment, but the porosity still remained. PANI showed aggregated granular morphology. In the case of zein-PANI product, the zein surface was covered with granular PANI particles and therefore, the morphology was quite similar to PANI itself. The *SEM* images of CGM and CGM-PANI product were shown in Fig. 7. A relatively smooth surface topography was observed for both as received and blank samples of CGM, whereas a nodular, aggregated rough surface was noted in the case of CGM-PANI product. The surface topography of the product resembles the presence of coherent PANI coating due to the *in situ* polymerisation of aniline monomer on the substrate, CGM. These results corroborate the similar finding as it was observed in FTIR and XPS studies.

Approach 2.2: In situ polymerisation of aniline in homogeneous conditions. This experiment was carried out by two different ways: adding an oxidiser (APS) to the aniline containing solution (**2.2.1**) as a conventional approach, and adding aniline to the oxidiser containing solution (**2.2.2**). The second way was attempted with the aim to study some possible interactions between zein and PANI reported already for some other products containing PANI prepared by *in situ* oxidative polymerisation, e.g. polysaccharide-PANI

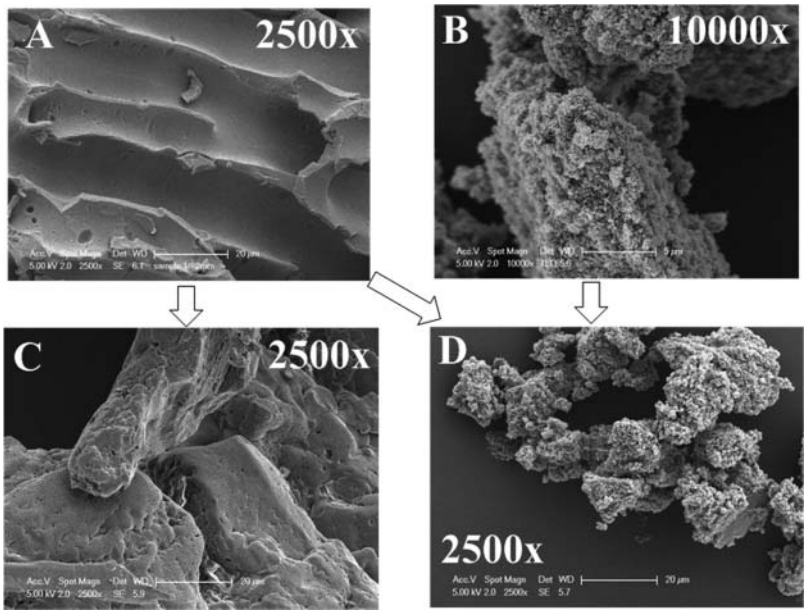

Figure 6. SEM images of (A) zein (as received), (B) PANI (Blank), (C) zein (Blank) and (D) zein-PANI product.

[10] and chitosan-PANI [19,20] because such an order of mixing ingredients is more favorable for a grafting polymerisation rather than formation of homopolymer.

The *Electrical conductivity* of the zein-PANI products from **2.2.1** and **2.2.2** approaches were $(8.0 \pm 0.1) \times 10^{-2}$ S cm^{-1} and $(1.8 \pm 0.2) \times 10^{-4}$ S cm^{-1} respectively.

FTIR spectra of the zein-PANI products performed by ATR on Ge crystal are shown in Fig. 8. The mass ratio of the reactants was 50:50 and hence for the comparison purpose, a physical mixture of PANI and zein in the mass ratio 50:50 was also examined. For a simple zein and PANI mixture, both zein and PANI were identified from their characteristic peaks described in Approach 1. The diagnostic signals of components in the zein-PANI products differ by intensity and more overlapping. The strong characteristic signals of PANI, e.g. in the area about 1500 cm^{-1} and 1600 cm^{-1} than that of the amide I signal from zein at about 1640 cm^{1} suggest PANI as a major component of the products. This fact also correlates with the *Elemental analysis* results (Table 2) where C:N atom ratio is shifted towards PANI.

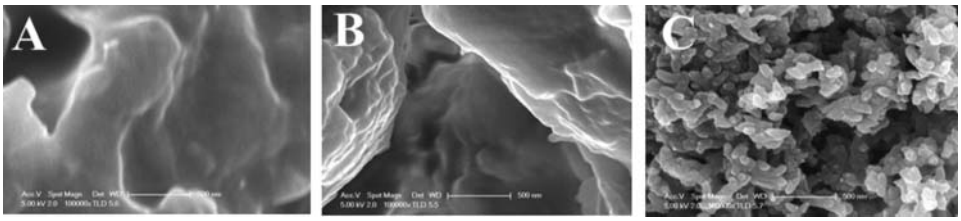

Figure 7. SEM images of (A) CGM (as received), (B) CGM (Blank) and (C) CGA-PANI product.

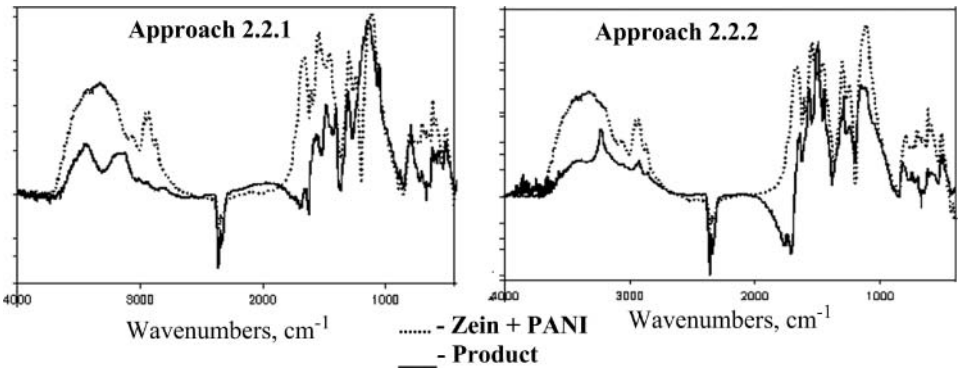

Figure 8. FTIR spectra of the physical Zein + PANI mixture (50:50) and the zein-PANI products obtained in the Approach **2.2**.

The FTIR spectra of the precipitates obtained from the supernatants from both ways of synthesis were found to be similar to zein (not shown in Fig.). Elemental analysis of the these precipitates (Table 2) where the atom ratio of C:N indicates the dominance of zein. The electrical conductivity of these precipitates obtained from the supernatants was too low to measure further supports this finding.

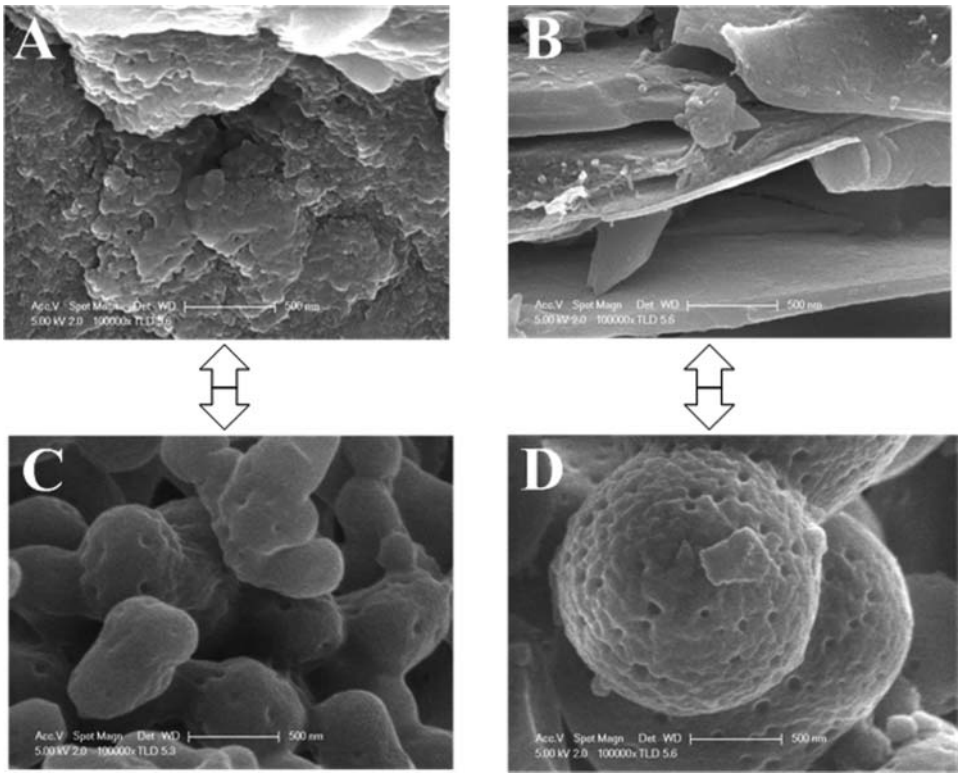

Figure 9. SEM images of zein-PANI products from (A) Approach 2.2:1, (B) Approach 2.2.2, (C) precipitate from the supernatant of 2.2.1, (D) precipitate from the supernatant of 2.2.2.

Table 2. Elemental analysis results for the Approach 2.2

SAMPLE	C, %	H, %	N, %	S, %	C:N, atom ratio
PANI-Zein (Approach 2.2.1)	53.81	5.84	10.85	5.75	5.78:1
PANI-Zein (Approach 2.2.2)	58.00	6.33	11.50	2.02	5.88:1
Precipitate from supernatant (2.2.1)	49.63	7.29	12.78	3.37	4.53:1
Precipitate from supernatant (2.2.2)	50.67	6.90	12.53	2.74	4.72:1

The zein-PANI product in both ways of synthesis showed flake-like morphology, whereas the precipitates obtained from the supernatants were globular in nature as observed from *SEM* images (Fig. 9).

Conclusions

Zein-PANI electrically conductive blends can be prepared by several routes either by casting films from homogeneous solutions or via in situ polymerisation. Due to the presence of conductive coating in situ polymerised products showed higher conductivity than the casted films. Blends made by in situ polymerisation show strong interaction between zein and PANI components. Incorporation of PANI in zein showed a plasticisation effect on zein. These materials could be useful for electrostatic dissipation or EMI applications.

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