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Substituted polyaniline/chitosan composites: Synthesis and characterization

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ABSTRACT

Substituted polyaniline/chitosan(PANIs/Ch) composites were chemically synthesized by using ammonium peroxydisulfate as oxidant and characterized by measurements of conductivity, FTIR, UV–vis, SEM and TGA techniques. FTIR spectra of the composites revealed that there is a strong interaction between substituted polyanilines and chitosan. Among the substituted polyaniline/chitosan composites synthesized, poly(*N*-ethylaniline)/chitosan PNEANI/Ch has the highest conductivity with a value of 1.68×10^{-4} S/cm. The P2EANI/Ch composite exhibited higher thermal stability than the other composites. SEM images of the composites showed an agglomerated granular morphology of substituted polyaniline particles coated on the surface of chitosan.

1. Introduction

Chitosan is one of the promising natural polymers with characteristics such as biodegradability, chemical inertness, biocompatibility, high mechanical strength, good film-forming properties, and low cost (Mucha, Wankowicz, & Balcerzak, 2007; Wang, Zhang, Cheng, & Dong, 2000). In addition, chitosan is a nontoxic cellulose-like polyelectrolyte polymer hydrogel that is suitable for the fabrication of artificial muscles, as this material undergoes a large volume change in response to changes in pH, temperature, or solvent composition (Kim, Shin, Kim, & Kim, 2004; Kim, Yoon, Kim, & Kim, 2004). Chitosan is used in a wide range of applications such as wastewater treatment (Crini, 2006), separation membranes (Won, Feng, & Lawless, 2002) food packaging (Arvanitoyannis, 1999; Arvanitoyannis, Kulokuris, Nakayama, Yamamoto, & Aiba, 1997; Arvanitoyannis, Nakayama, & Aiba, 1998), drug delivery systems (Nunthanid et al., 2004; Puttipipatkhachorn, Nunthanid, Yamamoto, & Peck, 2001), and biosensors (Tsai, Chen, & Liaw, 2007; Wu, Feng, et al., 2007; Wu, Hou, et al., 2007). However, in sensor applications, the poor electrical conductivity of hydrogels results in a poor response time and a high operational voltage limits its applicability in devices. Hence, composites have been attempted by incorporating a rigid conducting polymer (such as PANI) into a flexible matrix (such as chitosan) to combine the good processability of the matrix and the electrical conductivity of the conductive polymer (Xu et al., 2006).

Polyaniline (PANI) is an extensively studied conductive polymer. It is an easy-to-synthesize, light-weight polymer exhibiting high conductivity, low operational voltage and high stress. These properties make PANI a good candidate for the development of actuators (Kaneto, Kaneko, & MacDiarmid, 1995; Madden, Madden, Anquetil, Vandesteeg, & Hunter, 2004). Potential applications include utilization in rechargeable batteries, sensors, switchable membranes, anticorrosive coatings, and electronic devices (Cho, Park, Hwang, & Choi, 2004). However, the major disadvantage of PANI is its insolubility in common organic solvents and its infusibility. There are some possible methods for preparing soluble PANIs. One of these methods is to substitute one or more hydrogens by an alkyl, an alkoxy, an aryl hydroxyl, an amino group, or halogen group in an aniline nucleus (Cataldo & Paolo, 2002; Gök, Sarı, & Talu, 2004; Sari, Gök, & Şahin, 2006; Sarı, Talu, & Gok, 2003).

Recently, substituted polyaniline composites have been prepared with Nylon6 (Sarı et al., 2003), molybdenum disulfide (Bissessur & White, 2006; Bissessur, White, & Dahn, 2006)multi-walled carbon nanotubes (Lu et al., 2006), and polyimide (Iroh et al., 2004).

Some recent work has been reproted on the synthesis of PANI/chitosan composites and blends (Ismail et al., 2008; Kim et al., 2005; Shin et al., 2005; Thanpitcha, Sirivat, Jamieson, & Rujiravanit, 2006). However, there is no reported study on substituted polyaniline/chitosan composites or blends. The aim of present study is to chemically synthesize substituted polyaniline/chitosan composites such as poly(*N*-methylaniline)/chitosan (PNMANI/Ch), poly(*N*-ethylaniline)/chitosan (PNEANI/Ch), poly(2-ethylaniline)/chitosan (P2EANI/Ch). Characterization of the composites has been carried out using FTIR and UV–vis spectroscopies, TGA and SEM tech-

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niques. Properties of the composites are compared with those of a polyaniline/chitosan (PANI/Ch) composite, synthesized at the same conditions.

2. Experimental

2.1. Materials

Aniline (ANI), *N*-methylaniline (NMANI), *N*-ethylaniline (NEANI), 2-ethylaniline (2EANI) were obtained from Aldrich and the monomers were under nitrogen prior to use. Chitosan with medium molecular weight was also purchased from Aldrich. Ammonium peroxydisulfate, hydrochloric acid, acetic acid, and *N*-methyl-2-pyrrolidone (NMP) (Fluka) were used as received.

2.2. Synthesis of substituted polyaniline/chitosan composites

In a typical procedure, an aqueous solution of chitosan (0.2 g) was prepared by dissolving chitosan in 40 ml of aqueous acetic acid (2 wt%) for 24 h and then adding 8.25×10^{-3} mol substituted aniline monomer in 40 ml 1 M HCl to form a homogeneous solution. Ammonium peroxydisulfate (APS, 0.0099 mol) solution in 1 M HCl was dropped into the above solution with vigorous stirring under N_2 atmosphere. The molar ratio of oxidant/monomer was 1.2. The polymerization was carried out for 24 h at room temperature. After that, the solution was centrifuged for 10 min at 8000 rpm and precipitation was then redispersed in 2 wt% acetic acid and then washed with deionized water and centrifuged again. The washing procedure was repeated four times. The final composite was dried at 50 °C for 24 h. PANI/Ch composite was synthesized utilizing the same conditions to compare its properties with substituted polyaniline/chitosan composites. Fig. 1a–b shows the general polymerization mechanisms of substituted polyaniline homopolymer (a) and substituted polyaniline/Ch composite (b).

2.3. Instrumental

Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm^{-1} with a 4 cm^{-1} resolution from KBr pellets on a Perkin Elmer Spectrum BX FTIR system (Beaconsfield, Beuckinghamshire, HP91QA, England). The direct current electrical conductivity of the composites was measured by the standard four point probe method using PCI-DAS6014 for a current source, voltameter and temperature controller. Dry, powdered samples were made into pellets using a steel die of 13 mm diameter in a hydraulic press under a pressure of 700 MPa. For SEM analysis, samples were sputter coated with gold layers and images were taken on a scanning electron microscope model Philips XL-30 S FEG. Thermograms of the polymers were recorded using a Perkin Elmer thermogravimetric analyzer in the presence of N_2 atmosphere from 30 to 900 °C with a heating rate of 10 °C min^{-1}. UV–vis analysis of the composites was carried out in NMP using the Jasco V-530 model UV–vis spectrophotometer.

3. Results and discussion

3.1. FTIR results

The FTIR spectra of the composites are shown in Fig. 2. In the spectrum of chitosan, the band at 3435 cm^{-1} is due to —OH vibration. This band is quite broad and has covered characteristic —NH band for chitosan 1654 and 1597 cm^{-1} band belonging to $-NH_2$ bending. The bands occuring at 1379 cm^{-1} are ascribed to the C—OH vibration of the alcohol groups in the chitosan and the band around 2861 cm^{-1} is ascribed to the C—H stretching mode in chitosan (Ismail et al., 2008). The absorption bands at 1155 cm^{-1} due to anti-symmetric stretching of C—O—C bridge, and the 1075 cm^{-1} skeletal vibration involving the C—O stretching are characteristics of its saccharide structure (Kim et al., 2004).

It can be seen from the FTIR spectra that the composites have the characteristic bands of both chitosan and substituted PANI. Table 1 shows characteristic frequencies of chemically synthesized composites. The 1559, 1570 and 1596 cm^{-1} bands are characteristic of the nitrogen quinone (Q) structure, and the 1497 and 1502 cm^{-1} bands are related to the benzene ring (B) structure. The intensity ratio of the Q/B absorption peaks is indicative of the extent of oxidation. On comparing the relative intensities of these peaks for the composites, P2EANI/Ch and PNMANI/Ch have contained oxidized quinoid and reduced benzenoid units in equal proportion. However, PNEANI/Ch and PANI/Ch have shown lower oxidization degree than other composites. The –NH bands belong-

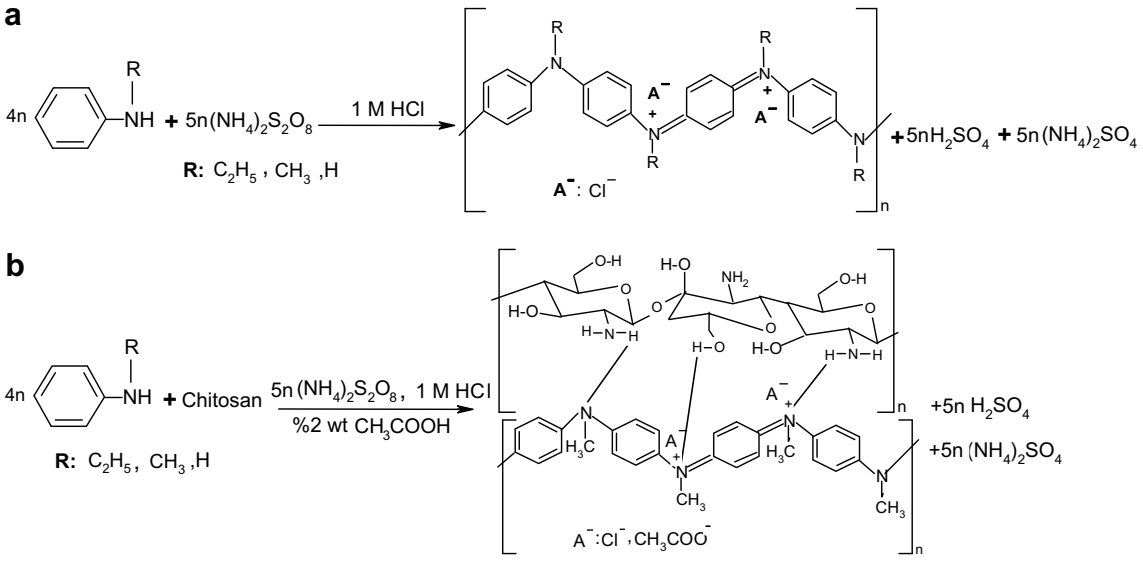

Fig. 1. Polymerization mechanism of (a) homopolyanilines (b) substituted polyaniline/Ch composite.

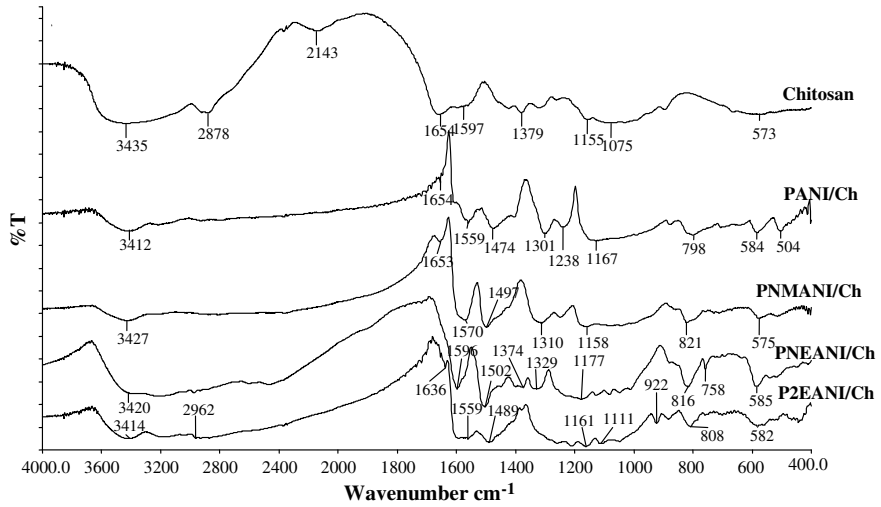

Fig. 2. Infrared spectra of Chitosan, PANI/Ch and substituted PANIs/Ch composites.

Table 1
Characteristic frequencies of the composites

Wavenumber (cm^{-1})				Band characteristics
PANI/Ch	PNMANI/Ch	P2EANI/Ch	PNEANI/Ch	
798	821	809	816	Paradisubstituted aromatic rings
1167	1158	1161	1177	N=Q=N vibrations
1301	1310	–	1330	Aromatic C—N stretching
1474	1497	1489	1502	C=C, C=N streching of benzenoid rings
1570	1570	1559	1596	C=C, C=N streching of quinoid rings
3412	3435	3436	3435	>N—H stretching vibration

ing to chitosan are seen around 1654 cm^{-1} in the spectra of composites. However, the band has shifted to lower wavenumber in the PNEANI/Ch composite. This result indicates larger interaction between PNEANI and Ch.

3.2. Conductivy and UV–vis spectra of composites

Table 2 exhibits polymerization yields (g) and room temperature electrical conductivity values and UV–vis spectra results of the composites. The yield (g) of the composites is approximately the same for all, however the degree of oxidation is different. The P2EANI/Ch composite has the highest yield. While chitosan is an insulating material, the PNEANI/Ch composite has the highest conductivity of 1.68×10^{-4} S/cm. Although the P2EANI/Ch and PNEANI/Ch composites include substituted groups, they exhibit nearly the same electrical conductivity, of 10^{-4} S/cm, to the reported conductivity of PANI/Ch composite (Shin et al., 2005). In general, substituted PANIs have lower conductivity than the pure-PANI composites (Kulkarni, Viswanath, & Khanna, 2006). Substituted PANI/Ch composites are quite useful materials because of their nearly similar conductivity and higher solubility than PANI composites.

The UV–vis spectra of the composites are shown in Fig. 3. All samples show two absorption bands in NMP. We clearly observe the characteristic bands of polyaniline and substituted polyanilines

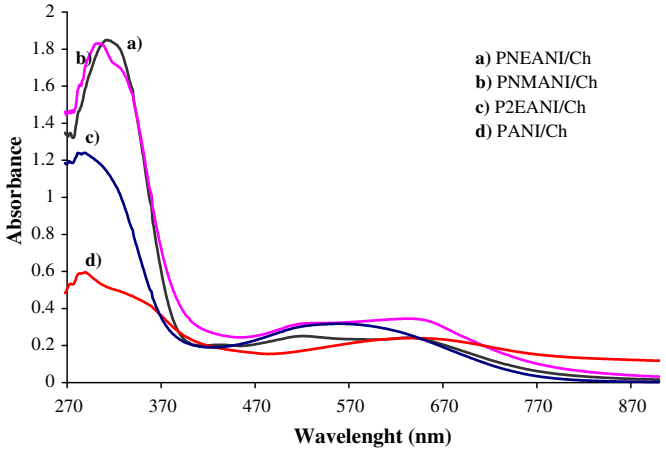

Fig. 3. UV–vis spectra of the composites.

Table 2
Polymerization yield, conductivity, maximum absorbance wavelengths and intensity ratios of A_Q/A_B

Polymer	λ_1 (nm) $\pi \rightarrow \pi^*$	λ_2 (nm) $n \rightarrow \pi^*$	A_Q/A_B	Polymerization yield (g)	Conductivity (S/cm^{-1})
PANI/Ch	283	634	0.42	1.199	7.73×10^{-5}
PNEANI/Ch	308	571	0.14	1.125	1.68×10^{-4}
PNMANI/Ch	299	639	0.19	1.058	6.84×10^{-6}
P2EANI/Ch	282	560	0.26	1.262	1.53×10^{-4}

at 283–308 and 571–639 nm (Table 2). The absorbance maxima at 283–308 nm are ascribed to the $\pi \rightarrow \pi^*$ (λ_1) transition within the benzenoid segment. The band at 571–639 nm shows $n \rightarrow \pi^*$ (λ_2) transitions within the quinoid structure (Yavuz & Gok, 2007). The wavelength of the quinoid band plays an important role in switching polyaniline from an electric insulator to a conductor upon doping. Furthermore, the intensity of ratio of A_Q/A_B indicates the relative amount of quinoid unit in polyaniline. In this work, the intensity ratio of A_Q/A_B was calculated from the UV–vis spectra. The PANI/Ch composite has the highest value. This means it has the highest oxidation state. PNEANI/Ch composite has the lowest A_Q/A_B showing less oxidation than other composites. It is also confirmed by FTIR results.

3.3. Morphology

Fig. 4a–e shows scanning electron micrographs of Chitosan (Ch), PANI/Ch, P2EANI/Ch, PNEANI/Ch and PNMANI/Ch, respectively. The morphology of chitosan and composites is compared at a magnification of 50.000×. From these figures, it can be deduced that P2EANI/Ch (Fig. 4c) has granular structure and the smallest particle size, whereas PNEANI/Ch (Fig. 4d) has the tightest structure. For all composites, size scale is smaller than 500 nm. When the morphology and conductivity of samples are compared, P2EANI/Ch has more unique and homogenous structure than others. This could be a reason for higher conductivity. It appears that morphology has some influence on electrical conductivity (Gök, Omastova, & Yavuz, 2007).

3.4. Thermal stability

Fig. 5 shows the TGA thermogram of Chitosan (Ch), PANI/Ch and substituted PANI/Ch composites. Decomposition temperatures obtained from TGA curves are listed in Table 3.

The first weight loss of 5–10% observed up to 100 °C is due to loss of water from the polymer composites (Chan et al., 1989;

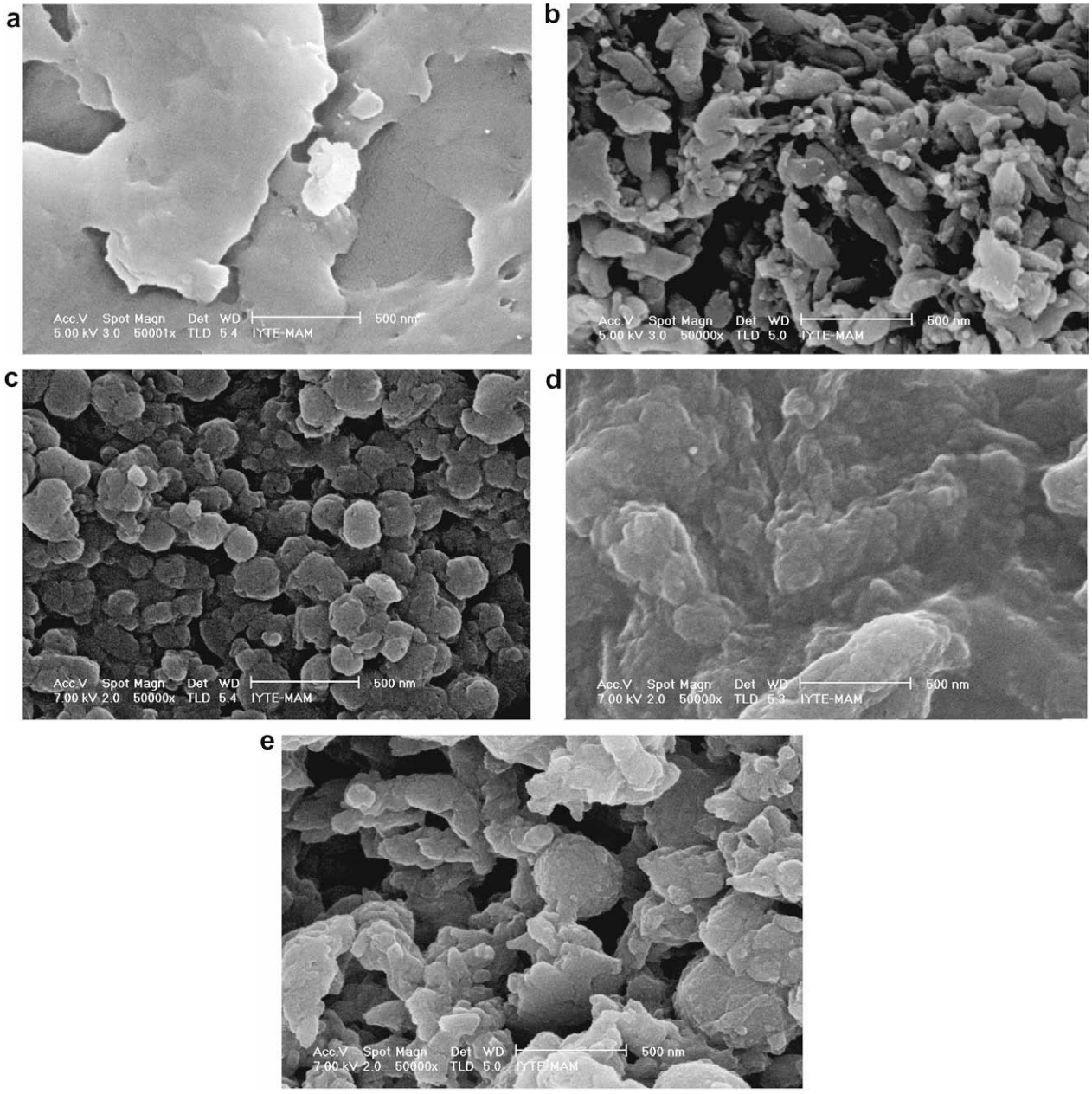

Fig. 4. Scanning electron micrographs of the composites; (a) Chitosan(Ch), (b) PANI/Ch, (c) P2EANI/Ch, (d) PNEANI/Ch and (e) PNMANI/Ch.

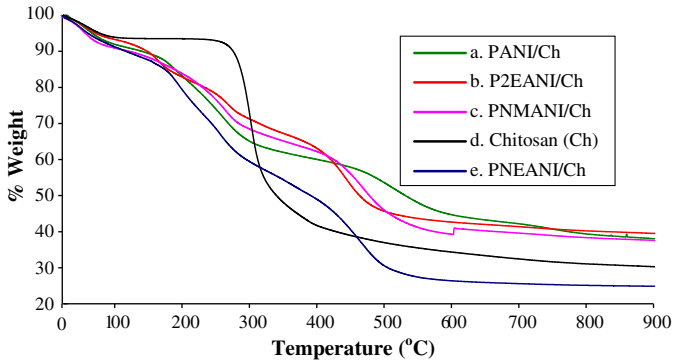

Fig. 5. TGA curves for chitosan, PANI/Ch and substituted PANIs/Ch composites.

Table 3
Thermal degradation temperatures of the composites

Sample	T_i	T_m	T_f	% Residue at 900 °C
Chitosan (Ch)	286	313	340	30
PNMANI/Ch	180	232	283	38
	429	480	530	
PANI/Ch	170	232	293	39
	465	522	579	
PNEANI/Ch	164	222	279	26
	410	465	520	
P2EANI/Ch	244	263	282	40
	408	446	484	

T_i, initial degradation temperature; T_m, maximum degradation temperature; T_f, final degradation temperature.

Yue, Epstein, Zhong, Gallagher, & MacDiarmid, 1991). Chitosan shows a discrete weight loss at 286 °C, attributable to the degradation of chitosan chains (Thanpitcha et al., 2006). The composites exhibit two steps as seen from Table 3. The first stage observed within the temperature range of 164–244 °C is related to removal of dopant molecules from the polymer structure. The weight loss observed between 408 and 465 °C after the removal of the dopant molecules corresponds to the degradation of the polymer chain. P2EANI/Ch composite exhibits the highest thermal stability, whereas the final thermal degradation temperature of P2EANI/Ch was observed to be lower than that of the other composites.

4. Conclusions

Substituted polyaniline/chitosan composites were synthesized by *in-situ* chemical oxidation using ammonium persulfate as an oxidant in HCl and CH_3COOH acid medium. The FTIR results confirmed that there is an strong interaction between substituted polyanilines and chitosan. All composites exhibited a better final degradation temperature than chitosan. The thermal stability of composites at 900 °C was higher than that of chitosan except for the P2EANI/Ch composite. P2EANI/Ch composite has more unique and homogenous structure than others. This smooth morphology can be a reason for its higher conductivity. These substituted polyaniline/Ch composites are promising candidates for glucose biosensor applications, which is currently under investigation in our group.

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