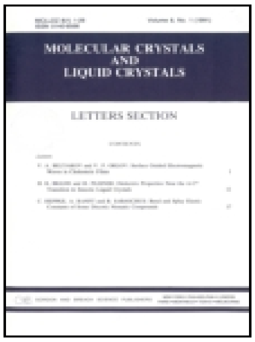

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Studies of Interfacial Interaction between Polyaniline and Corn Gluten Meal and their Effect on Electroactive and Free Radical Scavenging Properties

WALT V. K. WHEELWRIGHT,* SUDIP RAY, AND RALPH P. COONEY

School of Chemical Sciences, The University of Auckland, Auckland, New Zealand

Preparation and characterisation of Corn Gluten Meal (CGM)-polyaniline (PANI) blends by direct deposition of PANI onto the CGM surface via in situ oxidative polymerisation of aniline was studied. A series of different CGM-PANI blends were prepared by varying CGM-aniline feed mass ratios 95:5, 90:10, 80:20, 70:30, 60:40 and 50:50. The blend compositions were studied by Elemental analysis. Interfacial interactions between nitrogen containing groups from CGM and PANI were detected by X-ray photoelectron spectroscopy and FTIR spectroscopy. Formation of electrically conductive emeraldine salt form of PANI in these blends was evident from their characteristic dark green colour. The conductivity of the blends was increased with increasing PANI content in the blends in the range between 10^{-2} *S·cm*$^{-1}$ *to 2 S·cm*$^{-1}$*. Similarly all these blends showed free radical scavenging activity and the effect was more pronounced at higher PANI content. Therefore inclusion of PANI introduced valuable functional properties in CGM which can be applicable for commercial uses.*

Keywords Corn gluten meal; electrical conductivity, polyaniline; *in situ* polymerisation; free radical scavenging

Introduction

Corn Gluten Meal (CGM) is a by-product of starch extraction from corn [1, 2]. CGM plasticised with water, glycerol and octanoic acid was reported as a candidate to prepare biodegradable packaging material with good mechanical and water barrier properties [3]. It can also be used as a biodegradable matrix in the blends reinforced by the wood fibres [4]. CGM/wood fibres composites plasticised with water, glycerol and ethanol were proposed

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*Address correspondence to Walt V. K. Wheelwright, School of Chemical Sciences, The University of Auckland, Private Bag 92019, Auckland, New Zealand. E-mail: vkol006@aucklanduni.ac.nz

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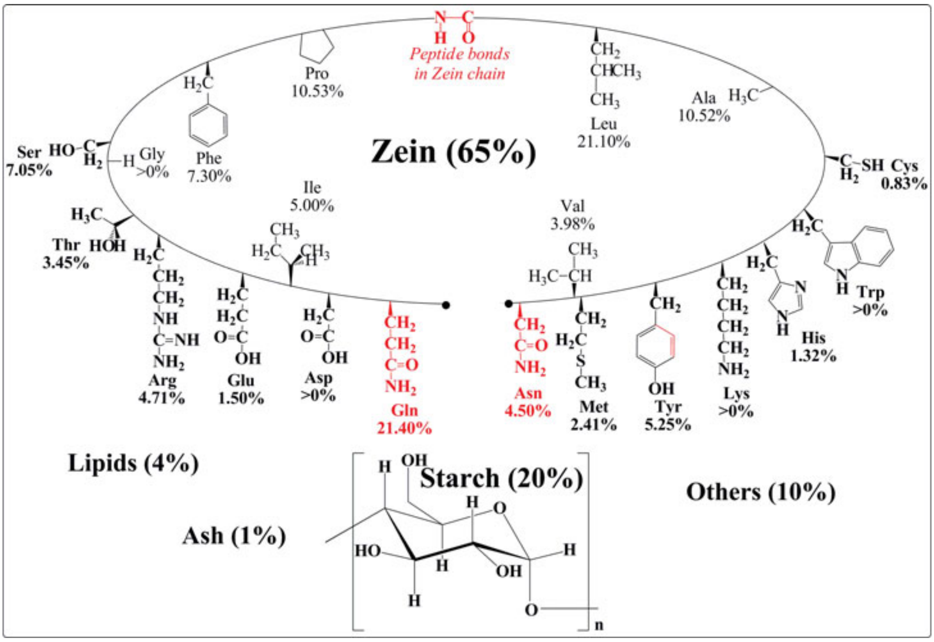

Figure 1. Chemical composition of Corn Gluten Meal.

to develop low cost biodegradable containers with potential application in agriculture [5]. Amongst the proteins and protein containing materials, CGM was also utilised as an agricultural polymer for packaging application [6]. Different aspects of CGM including its thermal properties and interactions of its protein components at elevated temperatures were reported [7].

The general composition of CGM has been discussed in the literature [2, 4, 5, 8] and is shown in Fig. 1. The main component of CGM is zein comprising up to 65% of its contents [4, 5]. Amino acid composition of zein was reported in a number of publications [9, 10] and is summarised in Fig. 1 with their typical proportions. The amino acids shown in bold can provide sites for various chemical interactions. The major amino acid component of zein is Glutamine (Gln) and that together with Asparagine (Asn) comprises about 26% of all the amino acids in zein. Starch is another component of CGM found in high quantity, about 20% [4]. Other components shown in Fig. 1, have relatively low content, but can also contribute in physical and chemical properties of CGM.

Polyaniline (PANI) [11, 12] has been reported in combination with biopolymers [13-16] to procure useful properties, primarily based on PANI's electrical conductivity [17]. The electrically conductive PANI form is emeraldine salt (ES) that can be obtained by acid doping.

A possibility to prepare electrically conductive zein and CGM-PANI blends has been recently reported [1]. Based on this previous research on zein-PANI blends, the present work is focused on detailed investigation on the preparation of CGM based blends and the influence of PANI on the functional properties, namely electrical conductivity and free radical scavenging activity. Further emphasis has also been given to understand the interaction between each component of the blends.

Experimental

Materials

CGM ("Avongold") was supplied by Penford (New Zealand). Aniline, ammonium persulfate (APS), methanesulfonic acid (MSA), 2,2-diphenyl-1-picrylhydrazyl (DPPH) and methanol (99%) were supplied by Sigma-Aldrich as analytical grade reagents. Aniline was freshly distilled while other chemicals were used as supplied.

Measurements

Elemental analysis was carried out using Carlo Erba Elemental Analyser EA 1108. The analytical method was based on the complete and instantaneous oxidation of the sample by "flash combustion" at 1020°C which converts all organic and inorganic substances into combustion products.

The *XPS* 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 on a Kratos Axis UltraDLD equipped with a hemispherical electron energy analyser with 160 eV pass energy, whilst core level scans were collected with pass energy of 20 eV. Data analysis was performed using CasaXPS software.

Electrical conductivity was measured by four-point probe measurement technique at room temperature (20°C) using Jandel RM2 instrument.

FTIR spectra were taken in the solid state of analysed samples using a Thermo Electron NICOLET 8700 FT-IR spectrometer with Diamond or Germanium crystal ATR attachment. Germanium crystal ATR was applied for all the PANI containing samples. The signals were processed by means of "OMNIC" software. 64 scans at resolution 4 cm^{-1} were averaged for each sample.

Radical Scavenging Activity Assay

Radical scavenging was performed using solution of DPPH• in methanol [18]. 12.5 mg of DPPH• was dissolved in absolute methanol (98–99%) in a 500 mL volumetric flask. This corresponds to a 63.4 μM (0.025 g in 1 L) solution of DPPH• in methanol. 20 mL of the DPPH• solution was added to 2 ± 0.5 mg of each sample of CGM-PANI blends and left at ambient temperature (20°C) for 24 hours. The absorbance of the supernatant was the measured using a Shimadzu UV-1700 UV–visible spectrophotometer (at 516 nm, λ_{max} of the DPPH• solution). Three trials of each sample were undertaken. Due to very low free radical scavenging activity, the amount of pure CGM in the experiment was increased to 10 mg. On contrary, the amount of highly active PANI in the experiment was 1±0.2 mg. The results were calculated on the basis of remaining DPPH• at the end of the experiment in comparison with a control experiment (DPPH• methanol solution without added test sample) by subtracting away the background loss of DPPH•.

Scanning Electron Microscope (*SEM*) study was carried out using a Philips XL30S FEG. Due to the charging effects, the samples were prepared on the surface of a carbon film and coated in vacuum with platinum by PVD (physical vapour deposition) method.

Preparation of the Blends

The amount of initial ingredients for the blend preparation is shown in Table 1.

Table 1. Initial amount of reactants for the various CGM-PANI blends preparation

Initial Ingredients	Sample A5	Sample A10	Sample A20	Sample A30	Sample A40	Sample A50
1 M MSA, mL Aniline+CGM/ APS	40/10	40/10	40/10	40/10	40/10	40/10
Aniline, g	0.1	0.2	0.4	0.6	0.8	1.0
CGM, g	1.9	1.8	1.6	1.4	1.2	1.0
APS, g	0.274	0.548	1.096	1.644	2.192	2.740

Aniline was dissolved in 40 mL of 1 M aqueous MSA. CGM was suspended in the solution while being stirred magnetically. APS was dissolved in 10 mL of 1 M aqueous MSA and added dropwise to the aniline-CGM system. After the addition of the full amount of APS (about 30 min.) the mixture was additionally stirred at 20-23°C for 20 h. The resulting product was filtered, washed with 200 mL of water and dried in vacuum for 48 h at 25°C.

Results and Discussion

Influence of Aniline Content on the in situ *Polymerisation*

Compared to conventional aniline polymerisation [19] in this study a retarding effect was observed while aniline was *in situ* polymerised in the reaction medium containing CGM. With the addition of oxidant solution in the reaction medium, the colourless reaction solution gradually became dark in colour indicating the initiation of aniline polymerisation. When the amount of aniline in the feed solution was highest (sample A50) this time was about 10 to 15 min. With decreasing the amount of aniline in feed solution, this formation time was progressively increased and in case of A5 this was about 4 h. The complexation of aniline onto this CGM substrate induced a retarding effect and thereby diminished the polymerisation rate. Usually the induction of polymerisation originates in competitive reactions of initiator or of primary radicals, which is the case here, with the components of CGM. Also, this is evident that hydroxyl or amine (primary or secondary) functionalised compounds can strongly influence the kinetics of scission of persulfates. In addition, the efficiency of initiation can be strongly diminished by primary radicals resulted from thermal activation which undergo mainly hydrogen abstraction rather than polymerisation reactions.

Influence of Aniline Content on the CGM-PANI Blend Composition

Bulk composition of various CGM-PANI blends and the individual components CGM and PANI were determined by *Elemental analysis* and the results are shown in Table 2. *Elemental analysis* of CGM as received, denoted as CGM(r), was compared with blank CGM, denoted as CGM(b), where CGM was treated at the same experimental conditions but without aniline. Blank polyaniline (PANI) was also prepared under the same experimental conditions but without the presence of CGM for comparison purpose. The C:N atom ratio of PANI was higher than CGM and hence in the CGM-PANI blends, this ratio was increased in the samples A5 to A50 with increasing the amount of PANI in the blends. On the other hand, N:S atom ratio of PANI was significantly lower than CGM due to higher sulphur

Table 2. Results of the elemental analysis

Sample code	Aniline monomer content,%	C,%	H,%	N,%	S,%	C:N atom ratio	N:S atom ratio
A5	5	52.51	7.67	11.31	1.20	5.41 : 1	21.67 : 1
A10	10	53.51	7.17	11.18	1.98	5.58 : 1	12.95 : 1
A20	20	52.46	7.15	10.93	1.86	5.60 : 1	13.49 : 1
A30	30	54.61	7.00	11.19	2.49	5.69 : 1	10.28 : 1
A40	40	55.07	6.61	11.16	3.06	5.76 : 1	8.36 : 1
A50	50	54.70	6.26	10.86	2.95	5.88 : 1	8.44 : 1
CGM(b)	n/a	50.00	7.57	10.79	1.25	5.40 : 1	19.76 : 1
CGM(r)	n/a	50.40	7.63	10.68	0.62	5.51 : 1	39.74 : 1
PANI	100	58.01	1.17	11.04	6.38	6.13 : 1	3.96 : 1

content in PANI. The primary source of this high sulphur content was MSA as PANI was doped with this acid. Progressive decrease in N:S atom ratio in the samples A5 to A50 with increasing the amount of PANI in the blends validates the previous findings. Compared to CGM(r), lower C:N atom ratio in CGM(b) possibly indicates the removal of some starch due to partial solubility at the conditions of experiments.

Spectroscopic Studies on the Chemical Interactions between CGM and PANI

Surface compositions of CGM-PANI blends and also CGM(r), CGM(b) and PANI were determined by *XPS* studies and the results are presented in Tables 3 and 4. All the spectra were calibrated on the basis of C(1s) signal. Due to the differences of carbon atoms in CGM where the majority of them are saturated whereas PANI and the blends containing high PANI content carbon is unsaturated, and accordingly the carbon peak was calibrated at

Table 3. XPS binding energies (eV) and atomic percentage (At%) values of C(1s) deconvoluted spectra

	C−C/C−H		C−N		C−O		C=O O−C−O C−S		O−C=O	
Sample code	eV	At%	eV	At%	eV	At%	eV	At%	eV	At%
CGM(r)	285.0	61.5	285.9	12.1	286.8	13.5	288.1	7.8	289.1	4.7
CGM(b)	285.0	60.7	286.2	12.0	286.9	9.9	288.2	9.7	289.0	7.7
A5	284.9	68.3	285.6	12.3	286.6	11.4	287.7	3.5	289.2	4.4
A10	285.2	73.8	286.8	13.1	—	—	288.6	3.1	289.2	3.8
A20	284.5	81.4	286.1	15.6	—	—	288.4	3.1	—	—
A30	284.5	79.5	286.1	17.2	—	—	288.2	3.3	—	—
A40	284.5	77.3	286.1	18.1	—	—	288.2	4.6	—	—
A50	284.5	73.9	286.0	19.6	—	—	287.9	6.4	—	—
PANI	284.5	52.1	285.7	36.0			287.0	11.9		

Table 4. XPS binding energies (eV) and atomic percentage (At%) values of C(1s), N(1s), S(2p) and O(1s) peaks from the survey scans

	C (1s)		N 1s		S 2p		O 1s		
Sample code	eV	At%	eV	At%	eV	At%	eV	At%	C:N
CGM(r)	284.8	83.0	399.8	1.4	—	—	532.8	15.7	59:1
CGM(b)	284.8	80.7	399.8	1.1	167.0	0.1	531.0	22.4	73:1
A5	284.9	84.4	399.9	1.7	168.9	0.2	531.9	13.7	50:1
A10	285.2	81.8	399.2	2.7	168.2	0.7	532.2	14.8	30:1
A20	284.0	81.5	398.0	4.2	167.0	1.0	531.0	13.3	19:1
A30	284.6	80.2	398.6	5.2	167.6	1.2	531.6	13.4	15:1
A40	284.6	78.9	398.6	6.2	167.6	1.5	531.6	13.4	13:1
A50	284.6	69.0	399.6	6.6	168.6	3.1	531.6	21.4	10:1
PANI	284.1	72.2	399.1	8.4	168.1	2.1	531.1	17.2	8:1

285.0 eV [20, 21] in the case of CGMs, A5 and A10 samples and at 284.6 [21–23] for other blend samples and PANI. *XPS* studies allowed comparing CGM(r) and after the treatment at the experimental conditions, CGM(b). Increased amount of C—S content (At%) was observed in oxidant treated CGM(b) indicating possible interaction between the substrate and the persulfate oxidant. An increase of the amount of O—C=O carbon can be due to the removal of some starch from the surface while the lipids contents remains the same. The removal of starch is also confirmed by a decrease of the C—O carbon amount partially coming from starch [24].

The amount of saturated carbon decreased from A5 to A50 due to the PANI deposition. This was confirmed by a decrease of the binding energy in the column C—C/C—H from a value about 285 eV to a lower value 284.5 eV. This change occurs between the samples A10 and A20 and remains the same for all other samples with a larger amount of PANI. The amount (At%) of carbon connected to nitrogen (C—N column; Table 3) increases from CGMs to PANI due to possible interaction between NH_2 and OH groups of CGM with PANI. It can be a hydrogen bonding or even a covalent bond between the components reported few times in the literature for chitosan and other carbohydrates [15, 25, 26]. A similar trend is shown for the O—C=O column (Table 3). This kind of carbon atom is derived from lipids of CGM and some acids in zein chain of CGM [27]. However, these interfacial interactions become undetectable as it goes beyond the detection limit of XPS with gradual deposition of PANI on the CGM substrate with increasing aniline concentration.

The *XPS* data from the survey scans for C(1s), N(1s), S(2p) and O(1s) are shown in Table 4. The peak maxima for C(1s) was occurred at 284.8 eV for both CGM(r) and CGM(b) samples. It also remained at about 285 eV in A5 and A10 that is characteristic for saturated carbon atoms. When the amount of PANI on the surface increases, this value drops to 284.6 eV and even lower that corresponds to the unsaturated atoms of carbon. The main trend in the nitrogen binding energy was a decrease from 399.9 eV in A5 (binding energy in the pristine CGM(r) and CGM(b) was 284.8 eV) to the lower values, characteristic for PANI (398.3 eV in quinoid imine, 399.7 eV in benzenoid amine [18] and 399.1 eV in the survey scan [1]).

From Table 4, it has been found that the nitrogen content (At%) for CGM(b) was only 1.1% and C:N was 73:1 and those values for PANI were 8.4% and 8:1 respectively. In case of CGM-PANI blends, from A5 to A50, this nitrogen content gradually increased from 1.7 to

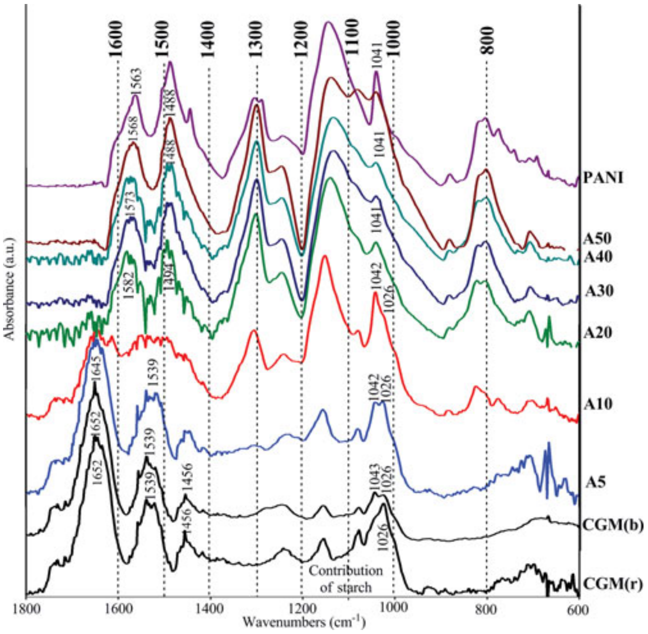

Figure 2. FTIR spectra of the blends and the individual components in the fingerprint region.

6.6% and the C:N values decreased from 50:1 to 10:1 respectively. This progressive increase in nitrogen content and decrease in C:N values in these blend samples with increasing the aniline concentration in the reaction medium suggests the formation and the deposition of additional PANI on the CGM substrate.

Sulfur is distributed on the surface of PANI and also showed a gradual increase in the CGM-PANI blend samples (A5 to A50) due to an increased amount of the MSA doped PANI. The peak maxima are focused at the area 167.0–168.9 eV characteristic for S(2p) in sulfonic acids [28]. Oxygen contents remains relatively stable with the O(s1) peak maxima at 532.8 eV in CGM(r) and at 531.0–532.2 eV in other samples [20, 28].

In addition to interactions between *in situ* polymerised aniline and the substrate, any possible interaction between the substrate and the oxidant was also investigated by *FTIR* spectroscopic studies. The comparison of the spectra of the pristine CGM(r) and CMG(b) treated with APS are shown in Figs. 2 and 3. A new band at 1043 cm^{-1} due to S=O stretching was observed in CGM(b) sample (Fig. 2) indicating that the raw substrate CGM(r) was modified by persulfate. Also, the increment in S content in CGM(b) compared to CGM(r) from 0.62% to 1.25% (Table 2) in bulk studies by elemental analysis and an increment in C—S content from 7.8 to 9.7 At% (Table 3) in CGM(b) on its surface by XPS studies further corroborate the findings from FTIR (Table 2).

Interactions between CGM and PANI were also evident from *FTIR* studies. In case of A5, the Amide I band at 1652 cm^{-1} in CGM(b) (mostly C=O stretch mode of the primary and secondary amides with some contribution of C—N deformation [29–32]) was slightly red-shifted to 1645 cm^{-1}. However, the frequency of Amide II band at 1539 cm^{-1} and of Amide III band at 1456 cm^{-1} (C—N stretch and N—H deformation modes of the secondary amides [31, 33]) were not affected. A red shift of the Amide I band was reported for a change of a secondary structure in protein chains when it was affected by some conformational influences, such as hydrogen bonding [29]. This suggests the interfacial

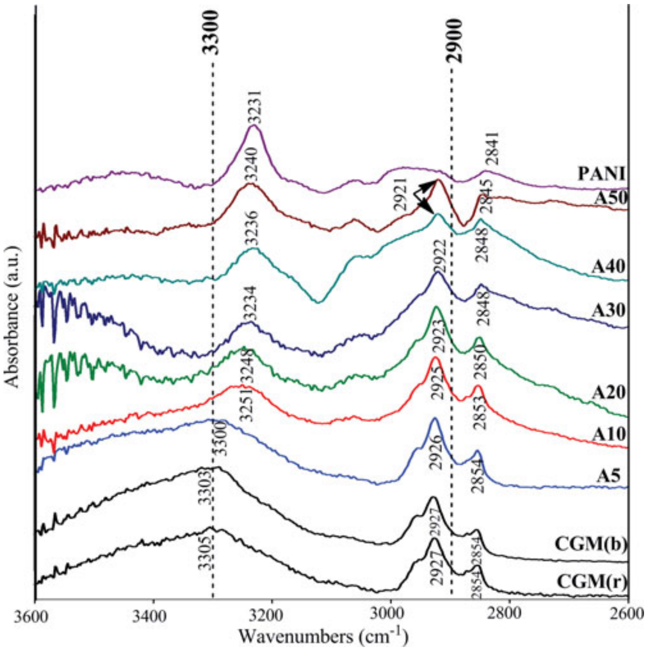

Figure 3. FTIR spectra of the blends and the individual components in the N—H and C—H stretch mode region.

interactions between oxidant modified CGM and PANI occurred through amino acid groups from CGM that contain the primary amide functionality (Fig. 1), such as Glutamine (Gln) and Asparagine (Asn). When the amount of PANI was increased (A10), intensity of these bands was reduced and a shoulder peak at 1614 cm^{-1} was appeared due to interaction between CGM and PANI. Further increase in aniline concentration in the reaction medium (A20 to A50) resulted in deposition of additional PANI on the CGM substrate and the Amide I band becomes almost undetectable. FTIR spectra of these blends resembled like PANI. This could happen due to strong IR absorption of PANI. Also, with increasing PANI thickness on the surface, the CGM-PANI interactions goes beyond the detection limit of the instrument as noted in XPS studies. At the higher concentrations of PANI (A20 to A50) Amide II band at 1539 cm^{-1} and Amide III band at 1456 cm^{-} are mostly overlapped by the intensive PANI bands at the area of 1600 cm^{-1} (quinoid form of the PANI rings) and 1500 cm^{-1} (benzenoid form of the PANI rings). Moreover, the appearance of peaks at 1568 cm^{-1} and 1488 cm^{-1} confirms the conductive form of PANI in the blends as they were doped with MSA [34].

When the amount of PANI was not high in the blends, i.e. in case of samples A5 and A10, the characteristic groups, such as C—O and C—O—C of starch, one of the major component of CGM, were also detected in the wavelength range between 1200 cm^{-1} and 900 cm^{-1} (Fig. 2) [27, 35]. With a higher PANI concentration they were overlapped by the intensive PANI bands. For example, peak at 1025 cm^{-1} due to C—O stretching in CGM, this band was masked by 1041 cm^{-1} band originated from S=O group of the MSA doped PANI [36].

Changes in C—H and N—H stretching regions were also noted in the blend samples (Fig. 3). C—H stretching bands at 2927 cm^{-1} and 2853 cm^{-1} and N—H stretching vibration at 3305 cm^{-1} from CGM were red-shifted in the blended samples.

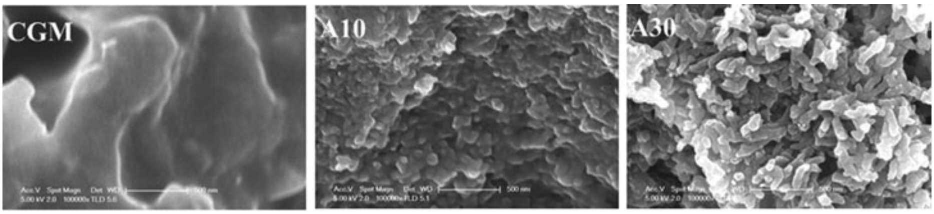

Figure 4. SEM images of CGM(r) [1] and CGM-PANI representative blends at 100,000x magnification.

In the samples with a higher amount of PANI these values remained almost the same, resembling the characteristic H-bonded N—H stretch mode in PANI [36]. The N—H stretching band centred at 3305 cm $^{-1}$ was multicomponent, involving primary amides from lateral chains of amino acids at 3203 cm^{-1}, 3295 cm^{-1} and 3450 cm^{-1} and also secondary amides of the zein backbone at 3300 cm^{-1} [8, 33]. With increasing PANI content in the blends, this band became sharp by losing the contribution from primary amides. This further suggests that the preferable CGM-PANI interaction site was located on the lateral amino acids with primary amide functionality, such as Gln and Asn.

Influence of PANI Content on the CGM-PANI Blend Morphology

The *SEM* images of CGM(r) and representative CGM-PANI blends (A10 and A30 samples) are shown in Fig. 4. In both the CGM-PANI blend samples the presence of PANI on CGM surface is clearly evident. A relatively smooth surface topography was observed in untreated substrate CGM(r), whereas a nodular, aggregated rough surface was noted in the blend samples. Moreover, the PANI seemed to be submerged into the CGM matrix that can be a consequence of the aniline absorption [37, 38] and formation of the PANI on the CGM substrate. The A30 sample represents a conventional elongated morphology [39, 40]. This could happen due to slow polymerisation of additional aniline monomer which leads to rod-like structures.

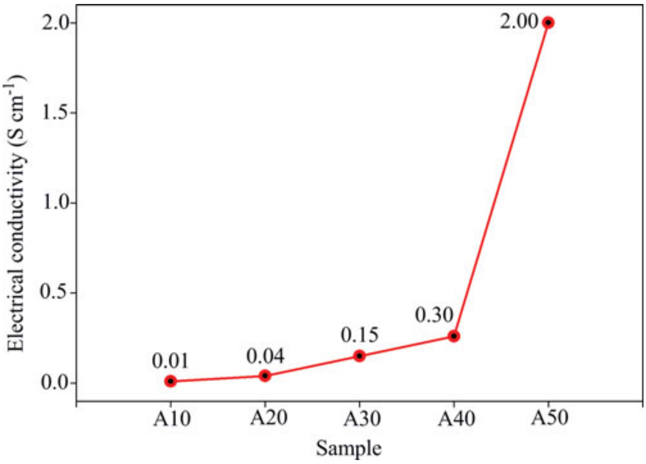

Figure 5. Plot of the Electrical conductivity values of CGM-PANI blends.

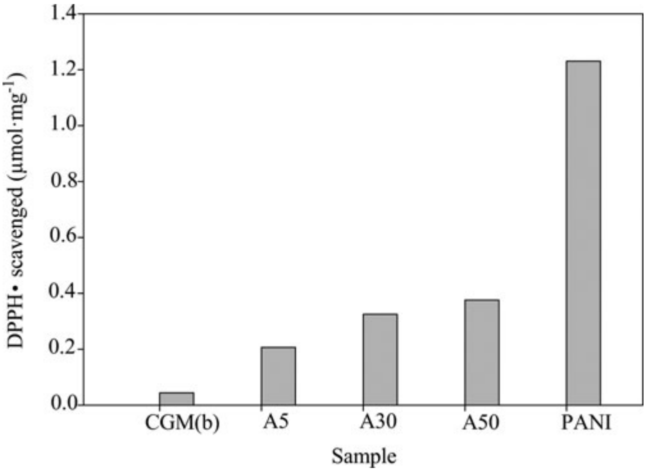

Figure 6. Free radical scavenging capacity values of CGM-PANI blends and the individual components.

Influence of PANI Content on the Electrical Conductivity of the CGM-PANI Blends

The *Electrical conductivity* of the CGM-PANI blended samples was in agreement with the amount of applied aniline monomer in the reaction feed and with the amount of PANI deposited on the CGM surface. However, it was not possible to measure the conductivity of A5 samples due to its value being lower than sensitivity of the method (below 10^{-8} $S{\cdot}cm^{-1}$). All other blended samples were electrically conductive and the conductivity was increased with increasing PANI content in the blends (Fig. 5).

Influence of PANI Content on the Free Radical Scavenging Property of the CGM-PANI Blends

Due to possible application of CGM as packaging material, free radical scavenging test has also been performed on the CGM-PANI blends. Representative blends (A5, A30 and A50) were tested in comparison with CGM and PANI. The results of this assay are shown in Fig. 6.

The blend samples demonstrated free radical scavenging capacity. With increasing PANI content in the blends, the free radical scavenging capacity was gradually improved. The low scavenging activity of pristine CGM was similar to the previously reported finding [41]. Inclusion of PANI even in small quantity substantially improves this functional property in CGM.

Conclusions

CGM-PANI(ES) MSA doped blends with various CGM to PANI ratio were prepared by *in situ* oxidative polymerisation of aniline resulted in the direct deposition of PANI onto the surface of CGM. Modification of substrate by the influence of oxidant was noted from spectroscopic and elemental analysis. The blends showed a strong interfacial interaction between this activated CGM and PANI components. On the basis of XPS and FTIR spectroscopic studies, the secondary amide groups of the lateral amino acids of zein in CGM were suggested as a preferable site for CGM-PANI interactions. The blends obtained from 10% and more aniline monomer contents in the reaction feed were electrically conductive. These blends also demonstrated noticeable free radical scavenging activity. The above findings suggest possible replacement of zein by more economic CGM and can be utilised in some applications where the materials require deriving from biological source. This approach can be applied in the preparation of other PANI-biopolymer containing blends with desirable characteristic features.

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