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# Conductive and Biodegradable Polyaniline/Starch Blends and Their Composites With Polystyrene

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## ABSTRACT

In recent years, polyaniline (PANI)/polymer conductive polymeric blends have attracted considerable attention. The majority of polymers selected to prepare PANI composites are insulating polymeric materials with excellent physical properties, e.g., rubbers, plastics and textiles. Generally, a large number of rubbers and plastics are synthesized by using petroleum feedstock as raw materials. However, the much limited and exhausting petroleum resources and most non-biodegradable plastics have become serious threats to living environment. In the present work, biodegradable conductive blends based on polyaniline/starch were prepared by in situ polymerization of aniline in the presence of starch activated in acidic medium. Various polyaniline/starch ratios (w/w%) were prepared to study the structure of the final blends. The conductivity of blends was measured and it was found that the electrical conductivity of the blends was increased by increasing the amount of polyaniline (PANI). In continuation of the study, various dopants such as organic and inorganic acids were tested to observe the electrical conductivity behaviour of the polyaniline/starch blends. Characterizations of the blends were accomplished by FTIR analysis, UV-Vis, XRD and DSC, and morphological studies were performed by scanning electronic microcopy (SEM). For improving the flexibility and mechanical properties of the blends, we introduced polystyrene of commercial type into the blends' structure to prepare polyaniline/starch/polystyrene blends. The biodegradability test was carried out to demonstrate the biodegradability characteristics in the prepared conducting composites.

**Key Words:**

biodegradable;
composite;
conductive polymer;
starch;
polyaniline.

## INTRODUCTION

In recent years, conductive polymeric composites of polyaniline (PANI)/polymer have attracted considerable research interest because of their potential applications as electrodes, biosensors, batteries, antistatic coatings, gas sensors, membranes and light emitting diodes [1-3]. Insulating polymeric materials, with excellent physical properties, e. g., rubber, plastics and textiles are seldom used to make PANI composites [3]. Some research works dealing with the preparation of the rubber-PANI, plastic-PANI, etc. have been published [1-3]. Generally, by using petroleum feedstock as raw materials, a large number of rubber and plastics are synthesized, worldwide. However, the much limited and exhausting petroleum

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resources and growing waste disposal of non-biodegradable plastics have become a serious threat to environment [3-5]. As a consequence, it is up to research programmes to look for natural and eco-friendly materials as substitutes for petroleum feedstock as more public communities are increasingly paying greater attention to this problem, in recent decades. Polymers from renewable resources have been the centre of world attention over the past two decades, mainly for two reasons: the environmental concerns and the realization that our petroleum resources are limited [6]. In addition, materials of renewable resources may provide additional revenues for those involved in agriculture.

Cellulose and their derivatives have been long used in preparation of PANI composites [2,7,8]. Additionally, the use of viscous and lyocell (regenerated cellulose) in combination with conductive polymers for the preparation of conductive materials has been reported in previous publication [3]. However, the disadvantage of cellulose is its extreme difficulty to dissolve in water and most common organic solvents. Thus, the preparation of conductive composites based on cellulose was encountered with major difficulties. In fact, their composites have not, so far, given rise to homogeneous structures.

Starch is a polysaccharide produced by higher plants as a means of storing energy. It is stored intracellularly in the form of spherical granules that are 2-100 mm in diameter. Most commercially available starches are isolated from grains such as corn, rice, wheat, and from tubers such as potato and tapioca. Chemically, starch is a heterogeneous substance and contains both linear (amylose) and branched (amylopectin) structures. Morphologically, it possesses both amorphous and crystalline regions. The ratio of amylose to amylopectin in starch varies as a function of the source, age, etc. Amylose is essentially a linear structure of $\alpha$-1,4-linked glucose units and amylopectin is a highly branched structure of short $\alpha$-1,4 chains linked by $\alpha$-1,6 bands. Most native starches are semicrystalline with a crystallinity of ~20-45%. Amylose and the branching points of amylopectin form the amorphous regions [9-14].

Since 1970s starch has been incorporated into polyethylene in order to enhance its biodegradability. Biodegradable composites of poly(propylene carbonate) reinforced with unmodified granular corn starch have been studied by several researchers [15,16]. Succinic anhydride as an active agent is introduced into poly(propylene carbonate)/granular starch composites. Succinic anhydride is prone to react with hydroxyl groups in starch, which introduce ester groups into starch and improve the compatibility between poly(propylene carbonate) matrix and starch [17]. Ge et al. have blended starch-*g*-poly (methyl acrylate) copolymer containing 28.6 wt% poly (methyl methacrylate) with poly(propylene carbonate) to improve phase adhesion between the granular reinforcement and poly(propylene carbonate) matrix [18]. Gelatinization (or plasticization) of starch is also a good method to enhance the interfacial affinity [19,20].

The aim of this work was the preparation of biodegradable conductive blends based on starch and polyaniline. For improving the flexibility and mechanical properties of the obtained blends, we introduced commercial polystyrene into the structure of blends and for that we prepared polyaniline/starch/polystyrene composites. The influence of various dopants such as organic and inorganic acids on the electrical conductivity of the PANI/starch blends was investigated, as well. The types of acids as dopant and the amount of aniline played major roles on the properties of the blends. As a result, the effects of these parameters on the electrical conductivity (EC) of the blends were studied. Conducting blends were characterized by means of FTIR, XRD, UV-Vis, DSC, and SEM studies.

## EXPERIMENTAL

### Materials

Aniline (Merck, Germany) was doubly distilled in the presence of zinc dust to eliminate the oxidation impurities. Starch, ammonium peroxydisulphate (APS) [$(NH_4)_2S_2O_8$], tetrahydrofuran (THF), camphorsulphonic acid, dodecyl benzene sulphonic acid, sulphuric acid, phosphoric acid, hydrochloric acid were purchased from Merck, Germany and they were all used without further purification. Commercial grade of polystyrene was donated by Tabriz

Petrochemical Co, Iran. All solvents (Merck, Germany) were used as received without further purification. Aqueous solutions were prepared with double distilled water.

### Characterization

FTIR spectra were recorded on a Thermonicolet (Nexus 670, USA) spectrometer and transmission spectra were obtained by forming thin transparent KBr pellets. The conductivity measurements were performed by a standard four probe technique on the flexible film samples obtained by pressing the powder at a pressure of 15 MPa. Vegetative growth images have been taken with an Olympus camera (DP 12, Japan) and an Olympus stereomicroscope (SZX 12, Japan). Particle size and morphology of the particles were examined via scanning electron microscopy (Bruker, Germany). The X-ray photoelectron spectra (XPS) were recorded on an X'pert Philips X-ray photoelectron spectrometer, Netherland, using non-monochromated Mg $K_a$ radiation as the excitation source. Differential thermal analyses were conducted (Mettler Toledo DSC 823e, USA) in an inert atmosphere and temperature rising rate was 10°C/min.

### Synthesis of PANI/Starch Blends

The polyaniline/starch blend was prepared by in situ polymerization of aniline in the presence of aqueous starch solution in acidic medium under ultrasonic irradiation or magnetic stirring in an inert atmosphere [20].

In a typical procedure, in a 250 mL three-necked flask equipped with inlet and outlet of inert gas, 100 mL hydrochloric acid (1.0 M) was added; followed by addition of 4 mL (0.0439 mol) of double distilled aniline. Then, 3 g starch was added into the above solution and kept standstill, until the starch was activated within a certain period of time. Then, the oxidant solution was prepared by dissolving 5 g (0.022 mol) APS in 50 mL water. Both solutions were cooled to 0-4°C in an ice bath. The solutions were degassed with inert gas. The oxidant solution was then added dropwise to aniline salt solution through a dropping funnel under ultrasonic irradiation with a power of 100 W and operated at 40 kHz over a period of 1 h. The mixture was kept under ultrasonic irradiation for additional 6 h in 0-4°C to ensure completion of in situ polymerization.

After 6 h, the ultrasonication was stopped and a dark green powder was collected on a filter paper by filtration and washed several times with distilled water and methanol. The filtrate was dried in vacuum (50°C). The same procedure was repeated for preparation of PANI-starch blends with deferent ratios of aniline to starch (w/w%).

### Preparation of PANI/Starch/PS Conductive Composites

In a typical procedure, PANI/starch blend (1.5 g) was added to 20 mL of THF at room temperature and stirred for 30 min. The obtained dispersion solution was then mixed with 20 mL solution of polystyrene (PS) (2.5 wt%) in THF and stirred for additional 2 h at room temperature. Finally a homogeneous coating solution was obtained. The coating solutions were cast on glass plates to obtain smooth films and dried at room temperature for 48 h.

### Biodegradable Test of PANI/Starch/PS Composite

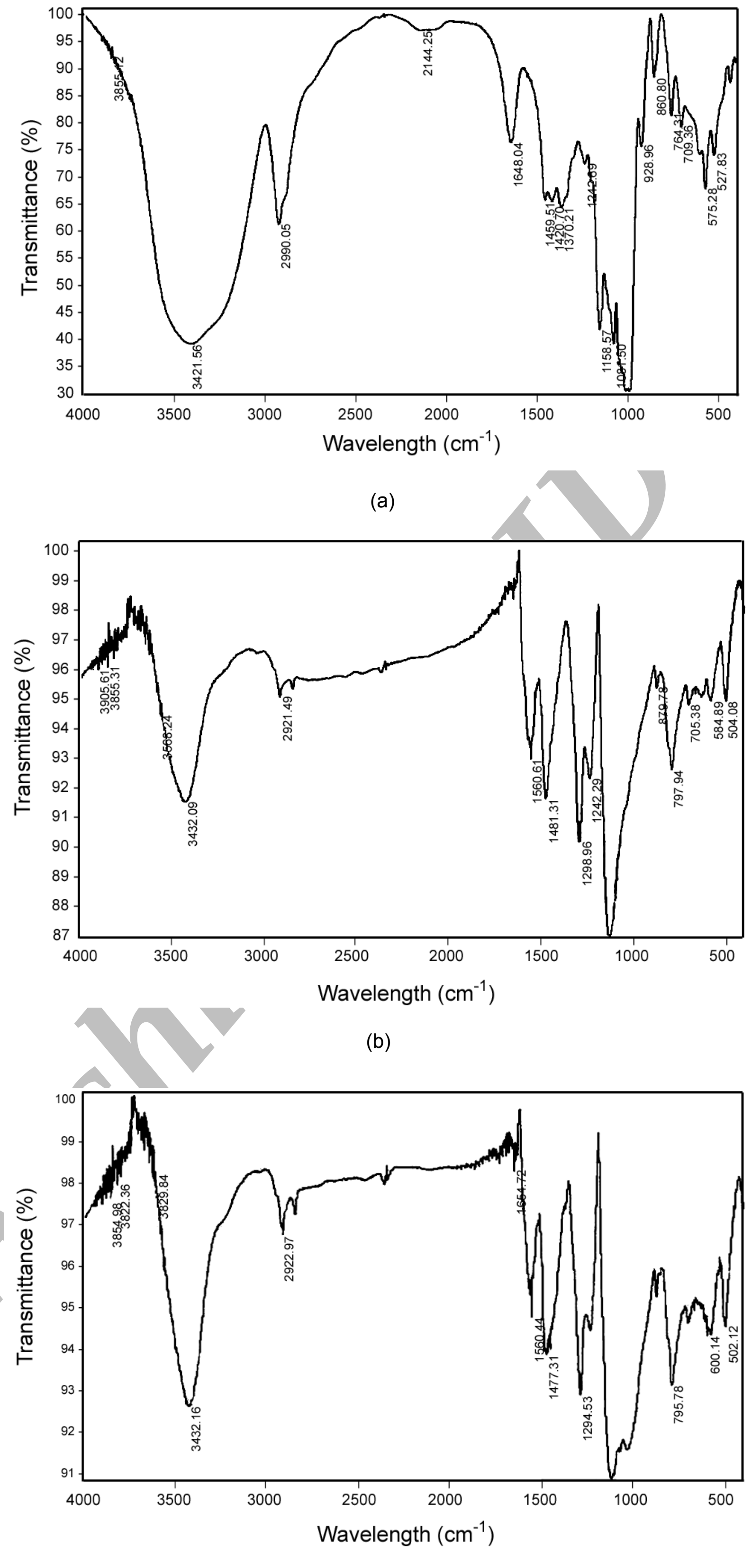
For demonstrating the biodegradable characteristics of PANI/starch/PS conductive composites, we placed the composite films in laboratory condition under perfect growth medium of soil born fungi. Biodegrada- bility test was carried out in Petri dishes of 8 cm diameter under relative humidity of 65% ± 5 and 25±2°C temperature. The gradual growth of mycelium and conidium production of most widespread genera of soil borne fungi (*Penicillium spp.*, *Aspergillus spp.*, and *Acremonium spp.,*) on composite pieces were observed after 1, 3 and 6 weeks.

## RESULTS AND DISCUSSION

The preparation of PANI/starch blends was carried out by in situ polymerization of aniline in the presence of aqueous starch solution in acidic medium.

### FTIR Analysis

The FTIR spectra of (a) pure starch, (b) PANI, and (c) PANI/starch blend are shown in Figure 1. The characteristic broad band for O-H group (in the presence of H-band) of starch appears at 3421 cm$^{-1}$. A



(a)

(b)

(c)

**Figure 1.** FTIR Spectra of (a) pure starch, (b) PANI, and (c) PANI/starch.

peak around 2930 cm$^{-1}$ is attributed to an asymmetrically stretching vibration of C-H band in pyranoid ring. The several absorption bands between 828-1158 cm$^{-1}$ are attributed to the contribution of various functional groups, such as C-O and C-O-C.

The typical feature of pure PANI is also well known in literature [21]. The peak corresponding to out-of-bending vibration of C-H band of *p*-disubstituted benzene ring appears at 797 cm$^{-1}$. The peaks around 1481 and 1560 cm$^{-1}$ result from stretching vibrations of N-B-N and N=Q=N structures, respectively (where -B- and =Q= stand for benzenoid and quinoid moieties in the PANI chains). The peaks at 1125 and 1298 cm$^{-1}$ due to vibrations of C-H and C-N stretching bands in benzene ring are being observed.

The characteristic absorption bands of pure starch (3432 cm$^{-1}$) and PANI (1560, 1477, 1294 and 795 cm$^{-1}$) have been both present in the spectrum of their blend, PANI/starch. Comparing the relative intensity band around 3432 cm$^{-1}$, we also find that the band of the stretching vibration of -OH group in the composite is apparently weaker than the same band in pure starch. Furthermore, the absorption peak at 3421 cm$^{-1}$ in the spectrum of pure starch is blue-shifted to 3432 cm$^{-1}$ in the spectrum of the composite. These phenomena confirm that starch is successfully activated by superfluous acids. The intermolecular hydrogen bonds are broken and the more hydrogen groups become accessible.

### UV-Vis Analysis

The UV-Vis spectrum of the blend is shown in Figure 2. Three bands are observed in the doped PANI/starch spectrum at 340, 415, and 800 nm. The bands are assigned as follows: $\pi$-$\pi^*$ transition of benzene rings in the first case and polaron bands in the last two cases, 415 nm is the typical transition between polaron and $\pi^*$ bands which is generally observed for emeraldine salts. The broad absorption band at 800 nm is assigned to the combination of transition from $\pi$ band to polaron band and "free-carrier tail" which stems from the formation of delocalized $\pi$ electrons.

The wavelength of the quinoid band plays an important role in switching polyaniline from an electric insulator to a conductor upon doping. In the PANI/starch blend, these last two bands are related to the doping process that is responsible for the polymer conductivity [13].

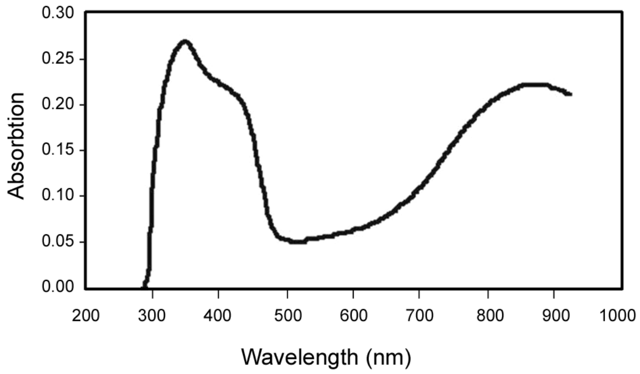


**Figure 2.** UV-Vis Spectra of the PANI/starch blend.

### SEM Analysis

In in situ polymerization of aniline in the presence of starch solution, ultrasonic irradiation has detrimental effect on polyaniline size and shape [21]. It is well known when the size of polyaniline granules is in the range of nanoscale, higher conductivity would be obtained. Figures 3a and 3b show scanning electron micrographs of PANI/starch blends prepared under ultrasonic irradiation. From these figures, it can be deduced that PANI/starch has granular structure in these blends and polyaniline is well dispersed in the starch matrix.

### XRD Analysis

It is very important to study the crystal structure of conductive PANI, because highly ordered chain structure of conductive polymer would endow highly electrical conductivity. Pouget et al. [22] investigated the crystal structure of PANI prepared through conventional polymerization in detail, suggesting a pseudo-orthorhombic crystal form. In the present study, we discuss the crystal structure of PANI component in a PANI/starch blend.

The XRD patterns of PANI/starch blend which was doped with HCl and PANI-HCl are shown in Figures 4a and 4b. It can be seen that pure PANI shows a typical noncrystalline pattern, while in the case of the PANI/starch blend, the XRD pattern shows nearly semicrystalline structure. In the XRD pattern

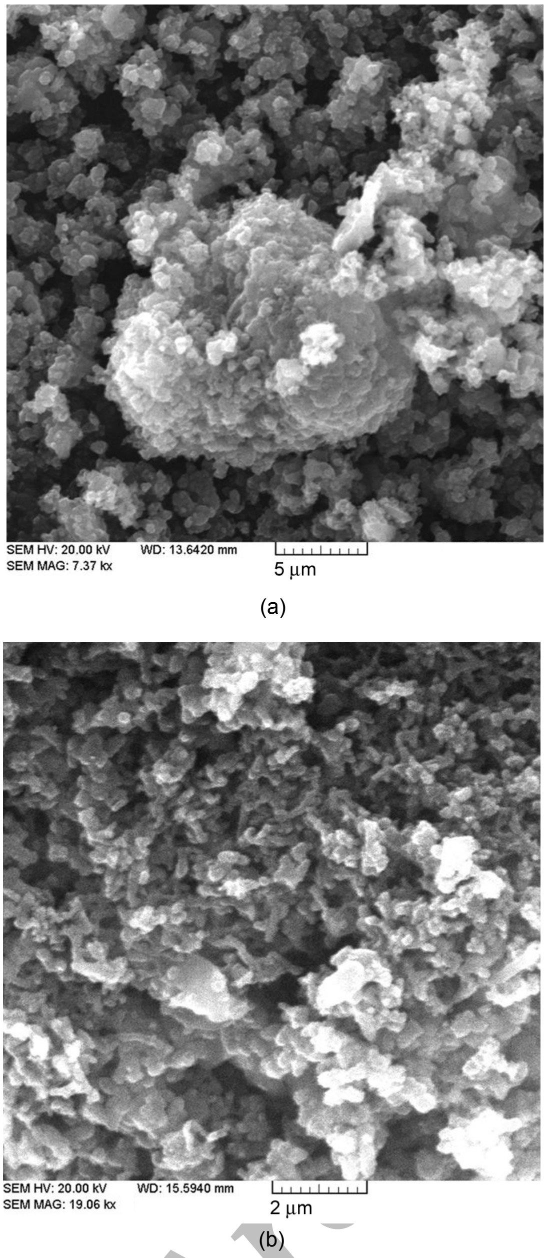


**Figure 3.** SEM Micrographs of PANI/starch blend at different magnifications: (a) ×734 and (b) ×1906.

of PANI/starch blend diffraction peaks at 2θ = 15.32°, 25.059° and 34.33° correspond to the emeraldine PANI. The peaks centered at 2θ = 15.32° and 25.059° are ascribed to the periodicity parallel and perpendicular to the PANI chains. From the XRD pattern of PANI/starch blend, the PANI has highly ordered crystal structure which is expected to exhibit high electrical conductivity.

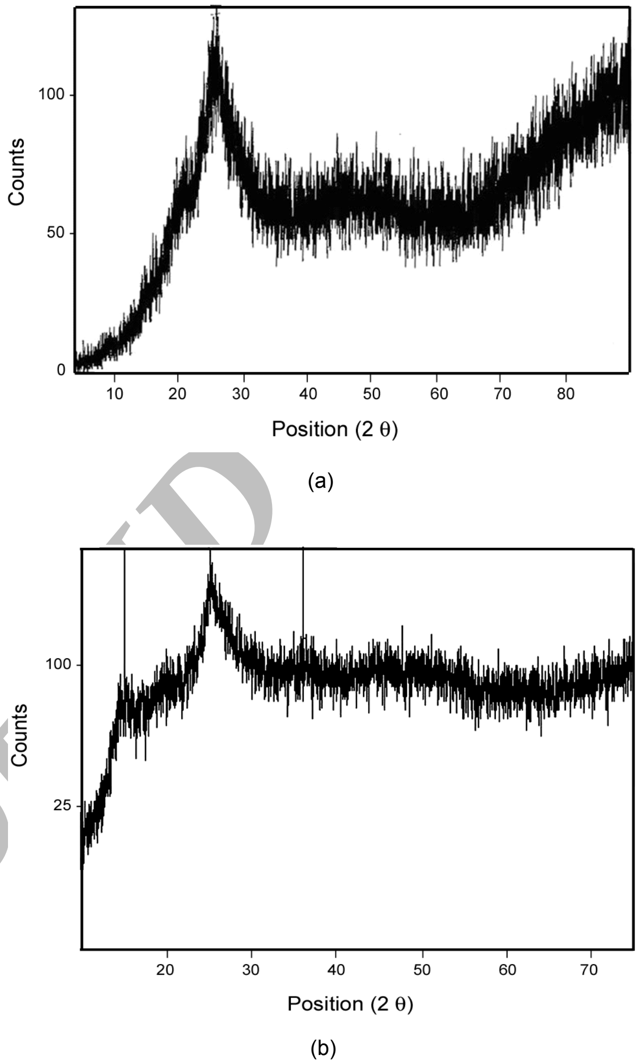


**Figure 4.** XRD Patterns of (a) PANI and (b) PANI/starch blend.

Comparing the XRD pattern of the blend with XRD pattern of polyaniline showed that the crystalline structure of has improved. The mean particles size can be calculated by the Scherrer equation as follows [23].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where $\lambda$ is the wavelength of X-ray source (Cu $K_a$=1.54056 Å), and $\beta$ is the full-width at half maximum (FWHM) of the X-ray diffraction peak at the diffraction angle $\theta$. Table 1 shows the mean diameter of PANI particles at various angles. The data show that the PANI nano-particles are present in the blend structure.

**Table 1.** Polyaniline mean diameter from Scherrer equation at different positions.

| Peak | Position Peak (2θ) | Height | FWHM (2π) | Diameter (nm) |
|---|---|---|---|---|
| 1 | 15.320 | 144.024 | 0.2387 | 33.62 |
| 2 | 25.059 | 142.040 | 0.4800 | 16.96 |
| 3 | 34.330 | 143.200 | 0.2972 | 28.05 |

**Table 2.** Conductivity results of PANI/starch synthesized under ultrasonic irradiation.

| Composites | Ratio of monomers in feed (aniline/starch) | Conductivity (S/cm) |
|---|---|---|
| 1 | 1/1 | 2.07 |
| 2 | 1/2 | 1.90 |
| 3 | 2/1 | 2.18 |

## Electrical Conductivity of the Blends

Four probe method was used for measurement of electrical conductivity of the prepared blends. For this purpose the powdered PANI/starch blend (0.5 g) was prepared in a pellet form (diameter: 13 mm, thickness: 1 mm) at pressure of 14 MPa.

The conductivity results of the blends, of various ratios of aniline to starch (w/w%), by ultrasonic irradiation or magnetic stirring are presented in Tables 2 and 3, respectively. Our results demonstrate that the higher the polyaniline content in the blends structure there is an increase in conductivity as well. Also, the conductive blends that were synthesized under ultrasonic irradiation showed higher conductivity compared to the blends synthesized via magnetic stirring. This effect can be interpreted by the fact that, ultrasonic irradiation of polymerization medium leads to production of polyaniline with greater dispersion and smaller particles size.

**Table 3.** Conductivity results of PANI/starch synthesized under magnetic stirring.

| Composites | Monomer feed ratio (aniline/starch) | Conductivity (S/cm) |
|---|---|---|
| 1 | 1/1 | 2.00 |
| 2 | 1/2 | 1.78 |
| 3 | 2/1 | 2.13 |

## Effect of Dopant Type

The electrical conductivity (EC) of PANI highly depends on the types of dopant, such as HCl, $H_2SO_4$, $H_3PO_4$, camphorsulphonic acid (CSA) and dodecyl benzene sulphonic acid (DBSA). These dopants were used for doping of polyaniline in blends of PANI/starch. The type of dopant which influenced the EC of the PANI/starch blends was investigated and the results are shown in Table 4.

It can be seen that the EC of the doped blends is increased by using dopants as follows: DBSA>HCl >CSA> $H_2SO_4$>$H_3PO_4$. The order could be attributed to anions ($HSO_4^-$) which is exclusively present in PANI/$H_2SO_4$. In other words, $H_2SO_4$ did not completely ionize to produce two hydrogen cations ($H^+$) and sulphate anion ($SO_4^{2-}$). This behaviour also confirms that the blends doped by dibasic acids were more protonated than the blends doped by monobasic acids.

Also, the acidity strength of these acids which are remarkably different has detrimental effect on the doping quality. At the same concentration, DBSA is markedly stronger than HCl. Similarly, $H_2SO_4$ is stronger than $H_3PO_4$. The weaker acids do not offer enough protonic hydrogen, thus, the doped PANI appears as unfavourable EC when the concentration

**Table 4.** Conductivity results of PANI/starch synthesized under ultrasonic irradiation re-doping with various dopants.

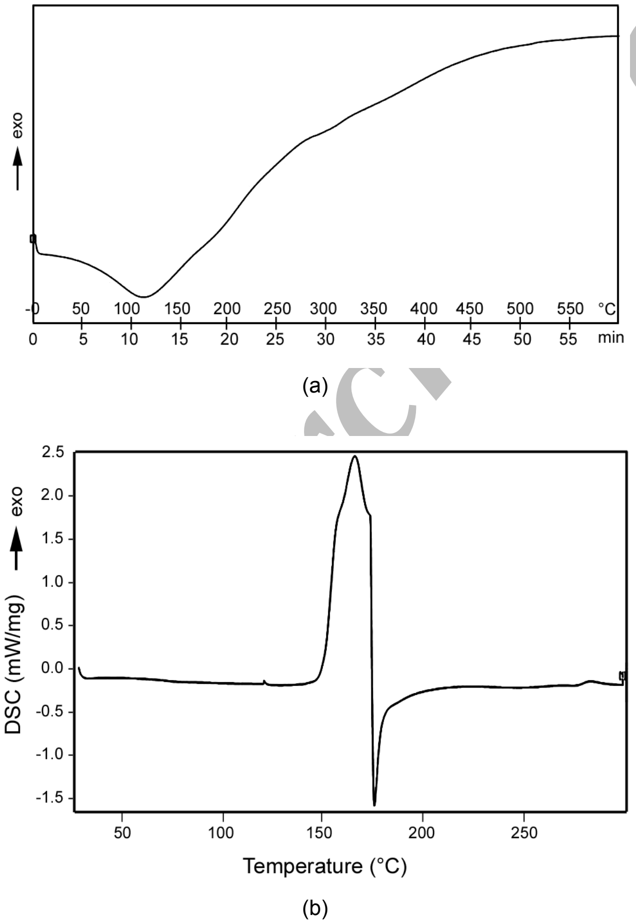
| Dopants | Monomer feed ratio (aniline/starch) | Conductivity (S/cm) |
|---|---|---|
| DBSA | 2/1 | 2.63 |
| HCl | 2/1 | 2.53 |
| CSA | 2/1 | 2.33 |
| $H_2SO_4$ | 2/1 | 2.20 |
| $H_3PO_4$ | 2/1 | 2.19 |

of oxidant is constant. It is also found that, the EC of PANI/$H_2SO_4$/starch is slightly lower than that of PANI/HCl/starch. Even there is a great difference in their concentration of hydrogen cations because hydrogen bands interaction may exist between $HSO_4^-$ and PANI chains. This result demonstrates that the better dopant for increasing blend conductivity is dodecyl benzene sulphonic acid (DBSA).

### Differential Scanning Calorimetry Analysis

In differential scanning calorimetry (DSC) analysis, a blend sample and an inert reference are heated under nitrogen atmosphere and thermal transitions of the sample are detected and measured.

Based on literature study it is well known that DSC curve of the starch shows a broad endothermic peak at 278°C with a glass transition temperature ($T_g$) observed at 146°C. The broad endothermic peak could be the result of the mixture of amorphous and crystalline phases in the starch structure [24].

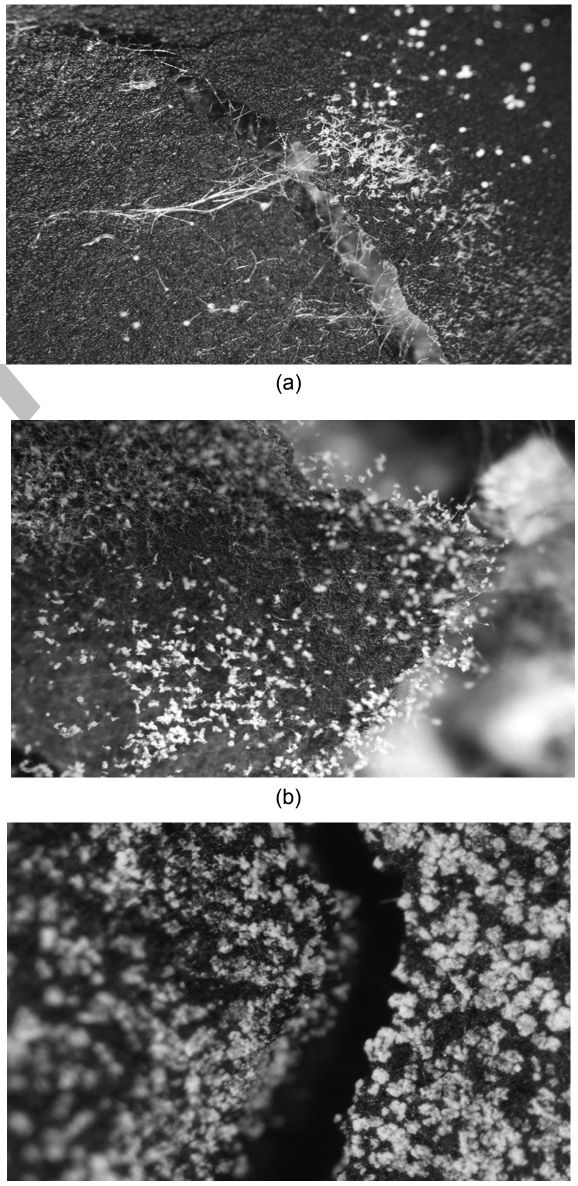


(a)

(b)

Figure 5. DSC curves of (a) polyaniline and (b) PANI/starch.

The DSC curves of polyaniline and PANI/starch blend were shown in Figures 5a and 5b, respectively. In the thermogram of PANI/starch blend one endothermic peak was observed at 168°C and $T_g$ at 120°C. It can be seen that PANI/starch has one endothermic peak, whereas polyaniline shows no endothermic peak. This is an indication of the presence of starch in the structure of the blend. Also, we observe the variation of glass transition temperature, $T_g$, indicating good miscibility of the blends' components.



(a)

(b)

(c)

**Figure 6.** Images of biodegradable conducting composite films penetrated with soil born fungi in several time durations: (a) one week, (b) three weeks, and (c) six weeks.

### PANI/Starch/PS Conductive Composite

The PANI/starch/PS conductive composite was obtained by physical solution blending of PANI/starch blend with polystyrene solution at room temperature. The inclusion of polystyrene in the blend structure increases the flexibility and mechanical strength of the obtained composites. The smooth films of PANI/starch/PS composite were obtained by evaporation of the organic solvent from a homogeneous coating solution spread on the surface of glass plate.

### Biodegradable Characterization

For demonstration of the biodegradable characteristics of PANI/starch/PS conducting composites, we placed the films of composites in a specific laboratory condition under soil born fungi effect. Biodegradability test was carried out in Petri dishes under relative humidity (RH) of 65% ±5 and temperature of 25±1°C. Gradual fungi vegetative growth with mycelium and conidium production on PANI/starch conducting composite demonstrated that the composite is potentially biodegradable. Mycelium growth and conidium production on composite pieces was observed within 1, 3 and 6 weeks intervals. Images of biodegradable conducting composite films penetrated with soil born fungi in several times are shown in Figure 6. The result of this work demonstrates that, the conducting composite is a suitable medium for fungi growth.

## CONCLUSION

In the present paper, PANI/starch conductive blends were prepared by in situ polymerization of aniline in presence of aqueous starch solution activated by hydrochloric acid under magnetic stirring or ultrasonic irradiation. The ultrasonic irradiation has considerable effect on the morphology and conductivity of obtained blends. Preparation of polyaniline/starch/ polystyrene blends was meanwhile performed. Conductivity of the blends was increased by increasing the PANI content in the blend structure. The characterization of blends was carried out by FTIR, UV-vis, SEM, XRD and DSC analysis. The differential scanning calorimetric study indicated that polyaniline/starch blends were more stable than pure starch. Also, the result of this work demonstrated that the best dopant for increasing the conductivity of blends is dodecyl benzene sulphonic acid (DBSA). The result of this work demonstrates that, the prepared conducting composites are suitable medium for fungi growth. Finally, we have provided a facile method for the synthesis of polyaniline/starch/ polystyrene conductive composites with biodegradable properties.

## REFERENCES

1. Soares BG, Leyva ME, Barra GMO, Khastgir D, Dielectric behavior of polyaniline synthesized by different techniques, *Eur Polym J*, **42**, 676-686, 2006.
2. Ahmeda AA, Mohammada F, Rahman MZA, Composites of polyaniline and cellulose acetate: preparation, characterization, thermo-oxidative degradation and stability in terms of DC electrical conductivity retention, *Syn Metals*, **144**, 29-49, 2004.
3. Mo Z-L, Zhao Z-L, Chen H, Niu G-P, Shi H-F, Heterogeneous preparation of cellulose-polyaniline conductive composites with cellulose activated by acids and its electrical properties, *Carbohyd Polym*, **75**, 660-664, 2009.
4. Bai H, Chen Q, Li C, Lu CH, Shi GQ, Electrosynthesis of polypyrrole/sulfonated polyaniline composite films and their applications for ammonia gas sensing, *Polymer*, **48**, 4015-4016, 2007.
5. Bolaos JF, Felizn B, Heredia A, Rodryguez R, Guillen R, Jiménez A, Steam-explosion of olive stones: hemicellulose solubilization and enhancement of enzymatic hydrolysis of cellulose, *Bioresource Tech*, **79**, 53-61, 2001.
6. Yavuz AG, Uygun A, Bhethanabotla VR, Substituted polyaniline/chitosan composites: synthesis and characterization, *Carbohyd Polym*, **75**, 448-453, 2009.
7. Pron A, Zagorska M, Nicolauc Y, Genoud F, Nechtschein M, Highly conductive composites of polyaniline with plasticized cellulose acetate, *Syn Metals*, **84**, 89-90, 1997.
8. Walter A, Banka E, Genoud F, Pron A,

Nechtschein M, Electronic transport in composites based on polyaniline blended with cellulose acetate-a DC-conductivity and ESR analysis, *Syn Metals*, **84**, 753-754, 1997.

9. Xiao CM, Tan J, Xue GN, Synthesis and properties of starch-*g*-poly(maleic anhydride-*co*-vinyl acetate), *Express Polym Lett*, **4**, 9-16, 2010.
10. Arvanitoyannis I, Nakayama A, Aiba S, Chitosan and gelatin based edible films: state diagrams, mechanical and premeation properties, *Carbohyd Polym*, **37**, 371-382, 1998.
11. Ismail YA, Shin SR, Shin KM, Yoon SG, Shon K, Kim SI, Electrochemical actuation in chitosan/polyaniline microfibers for artificial muscles fabricated using an in situ polymerization, *Sens Actuator B Chem*, **129**, 834-840, 2008.
12. Lu DR, Xiao CM, Xu SJ, Starch-based completely biodegradable polymer materials, *Express Polym Lett*, **3**, 366-375, 2009.
13. Xiaofei M, Peter R, Chang B, Jiuga Y, Wang N, Preparation and properties of biodegradable poly(propylene carbonate)/thermoplastic dried starch composites, *Carbohyd Polym*, **71**, 229-234, 2008.
14. Imam SH, Gordon SH, Shogrenr L, Tosteson TR, Goviden NS, Greene RV, Degradation of starch-poly(β-hydroxybutyrate-*co*-β-hydroxyvalerate) bioplastic in tropical coastal waters, *Appl Environ Microb*, **65**, 431-437, 1999.
15. Peng SW, Wang XY, Dong LS, Special interaction between poly (propylene carbonate) and corn starch, *Polym Compos*, **26**, 37-41, 2005.
16. Ge XC, Li XH, Zhu Q, Preparation and properties of biodegradable poly(propylene carbonate)/starch composites, *Polym Eng Sci*, **44**, 2134-2140, 2004.
17. Ma XF, Yu JG, Zhao A, Properties of biodegradable poly(propylene carbonate)/starch composites with succinic anhydride, *Compos Sci Tech*, **66**, 2360-2366, 2006.
18. Ge XC, Xu Y, Meng YZ, Thermal and mechanical properties of biodegradable composites of poly(propylene carbonate) and starch-poly(methyl acrylate) graft copolymer, *Compos Sci Tech*, **65**, 2219-2225, 2005.
19. Kim SH, Kim YH, Biodegradable polymer blends of poly(*L*-lactic acid) and gelatinized starch, *Polym Eng Sci*, **40**, 2539-2550, 2000.
20. Nazarzadeh Zareh E, Azariyan E, Najafi Moghadam P, Heterogeneous preparation of starch-polyaniline conductive composite, *9th Int Sem Polym Sci Technol (ISPST)*, Tehran, Iran, 17-21 Oct 2009.
21. Liu H, Hu XB, Wang JY, Boughton RI, Structure, conductivity, and thermopower of crystalline polyaniline synthesized by the ultrasonic irradiation polymerization method, *Macromolecules*, **35**, 9414-9419, 2002.
22. Pouget JP, Jozefowicz ME, Epstein AJ, Tang X, MacDiarmid AG , X-ray structure of polyaniline, *Macromolecules*, **24**, 779-789, 1991.
23. Jeon HJ, Yi SC, Oh SG, Preparation and antibacterial effects of Ag-$SiO_2$ thin films by sol-gel method, *Biomaterials*, **24**, 4921-4928, 2003.
24. Janarthanan P, Yunus WMZW, Bin Ahmad M, Thermal behavior and surface morphology studies on polystyrene grafted sago starch, *J Appl Polym Sci*, **90**, 2053-2058, 2003.