Sains Malaysiana 45(7)(2016): 1169–1176

Characterization of HEC/PANI Film as a Potential Electroactive Packaging with pH Sensor

(Pencirian Filem HEC/PANI sebagai Potensi Pembungkus Elektroaktif dengan Pengesanan pH)

NOORANIS MUSTAPHA, NOZIEANA KHAIRUDDIN, IDA IDAYU MUHAMAD*,
SHAHRIR HASHIM & MD. BAZLUL MOBIN SIDDIQUE

ABSTRACT

Interest in the use of intelligent packaging systems for food products has increased in recent years. Intelligent packaging systems are those that monitor the condition of packaged foods to give information regarding the quality of the packaged food during transport and storage. The potential of HEC/PANI film as pH indicator and pH sensor were evaluated. HEC/PANI film was prepared by solution blending and casting method. Fourier transform infrared (FTIR) spectroscopy showed that there was no chemical interaction between HEC and PANI. The film properties were retained chemically. The electrical conductivity increment from 1.14×10^{5} *to* 2.2×10^{5} *S/cm was observed when PANI was incorporated into the HEC film matrix. Field emission scanning electron microscopy (FESEM) showed that the electrical conductance network of PANI was formed in HEC/PANI film. The electrical sensitivity of the film has been studied with I-V characterization. The changes in color and current of HEC/PANI film on interaction to pH buffer 1-14 shows its suitability as pH indicator and pH sensor for food.*

Keywords: Intelligent packaging; hydroxyethylcellulose; pH indicator; pH sensor; polyaniline

ABSTRAK

Kepentingan dalam penggunaan sistem pembungkusan pintar bagi produk makanan telah meningkat sejak kebelakangan ini. Sistem pembungkusan pintar adalah pemantauan keadaan makanan yang dibungkus untuk memberikan maklumat mengenai kualiti makanan yang dibungkus semasa pengangkutan dan penyimpanan. Potensi HEC/PANI filem sebagai penunjuk pH dan sensor pH dinilai. HEC/PANI filem disediakan oleh pengadunan larutan dan kaedah tuangan. Transformasi Fourier inframerah (FTIR) spektroskopi menunjukkan bahawa tidak ada interaksi kimia antara HEC dan PANI. Ciri-ciri filem dikekalkan secara kimia. Peningkatan kekonduksian elektrik dari 1.14×10^{5} *kepada* 2.2×10^{5} *S/cm diperhatikan apabila PANI telah dimasukkan ke dalam filem matriks HEC. Pancaran medan mikroskop elektron imbasan (FESEM) menunjukkan bahawa rangkaian konduktans elektrik PANI terbentuk dalam filem HEC/PANI. Kepekaan filem elektrik telah dikaji dengan pencirian I-V. Perubahan dalam warna dan filem semasa HEC/PANI pada interaksi untuk penampan pH 1-14 menunjukkan kesesuaiannya sebagai penunjuk pH dan sensor pH untuk makanan.*

Kata kunci: Hidroksietilselulosa; pembungkusan pintar; pengesan pH; penunjuk pH; polianilina

INTRODUCTION

The most commonly encountered definition of intelligent packaging is provided by the European study 'Evaluating Safety, Effectiveness, Economic-environmental Impact and Consumer Acceptanceof Active and Intelligent Packaging (ACTIPAK-FAIRCT 98-4170, 1999-2001) as 'systems that monitor the condition of packaged foods to give information about the quality of the packaged food during transport and storage'. Many intelligent packaging concepts involve the use of sensors and indicators. A sensor is defined as a device used to detect, locate or quantify energy or matter, giving a signal for the detection or measurement of a physical or chemical property to which the device responds (Kress-Rogers 2001). Research and development of sensor technology has, until recently, been largely concentrated in biomedical and environmental applications (Demas et al. 1999). The specifications of such sensors are, however, quite different from those required for food packaging applications. The development of improved methods to determine food quality such as freshness, microbial spoilage, oxidative rancidity or oxygen and/or heat induced deterioration is extremely important to food manufacturers. An indicator may be defined as a substance that indicates the presence or absence of another substance or the degree of reaction between two or more substances by means of a characteristic change, especially in colour. In contrast with sensors, indicators do not comprise of receptor and transducer components and communicate information through direct visual change.

The oldest and most studied conducting polymers (CP) is polyaniline (PANI) (Lethaby 1862), which was reported as early as 1862, but rediscovered in the late 1970s and early 1980s. The advantages of PANI, compared to most other CPs, are its easy preparation procedure in acidic aqueous solutions, an in expensive monomer, high stability, process ability and solubility in common organic solvents, which allows for the blending of PANI with other bulk polymers. Some application areas of PANI were displays (LEDs), light weight batteries, antistatic materials, corrosion inhibitors and ion sensors (Yam 1995). It is well known that the chemistry of PANI is more complex than that of other CPs. PANI has a variety of oxidation states that are both pH and potential dependent. It is generally agreed that PANI exists in three different base forms: leucoemeraldine (LEB, fully reduced), emeraldine (EB, half-oxidised) and pernigraniline (PNB, fully oxidised) (Elsayed et al. 2011; Lindfors & Ivaska 2002). The only electrically conducting form is, however, the emeraldine salt (ES), which is the protonated form of EB. In contrast to other CPs, protons must thus be added to the PANI backbone in order to make it electrically conductive. The EB form of PANI can be protonated with sufficiently strong acids to ES due to the presence of basic sites (amine and imine groups) in the polymer structure (Lindfors & Ivaska 2002). The protonation process is reversible and the pH sensitivity of PANI is based on the equilibrium shown in Figure 1, which is also valid for alkyl substituted PANIs. The EB and ES forms are indicated in Figure 1 with (I) and (II), respectively. The strong pH sensitivity of PANI makes it most suitable as a membrane material for all-solid-state pH sensors.

Recently, films obtained from grafting reaction of hydroxyethyl cellulose (HEC) with oligoether-based diisocyanates and alkali salts have been proposed as polymer electrolytes (Pringsheim 1997). Cellulose is one of the world's most abundant, renewable and biodegradable natural polymer. Its mechanical properties, modest price, low density and organic character which allows further chemical modifications, made this macromolecule and its derivatives (as HEC) interesting to be processed as polymeric films.

In this research, the use of HEC/PANI film as pH indicator and pH sensor enabled the detection of milk spoilage. The film works based on pH increase resulting from the basic amines gradually produced by the spoilage process in the package. As a consequence, colour will change from green to blue, which is easily visible to the naked eyes.

EXPERIMENTAL DETAILS

MATERIALS

Ammonium persulphate (APS), hydrochloric acid (HCl) and aniline were all purchased from BDH chemicals. N-methyl pyrrolidone and HEC was obtained from Merck. Glycerol as a plasticizer was bought from Hmbg Chemicals (Malaysia). Standard buffer pH (2-14) was from Aldrich. All materials were used without further pretreatment.

METHODS

SYNTHESIS OF PANI

Green PANI (ES) was synthesized by chemical oxidation reaction which is the most feasible route to obtain large scale polyaniline production. The method was provided by Sunendar et al. (2008). 1.82 mL of aniline (20 mmol) was dissolved in 50 mL of 1 M HCl solution. 5.71 g APS (25 mmol) in 50 mL of water was added into the solution. The solution was stirred and left 24 h to polymerize. Green polyaniline was collected on a filter and washed with acetone, then dried in oven at 60°C. The solubility of the undoped of blue polyaniline (EB) is higher in a number of organic solvents than that of the doped form (green polyaniline). Therefore green polyaniline was converted into blue polyaniline using method by Thangaratinavelu et al. (1994). Green polyaniline (0.12 g) was placed in a 100 mL round-bottom flask. In order to transform green polyaniline to the blue polyaniline form, 3% solution of NH OH was added to green polyaniline powder and stirred until the colour of the powder changed from green to blue which indicates that blue polyaniline is formed. The suspension was stirred for 2 h and left for 48 h at room temperature to react well. Blue polyaniline that precipitated was collected on a filter and dried in oven at 60°C.

FILM PREPARATION

HEC/PANI film was formed by casting method. The films were prepared by slightly modifying the method provided by Mitchell and Murphy (1972). 9 g of HEC was dissolved in distilled water with stirring. After the solution was completely dissolved, 5 mL glycerin (HmbG Chemicals)

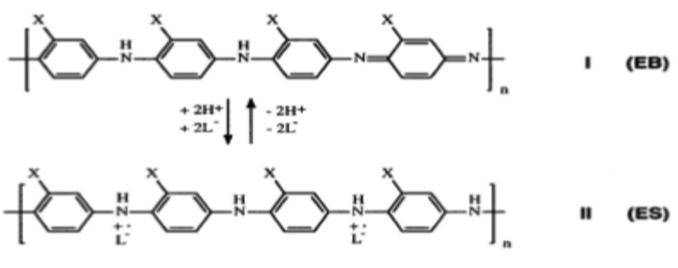


FIGURE 1. Schematic diagram and reaction process of protonation and deprotonation of PANI

was added as plasticizer and the mixture was heated slowly to a mild boiling at around 80°C. Polyaniline solution with 0.01 g/mL was mixed in the film solution at 3% (w/v). 10 mL of the film mixture was pipetted into petri dishes (100 mm diameter by 15 mm depth). The petri dishes were placed for 24 h in an oven (Memmert) set at 80°C. A thin transparent greenish film will thus be obtained. The films were placed in a desiccator. Silica gel was continually renewed allowing the samples to dry for one week before they were used for characterization (Osman et al. 2001).

FILM CHARACTERIZATION THROUGH FTIR AND FESEM

In this study, FTIR spectroscopy was used to study the characteristic vibration of the spesific bonds. These spesific bonds have their own wave numbers. FTIR spectroscopy measurements were carried out and recorded on a Perkin-Elmer Spectrum One FT-IR Spectrometer. FTIR analysis was performed with a resolution of 4 cm^{-1} in the range of 4000-400 cm^{-1} and was averaged over 16 scans.

Microstructural analysis was performed with a field emission scanning electron microscope (JEOL-JSM-7401F, Tokyo, Japan). It is critical that a cross-sectional cut be made in such a way as to minimize distortion of films morphology. Mechanical cut using devices such as a sharp razor blade creates compression, tearing and plastic deformation on the surface which severely distorts the fine structures of film surface. For this study, the sample films were prepared using the most commonly approach method which is to immerse the film samples in liquid nitrogen to make the material brittle and then quickly snap the film using forceps (Cao et al. 2007). Film pieces were mounted on aluminum stubs using a doublesided tape and coated with a 2-nm layer of platinum at 20 mA for 45 s and examined using an accelerating voltage of 2 kV.

APPLICATION: DETECTION OF MILK SPOILAGE

About 100 mL of UHT milk was used as samples in this study. The milk was stored in a closed container at different temperature of 25, 29, 37 and 43°C for 42 h. The pH of milk was recorded every 3 h and the conductivity of the HEC/PANI was measured using impedence (HP 4192A) analyser at initial condition, after 21 and 42 h. A graph was plotted for pH versus conductivity value at each storage temperature.

CONDUCTIVITY MEASUREMENT

Conductance is the reciprocal of resistance and therefore, the ease with which an electric current flows through the material. The standard unit of conductance is the siemens (abbreviated S), formerly known as the mho (a reciprocal ohm). When a current of 1A passes through a component across which a voltage of 1 V exists, then the conductance of that component is 1 S. Conductance (S/cm) is generally reported as a bulk property in conductive materials (Finkenstadt 2005).

For electronic conductivity measurement, impedence analyser was used with two probes at ambient temperature in the frequency range between 50 mHz and 100 kHz. The PANI pellet (100 ± 10 mg) with 1.33 cm in diameter and 0.07 ± 0.003 cm in height was produced by applying a pressure of 700 kg/cm^3 to PANI powder using a pump following the method reported by Wibowo et al. (2008). The measurement was carried out at temperature between 30 and 100°C for evaluation of temperature dependent conductance.

RESULTS AND DISCUSSION

FTIR ANALYSIS

FTIR spectroscopy was used to examine the interaction between HEC and polyaniline. The infra red spectra of HEC and HEC/PANI are shown in Figure 2. In the spectrum of HEC film, the broad band at 3391 cm^{-1} was the OH stretching. The peak at 2924 cm^{-1} corresponded to the C-H stretching, while the band at 1046 cm^{-1} and was assigned to the stretching vibration of C-O in C-O-C groups. Normally, when two or more substances were mixed, physical blends versus chemical interactions were reflected by the changes in characteristics spectral peaks (Guan et al. 1998; Yin et al. 1999). But in this study, the addition of PANI into the HEC did not change the original spectra peak of the based film. This showed that, there was no chemical interaction between PANI and HEC. The film properties were retained chemically. HEC/PANI film shows the band at 3355 cm^{-1} that was assigned to the stretching of N-H, representative of PANI in the film.

CONDUCTIVITY

Table 1 shows the electrical conductivity of HEC film and HEC/PANI film at room temperature. Electrical conductivity also refers to ion conductivity (Yoshida et al. 2002). Aday and Caner (2010) suggested that a large number of parameters, such as ionic strength, temperature, free water and solid content could give a significant influence on the electrical properties. The results showed incorporation of PANI into the HEC films increased the ion conductivity for both films. The increase of conductivity of the HEC/PANI film seems more than double, from its initial conductivity of the films without PANI.

FESEM MICROSCOPY

In order to understand the changes occurring to the conductivity, it was thought of interest to investigate the morphological features, in particular, the distribution of PANI in HEC film. Field emission scanning electron microscopy (FESEM) was used to image the nanostructure on the HEC/PANI film at the micrometer length scale. Figure 3 shows the FESEM images of the surfaces of nanocomposite films of HEC/PANI. Figure 3(a) shows morphology structure of HEC film with no loading of PANI. HEC exists in the form of granules, while a continuous phase is formed and only a few residual small granules appear in HEC film. It appeared

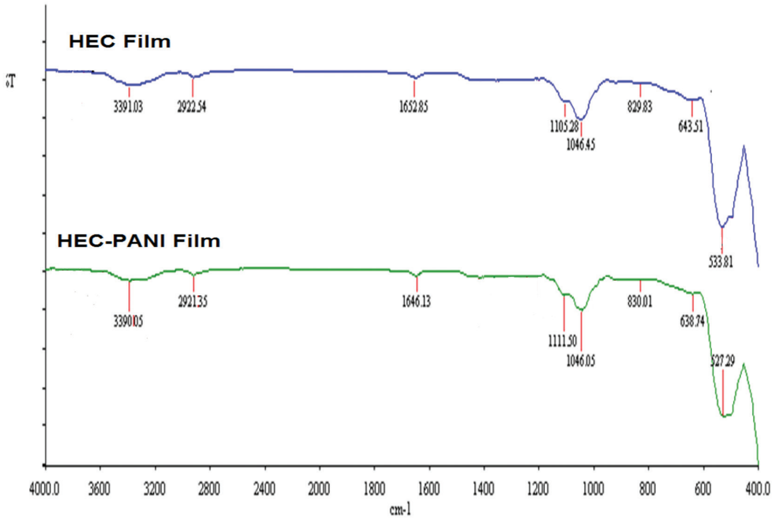


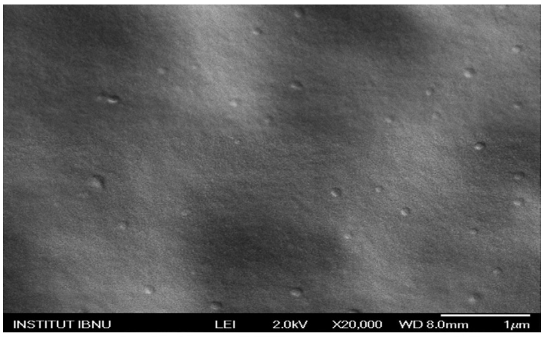
FIGURE 2. FTIR spectrum of HEC and HEC/PANI film

TABLE 1. Electrical conductivity of HEC film and HEC/PANI film at room temperature

Film	Conductivity (S/cm)
HEC	1.14×10^{-5}
HEC/PANI	2.20×10^{-5}

that only a very little of HEC did not melt during heating which was similar to the findings by Ramsay et al. (1993). Because of the stress and high temperature, HEC granules were molten or physically broken up and the continuous phase (i.e. HEC plasticization) was formed. There was no large aggregate and a homogeneous distribution of the HEC in the glycerol plasticized HEC film were observed, implying good adhesion between glycerol and HEC. This is attributed to the good compatibility resulting from the chemical similarities between starch and cellulose and the hydrogen bonding interactions existing in the interface between fillers and matrix (Cao et al. 2008).

In Figure 3(b), the nanoparticles of PANI were dispersed in the continuous HEC rich matrix and loosely adhering to it. The PANI aggregates formed network connection in HEC/PANI film. A high-structure PANI composed of many primary nanoparticles fuses together in a grape-like aggregate. During the casting, the high surface tension of PANI aggregates lead to flocculation in the quiescent melt (Yu et al. 2005). Flocculation makes PANI particles connect with each other and promotes the formation of a connected network, i.e. the electrical conductance network (Ma et al. 2008).



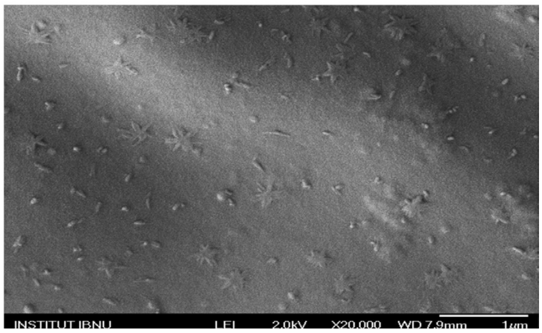


FIGURE 3. Field emission scanning electron microscopy of a (a) HEC film and (b) HEC/PANI film

I-V CHARACTERISTIC

A DC voltage sweep (-20 to 110 V) was applied to HEC and HEC/PANI films and the resulting current through the films was measured. The data obtained from these experiments can be seen in Figure 4.

The linear regression correlation coefficients was superior to 1.0 for both HEC and HEC/PANI film. Consequently, we can assume that the films showed a linear behavior from -20 to 110 V. The slopes of these linear regressions help us to compare the respond of electrical sensitivity of the films. The value of slope and correlation regression coefficients of the film was summarized in Table 2. Thus it appeared that HEC/PANI gave a better sensitivity to the electrical responses than HEC film. This characteristic will ensure that the film can function well as a sensor.

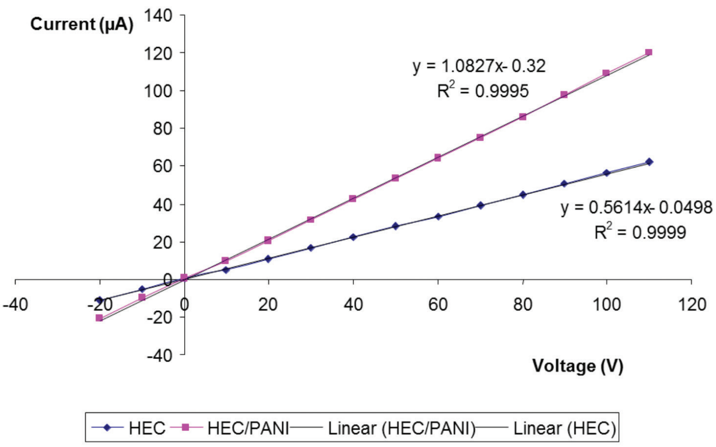


FIGURE 4. Current-Voltage characteristics of HEC and PANI/HEC films

TABLE 2. The slope and Correlation coefficient of film

Film	Slope of I (μA) = *f* (V) (in μA/ V unit)	Correlation coefficient (R^2)
HEC	0.5614	0.9999
HEC/PANI	1.0827	0.9995

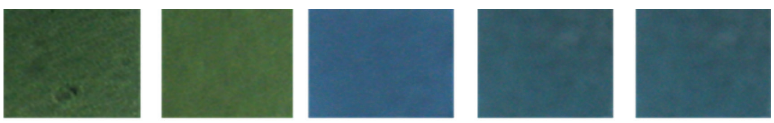
EFFECT OF pH

pH Indicator After each buffer was applied to the films, the change in color were recorded. The reaction between the films and the ions in the test buffers was instant. Figure 5 shows the dependence of color of HEC/PANI film at the different pH, respectively.

The color of PANI was much stronger than HEC/PANI since we only incorporated 3% of PANI into the HEC film. The color of PANI and HEC/PANI was observed ranging from green to yellow depending on the pH value. This behavior was suitable to be applied as pH indicator. The spoilage of milk and meat were easily detected by the changes of the color (Piletsky et al. 2006). As milk turns sour, lactic acid was released which caused a transition from blue to green. Other species such as ascorbic acid will also lead to colour changes due to oxidation/reduction reactions. Previous study showed that polyaniline has been converted from its initial green into blue by decomposing meat, due to the amines released (Piletsky et al. 2006).

pH Sensor The conductivity versus the pH values for the HEC/PANI film is shown in Figure 6. This measurement was used to evaluate the sensitivity of the film towards the changes of pH from 1-14. The responses of current measured at different pH can be modeled by polynomial regression. The model gives good agreement (R^2>90%) and can accurately represent the relationship between the current of the HEC/PANI film and pH values (1 to 14).

The conductivity increased both in strong acidic and strong basic conditions, which was attributed to the increse in the H^+ or OH^- concentrations. The conductivity value of the HEC/PANI film changes from 2.0×10^5 to 1.61×10^5 S/cm by varying buffer pH2-14 and this aspect can be utilized in the design of a pH sensor. It was found that the films demonstrated the highest conductivity value at pH2. The PANI behaves very similar to as if it were in ES form in pH range of 2 to 4 while at higher pH, deprotonation becomes favoured so the sensor response becomes better within the two ranges, 4 and below as well as 8 and above. This finding is in line with the result reported by Lindfors and Ivaska (2002). The degree of protonation and resulting electric conductivity thus become a function of pH. This implied that the degree and nature of cations which was an indirect consequence of the pH effect might have the influence on the properties of PANI.



pH1 pH4 pH7 pH10 pH14

FIGURE 5. The color of the HEC/PANI film at different pH

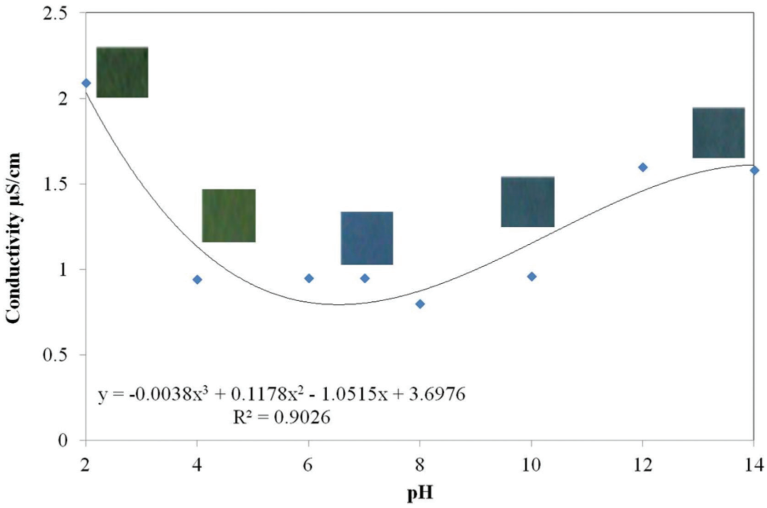


FIGURE 6. Variation in conductivity of the HEC/PANI film with the changes in pH

Application: Detection of Milk spoilage The results of the experiments conducted on it showed that the developed HEC/PANI film can be successfully used to detect changes that correlate between temperature and pH value in a defined condition. The theory of HEC film also supports the fact. Moreover, the efficiency of this film was tested using an application on milk storage in order to identify the sensitivity, accuracy and stability of the film indicator over the reducing freshness of milk vs time function.

Figure 7 shows the effect of storage temperature on the pH of milk as function of temperature. Storage temperatures of 10, 25, 29, 37 and 43°C were used in this study. It can be seen from the result obtained that the storage temperature of milk gives a significant effect to the pH of milk within 42 h of storage time. The pH of the tested milk and the corresponding conductivity of HEC/PANI film were recorded as in Figures 7 and 8, respectively. The same pattern was observed for both of the graph of effect of storage temperature on pH of milk and conductivity of HEC/PANI film. The milk stored at low temperatures (10 and 25°C) does not show any changes for both the pH of milk and film conductivity after 42 h of storage. When milk was stored at 29°C, the pH and conductivity of the film starts to change after 33 h of the storage. When the storage temperature was further increased to 37˚C, the change of the pH of milk was detected after 6 h of the storage. The milk stored at 43°C also showed a reduction from its initial pH after 21 h.

Milk and dairy products that have a pH of 6.6 were generally very rich in nutrients which provide an ideal growth environment for many microorganisms which have an almost neutral pH optimum (pH6-7.5)(Wouters et al. 2002). This comes in good agreement with the results that show changes of the pH/conductivity affected by the changes of temperature due to the growth of microorganism. According to Gunasakera et al. (2003) and Huang (2002), the temperature of 37°C is the optimum temperature for *Pseudomonas* spp. and *Staphylococcus*

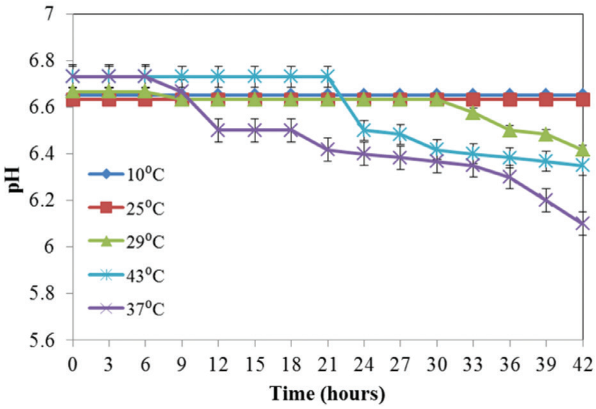


FIGURE 7. Changes in pH of milk due to the variation of aging and temperature

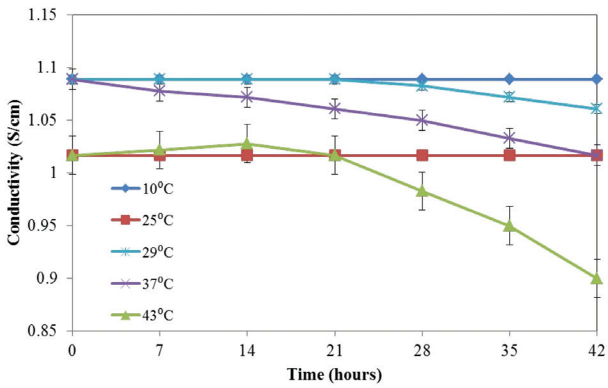


FIGURE 8. Difference in conductivity of HEC/PANI film at different temperature as a function of time

aureus ssp. Anaerobius is the most important organism contributing to the milk spoilage through the production of lipolytic and proteolytic enzymes. Microorganism have an optimum temperature for growth of about 37°C (Wouters et al. 2002). This statement can explain well why the changes of pH and conductivity of the HEC/PANI were detected earlier at 37°C. The storage temperature of 29°C and 43°C were also possible for the microbial growth but in a slower mode. So, the changes in the pH of milk and film conductivity at 29°C and 43°C were much slower than that at 37°C.

CONCLUSION

The HEC/PANI film was prepared by solution blending and casting method. The conductivity measurement and field emission scanning electron microscopy (FESEM) showed the electrical behaviour of PANI in the HEC/PANI film and it was in agreement with the FTIR. I-V characterization indicated that the film is sensitive to electrical responses. It was also possible to tune the pH sensitivity of HEC/PANI by using different pH buffer. The changes in color and electrical response were observed at different pH. It was suitable to be applied as pH indicator and pH sensor. Finally, the application of film indicator in milk storage demonstrated some useful findings for further study. However, the HEC-PANI film was not suitable for use as indicator of the ready-made food such as milk. That was due to the fact that the release of PANI into the food might caused toxicity, whilst, it was the perfect choice to detect the spoilage of raw food such as fish because it was usually washed and cooked before eaten. Recent study from Kuswandi et al. (2012) showed the effectiveness of PANI film as an indicator to detect the spoilage of fish. PANI film also appeared suitable to detect food spoilage that occurred in a large pH range.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by the Ministry of Science, Technology and Innovation Malaysia and Research Management Centre, UTM.

REFERENCES

Aday, M.S. & Caner, C. 2010. Understanding the effects of various edible coatings on the storability of fresh cherry. *Packaging Technology and Science* 23: 441-456.

Cao, X., Chang, P.R. & Huneault, M.A. 2007. Preparation and properties of plasticized starch modified with poly (ε-caprolactone) based waterborne polyurethane. *Carbohydrate Polymers* 71(1): 119-125.

Cao, X., Chen, Y., Peter, R., Chang, P.R., Stumborg, M., Michel, A. & Huneault, M.A. 2008. Green composites reinforced with hemp nanocrystals in plasticized starch. *Journal of Applied Polymer Science* 109(6): 3804-3810.

Demas, J.N., DeGraff, B.A. & Coleman, P.B. 1999. Oxygen sensors based on luminescence quenching. *Analytical Chemistry* 71: 793-800.

Elsayed, A.H., Elden, M.S., Elsyed, A.M., Elazm, A.H., Younes, E.M. & Motaweh, H.A. 2011. Synthesis and properties of polyaniline /ferrites nanocomposites. *International Journal of Electrochemical Science* 6: 206-221.

Finkenstadt, V.L. 2005. Natural polysaccharides as electroactive polymers. *Applied Microbiol Biotechnology* 67(6): 735-745.

Guan, Y.L., Liu, X.F., Zhang, Y.P. & Yao, K.D. 1998. Study of phase behavior on chitosan/viscose rayon blend film. *Journal of Applied Polymer Science* 67(12): 1965-1972.

Gunasakera, T.S., Dorsch, M.R., Slade, M.B. & Veal, D.A. 2003. Specific detection of *Pseudomonas* spp. by fluorescence *in situ* hybridization using ribosomal RNA directed probes. *Journal of Applied Microbiology* 94: 936-945.

Huang, J.C. 2002. Carbon black filled conducting polymers and polymer blends. *Advanced Polymer Technology* 21: 299-313.

Kress-Rogers, E. 2001. Instrumentation for food quality assurance. In *Instrumentation and Sensors for the Food Industry* (2nd ed.), edited by Kress-Rodgers, E. & Brimelow, C.J.B. Cambridge, UK: Woodhead Publishing Ltd. pp. 581-669.

Kuswandi, B., Jayus, Restyna, A., Abdullah, A., Heng, L.Y. & Ahmad, M. 2012. A novel colorimetric food package label for fish spoilage based on polyaniline film. *Food Control* 25: 184-189.

Lethaby, H. 1862. On the production of a blue substance by the electrolysis of sulphate of aniline. *Journal of the Chemical Society* 15: 161-163.

Lindfors, T. & Ivaska, A. 2002. pH sensitivity of polyaniline and its substituted derivatives. *Journal of Electroanalytical Chemistry* 531: 43-52.

Ma, X., Chang, P.R., Yu, J. & Lu, P. 2008. Characterizations of glycerol plasticized starch (GPS)/carbon black (CB) membranes prepared by melt extrusion and microwave radiation. *Carbohydrate Polymers* 74(4): 895-900.

Mitchell, R.L. & Murphy, C.F. 1972. Heat Sealable Hydroxyethyl Cellulose Film and Process for Preparing same. *US 3652316*.

Osman, Z., Ibrahim, Z.A. & Arof, A.K. 2001. Conductivity enhancement due to ion dissociation in plasticized chitosan based polymer electrolytes. *Carbohydrate Polymers* 44: 167-173.

Piletsky, S.A., Higson, S.P.J. & Davis, F. 2006. *Food Spoilage Sensor*. WIPO Patent Application WO/2006/024848.

Pringsheim, E., Terpetschig, E. & Wolfbeis, O.S. 1997. Optical sensing of pH using thin films of substituted polyanilines. *Analytical Chemical Act* 357: 247-252.

Ramsay, B.A., Langlade, V., Carreau, P.J. & Ramsay, J.A. 1993. Biodegradability and mechanical properties of poly-(ß-hydroxybutyrate-co-ß-hydroxyvalerate)/ starch blends. *Applied and Environmental Microbiology* 59(4): 1242-1246.

Sunendar, B., Wibowo, A., Nugraha, Y. & Bundjal, B. 2008. *An Electronic Structure Study of Polyaniline in Emeraldine salt and Emeraldine Base*. Institut Teknologi Bandung (ITB), Indonesia.

Thangarathinavelu, M., Tripathi, A.K., Goel, T.C. & Varma, I.K. 1994. Preparation and characterization of polyaniline-pvc polymer composite film. *Journal of Applied Polymer Science* 51: 1347-1349.

Wibowo, T., Bunjali, B. & Sunandar, B. 2008. An electric structure study of poyniline in emeraldine base form. *The 2nd South East Asian Technical University Consortium (SEATUC)*. 26-27 February. Institut Teknologi Bandung (ITB). Indonesia.

Wouters, J.T.M., Ayad, E.H.E., Hugenholtz, J. & Smit, G. 2002. Microbes from raw milk for fermented dairy products. *International Dairy Journal* 12: 91-109.

Yam, P. 1995. Plastics get wired. *Scientific American* 273(1): 82-87.

Yin, Y.J., Yao, K.D., Cheng, G.X. & Ma, J.B. 1999. Properties of polyelectrolyte complex films of the chitosan and gelatin. *Polymer International* 48(6): 429-43.

Yoshida, H., Takei, F. & Sawatari, N. 2002. High ionic conducting polymer with polysaccharide and its applications. *Fujitsu Science Technology Journal* 38(1): 39-45.

Yu, J., Zhang, L.Q., Rogunova, M., Summers, J., Hiltner, A. & Baer, E. 2005. Conductivity of polyolefins filled with high-structure carbon black. *Journal of Applied Polymer Science* 98(4): 1799-1805.

Nooranis Mustapha, Nozieana Khairuddin, Ida Idayu Muhamad* & Shahrir Hashim
Department of Bioprocess and Polymer Engineering
Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia
81310 Skudai, Johor Darul Takzim
Malaysia

Md. Bazlul Mobin Siddique
Division of Chemical Engineering
Faculty of Engineering, Computing and Science
Swinburne University of Technology
Sarawak Campus, Jalan Simpang Tiga
93350 Kuching, Sarawak
Malaysia

*Corresponding author; email: idayu@cheme.utm.my

Received: 12 May 2015
Accepted: 27 January 2016