CHAPTER V
PH SENSOR INCOPORATED PP/ORGANOCLAY NANOCOMPOSITES

5.1 Abstract

A novel color indicator for fresh fish packaging is developed to evaluate the fresh fish spoilage during storage and distribution. The processing of pH-sensitive material used for fish packaging based on layer of polypropylene/organoclay nanocomposites laminated with the layer of indicator dyes was focused. The nanoclay composites with indicator dye were compounding through a twin screw extruder using Surlyn® as a reactive compatibilizer. The nanoclay composites were fabricated into films and then attached onto a pH sensor disc by using a laminating machine (at 160°C). Fish spoilage was assessed through aerobic plate count (APC), total volatile basic nitrogen (TVB-N), and color changes of the pH sensor were measured and expressed as Hunter values as well as total color difference (TCD). TCD values of bromocresol green (BCG) type indicator also changed continuously. The color changes of the nanocomposite indicator film correlated well with APC, and TVB-N value of fresh fish. According to the changes in Hunter color values of the nanocomposte indicator film within the packages of fresh fish during storage at ambient temperature, the results show that the color of BCG type-film turned from initially yellow to finally green. The color changes of the developed indicator properly represented the degree of deterioration of fresh fish. Furthermore, they also retard fish spoilage due to the improvement of oxygen barrier property of packaging. The nanocomposite indicator films both could be employed as an effective smart packaging technology for evaluating fresh fish and extent shelf life of fresh fish.

5.2 Introduction

Nowadays, there is a large amount of emphasis in developing rapid methods to evaluate fish freshness by using general quality indicators. One concept to meet this requirement is by using a smart packaging in cooperation with a simple pH-sensitive color indicator that monitors the microbial breakdown products in the headspace of the packaged fish. When fish spoils, it releases a variety of basic volatile amines which are detectable with appropriate pH indicating sensors through visible color changes to the spoilage-volatile compounds that contribute to a quantity known as total volatile basic nitrogen (TVB-N) and the response of changing microbial populations (aerobic plate count (APC) or total viable count (TVC)).

According polymer/clay nanocomposites, the property improvements over polymers are high mechanical properties, excellent heat resistance, dimension stability, low gas permeability and improved die-ability. Bentonite clay is selected for modifying as an organoclay because of low price and widely available in the market. Due to the incorporation of organoclay and indicator not only the nanoparticles of organoclay are able to block oxygen, carbon dioxide and moisture but also make the plastic lighter, stronger and more heat resistance. [1]

After fish becomes spoiling, pH of fresh fish increases from 6.2 to 7.5. The reason why bromocresol green (BCG) was selected to be incorporated to nanocomposite films. Moreover, BCG was found to offer excellent sensitivity towards ammonia (~6 ppb) [3] and color change in range of pH 3.8 to 5.4 (yellow to blue), though the low pKa meant they were also susceptible to water interference.

In this work, Na-bentonite was treated with the cationic surfactant, Dipalmitoylethy Hydroxyethylmonium Methosulfate to obtain the organoclay for use as a nano-reinforcement in polymer matrix (PP). The pH sensor discs were attached in nanocomposite films by using a laminating machine (at 160°C). The capability to use this film as pH sensitive packaging is demonstrated in term of change in total color difference (TCD) and Aerobic Plate Count (APC) or Total Volatile Basic Nitrogen (TVB-N). So, the smart packing can indicate directly the quality of the fresh fish instead of following the designated expiry date. [2]

5.3 Experimental

A. The nanocomposite pH sensor fabrication

A typical pH sensor solution contained a binder, such as cellulose acetate (70%, w/w), a dye, such as bromocresol green, BCG (1, 3, 5%, w/w), and a plasticiser, dibutyl sebacate (DBP) (30%, w/w). The mixture was sonicated for 45–60 min until dissolution was completed. Subsequently, the pH sensor was made by using an automatic pipette and simply deposited 3–4 μl of the pH sensor solution on a mirror substrate. Then, spin-coated at 1,000, 2,000 and 3,000 rpm for approximately 2 min. Films generated at different rotation speed would be varied in thickness. The coated discs were peeled from the mirror substrate then placed in an open container, subsequently in a dark cupboard for overnight at room temperature to complete the drying process. The pH sensor discs of 5 cm diameter were attached onto PP/clay nanocomposite films at different clay content (1, 3, 5 %wt) using a laminating machine (at 160°C). The resulting nanocomposite pH sensor films could be used for the color change testing. The fresh fish (Barramundi or Giant Perch) were obtained from Sam Yarn Market and filleted. Aseptic techniques such as the use of disposable gloves, bactericide built-in cutting board and flame sterilized scalpel were used to avoid sample contamination.

B. Sensor Response to Standard Ammonia

Ammonia was selected from the amine group for color response of a pH sensor. Standard ammonia (10-1000 ppm) in aqueous solutions was prepared in various concentrations. Then, 25 ml aliquots of ammonia standard were pipetted into a polypropylene cup (7x4cm), and closed with nanocomposite pH sensor film. Each cup was sealed with fast cure epoxy to create a permanent gas-tight seal and prevent leakage of ammonia. Stand them at room temperature for 12 hr. Subsequently, investigation of film thickness, amount of dye and different of clay content were performed in the same method and measured two times each.

Color changes of the pH sensor were measured from the pH sensor with a Chroma Meter and expressed as Hunter system (L, a and b) values and total color difference (TCD). The TCD value (ΔE) was calculated by the following equation (Francis, 1983):

$$\Delta E = \left[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\right]^{1/2}$$

Here, ΔL is the brightness difference between sample and target, Δa the redness difference between sample and target, and Δb is the yellowness difference between sample and target. The target color is (93.13, -0.96, 1.69) corresponding to (*L, a, b*) for white standard color in Hunter system.

C. Study of Films Thickness, Amount of Dye, Clay Content, and Quantity of fish tissue on Color Response of nanocomposite pH sensor to TVB-N

For a set of sensors, fourteen replicate fish meat samples of approximately 20 g were placed in separate individual polypropylene caps. Each cap was sealed with fast cure epoxy to create a permanent gas-tight seal and prevent leakage of amines. Samples were at no time indirect contact with the sensors (i.e. only head-space was sampled). The response of fish tissue samples, allowed to spoil at room temperature, was monitored every 3 h with chroma meter for 42 h. Experimental design for fish spoilage monitoring is shown in Figure 5.1 below.

Same measurements were carried out for the nanocomposite sensor film of different thickness prepared by changing spin coating speeds (1000, 2000, and 3000 rpm), amount of dye (1, 3, and 5 %wt BCG), and clay content from 1-5%wt clay. Moreover, the color change was also monitored for different fish meat content (20, 40, and 60 g) and for the nanocomposite sensor film with various dye content.

Color changes of the pH sensor were measured from the pH sensor with a chroma meter as performed in sensor response to standard ammonia.

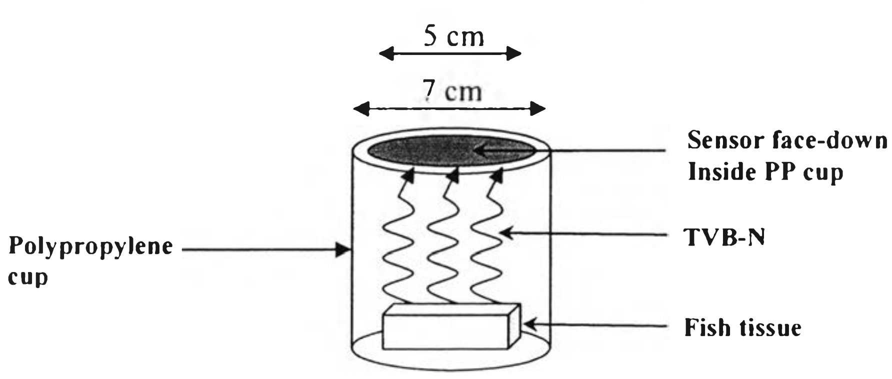


Figure 5.1 Experimental design for fish spoilage monitoring.

D. Leaching Studies

Indicator dyes (BCG) were dissolved in water to prepare standard solutions of 1, 2, 5, and 10 ppm. Then the absorbance of the standard solutions was investigated by using UV-vis spectroscopy (SHIMADZU model UV-2550) with medium scan rate and sampling the data every 1 nm. Spin-coated nanocomposite sensors were cut into rectangular shape with 4x4 cm and soaked with 10 ml of water in a small container for approximately 48 h, after which wavelength spectrum of the water (400–700 nm) was carried out to detect the presence of BCG, if any. The absorbance of the indicator dye standard solutions was observed by UV-vis spectroscopy. Calibration curve was plotted between absorbance versus concentration.

5.4 Results and Discussion

A. Film Thickness of nanocomposite pH Sensor

The pH measurement and APC or TVB-N was investigated in order to find the fish spoilage period. Furthermore, the relationship between sensor response and fish spoilage period was studied in this step.

Table 5.1 shows the effect of spin coating-speed on sensor thickness of BCG type by spin-coated with the sensor solution at 1000, 2000 and 3000 rpm to generate film of different thicknesses. Result indicated that the higher the spin-coating speed, the thinner the sensor film with the average thickness results being 2.40, 2.08 and 1.94 μm at a spin rate of 1000, 2000 and 3000 rpm, respectively. At spin rates higher than 3000 rpm, such as 4000 rpm, the decrease in film thickness became marginal, whereas at spin rates less than 1000 rpm, such as 500 rpm, the films obtained were difficult to dry and could not form a sensor film. Therefore, film at 1000, 2000 and 3000 rpm was chosen as appropriate thickness for sensor response testing in the following studied.

Table 5.1 Effect of spin coating-speed on sensor thickness of BCG type film

Speed (rpm)	**Thickness (microns)**					
	no.1	no.2	no.3	no.4	no.5	average
1000	2.7	2.3	2.3	2.4	2.3	2.40
2000	1.9	2.1	2.2	2.1	2.1	2.08
3000	1.9	1.9	2.0	2.1	1.8	1.94

Table 5.2 Weight of sensor disc and nanocomposite film

Average weight (mg)										
Sensor disc (diameter 5 cm)						Nanocomposite film (diameter 7 cm)			PP	PP/Surlyn
Spin speed (rpm)			Amount of BCG (%wt)			Clay content (%wt)				
1000	2000	3000	1	3	5	1	3	5		
58.9	50.2	45.2	58.9	59.3	59.6	93.4	.105.2	112.1	90.6	91.1

B. Sensor Response to Standard Ammonia

Ammonia is one of the compounds produced as fish spoil. The study of the sensor response to standard ammonia gas provided a model of the response to TVB-N.

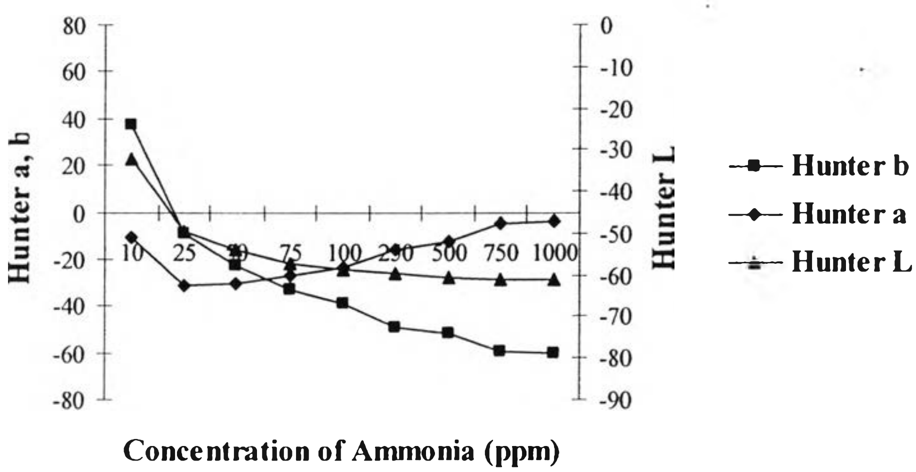
All sensors indirect contact with the standard ammonia responded to the increasing ammonia concentration with a very distinct color change from yellow to blue for BCG type films. Sensors were monitored after 12 h. The changes in Hunter color values for BCG indicator response to increasing ammonia concentration during storage at room temperature is shown in Figures 5.2, 5.3, and 5.4. Prior to the first stage, Hunter *L*, a, and *b* decreases slowly. Thereafter, Hunter *L* and *b* gradually decreases at the middle and the final stage while Hunter *a* slightly increases with time.

The TCD values (ΔE) of BCG indicator films for fresh fish packaging during storage at ambient temperature are calculated and depicted in Figure 5.5. The TCD value also changes continuously with the response of the indicator films. The TCD values significantly increased and then remain constant with time when the concentration of ammonia increase.

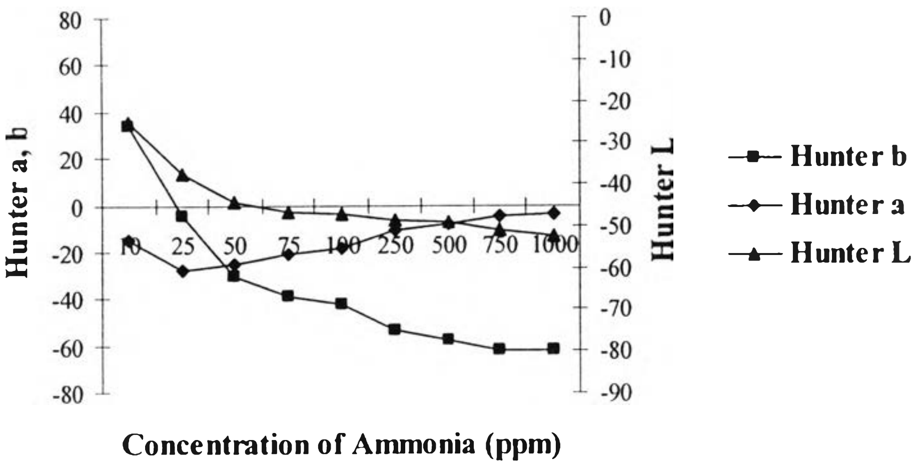
The data indicated that the sensor was sensitive to relatively low concentrations of ammonia (10 ppm). Moreover, the saturation of sensor with standard ammonia was appeared at high concentration of ammonia.

Furthermore, responses of the sensors spin-coated at 1000 rpm show the highest TCD value that mean the thicker sensor contains more dye content so color change can be enhanced. TCD value of 3%wt of BCG close to 5%wt of BCG, so 3%wt of BCG was selected for further study due to saving cost. Additionally, amount of clay content not affect the sensor response when the ammonia concentrations increase.

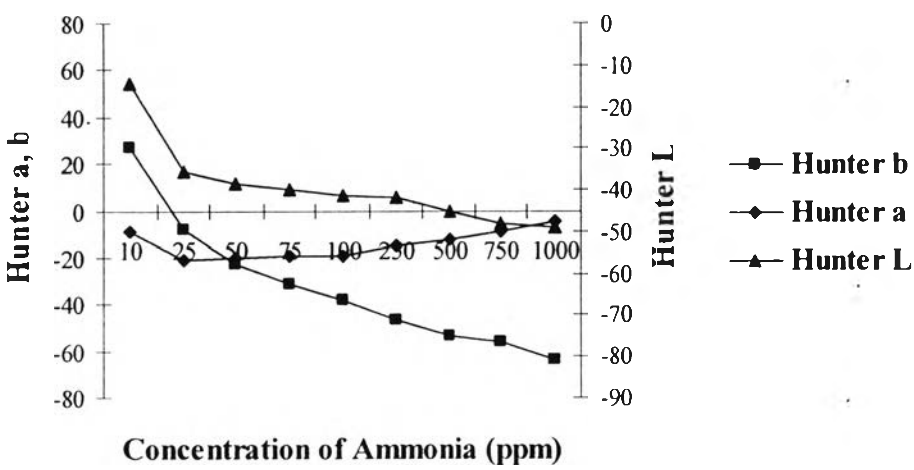
Hence, spoiling fish produces a mixture of amines and ammonia, the concentration of TVB-N in the headspace is therefore likely to be sufficiently high to be detected by this proposed sensor.



(A)

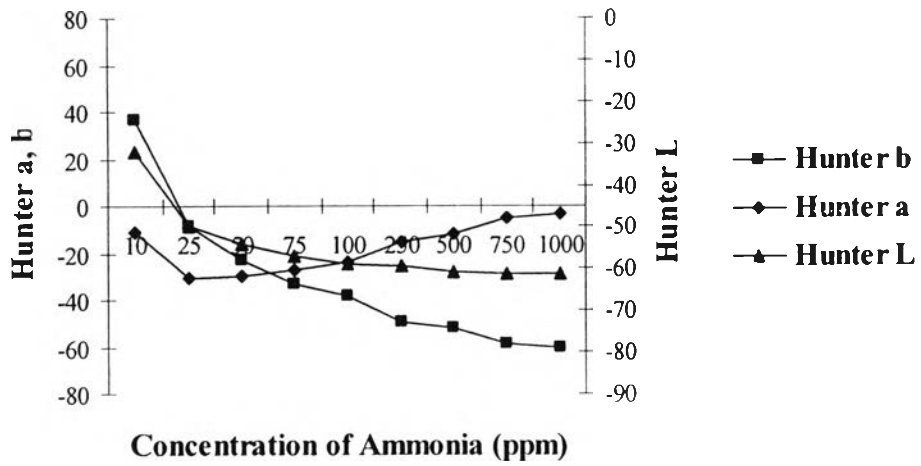


(B)



(C)

Figure 5.2 Changes in Hunter color values for BCG indicator response to increasing ammonia concentration after standing at 12 hr during storage at room temperature: (A) 1,000 rpm, (B) 2,000 rpm and (C) 3,000 rpm.


80
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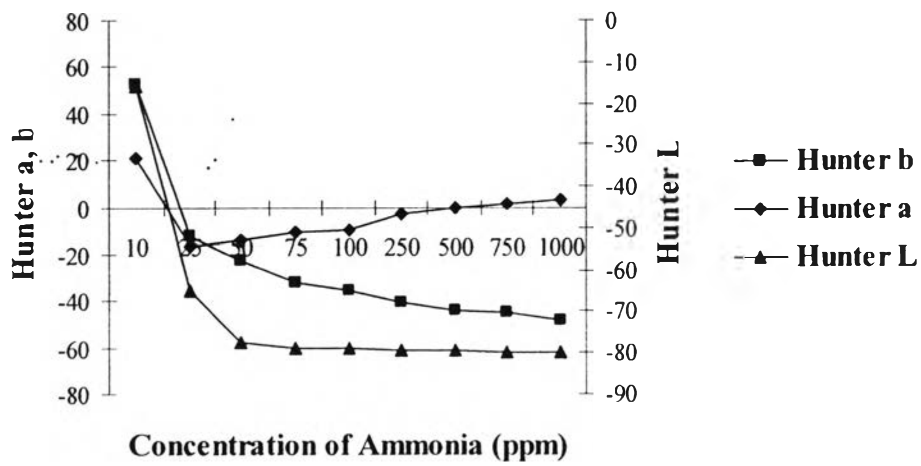
40
20
0
-20
-40
-60
-80
Hunter a, b
10
25
50
75
100
250
500
750
1000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Hunter L
Hunter b
Hunter a
Hunter L
Concentration of Ammonia (ppm)

(A)


80
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-20
-40
-60
-80
Hunter a, b
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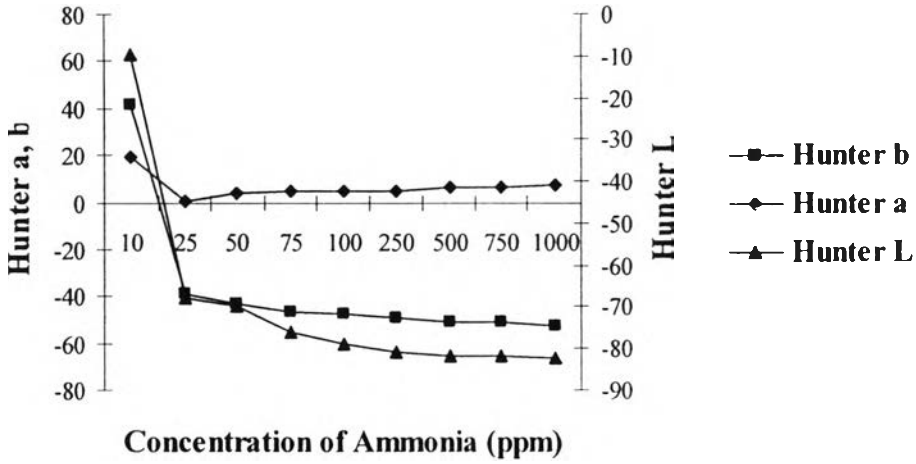
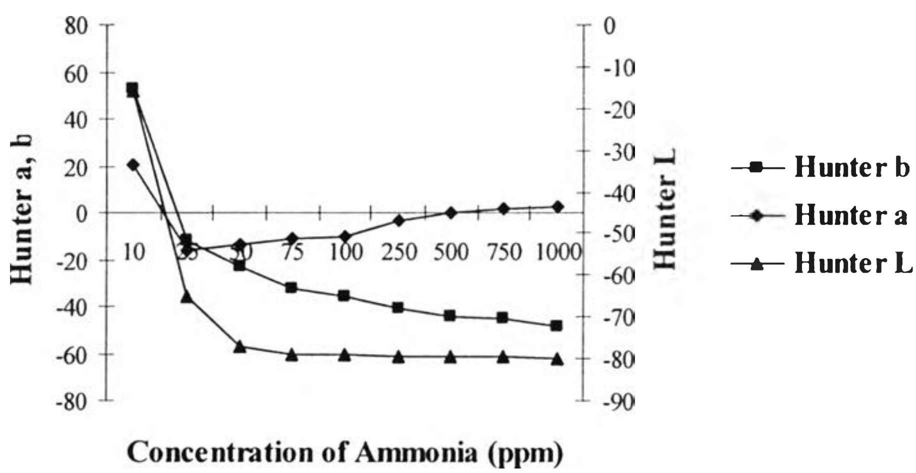
50
75
100
250
500
750
1000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Hunter L
Hunter b
Hunter a
Hunter L
Concentration of Ammonia (ppm)

(B)

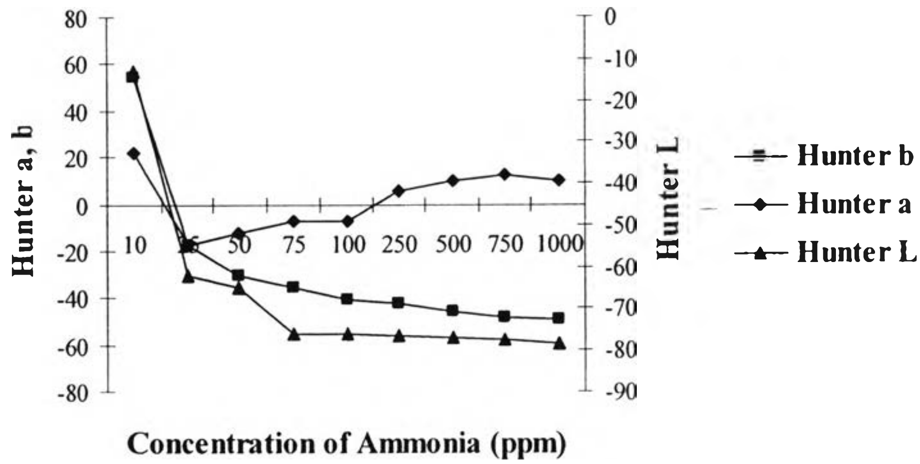


(C)

Figure 5.3 Changes in Hunter color values for BCG indicator response to increasing ammonia concentration after standing at 12 hr during storage at room temperature: (A) 1%wt BCG, (B) 3%wt BCG and (C) 5%wt BCG.



(A)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-60
-80
Hunter a, b
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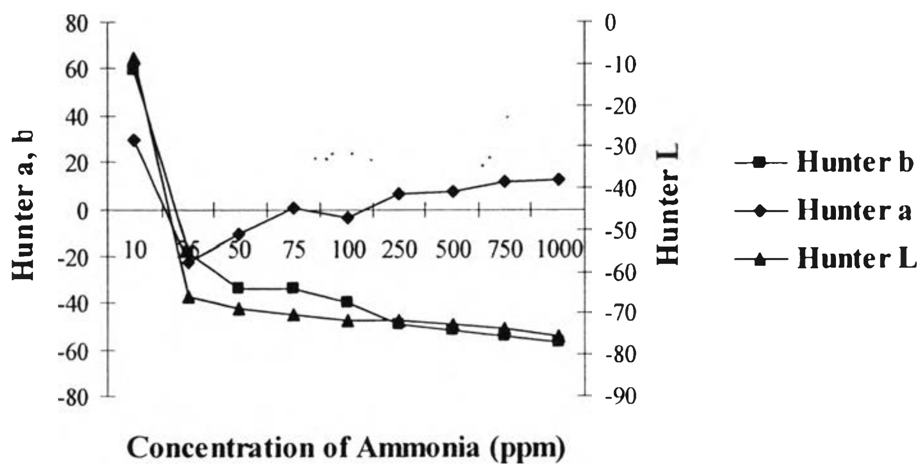
50
75
100
250
500
750
1000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Hunter L
Hunter b
Hunter a
Hunter L
Concentration of Ammonia (ppm)

(B)


80
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-20
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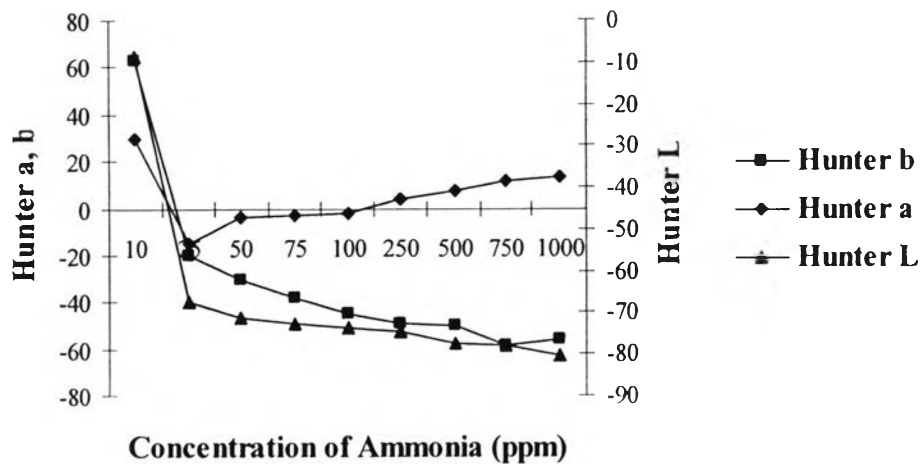
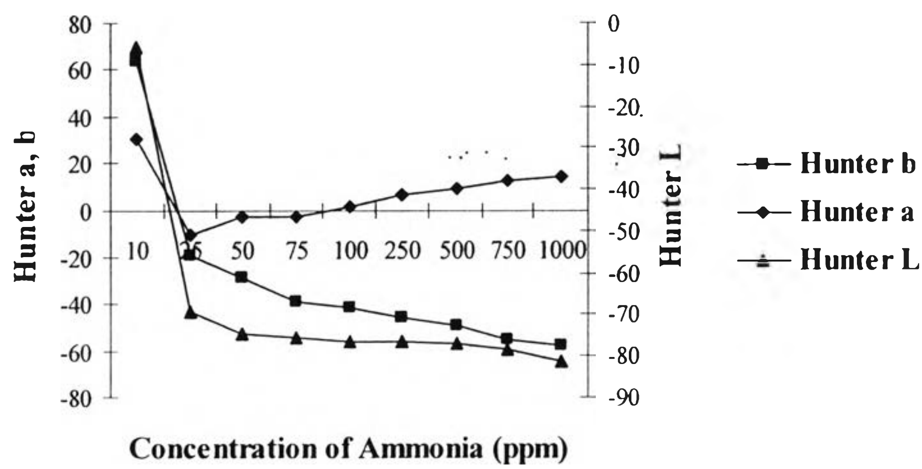
-60
-80
Hunter a, b
10
25
50
75
100
250
500
750
1000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Hunter L
Hunter b
Hunter a
Hunter L
Concentration of Ammonia (ppm)

(C)

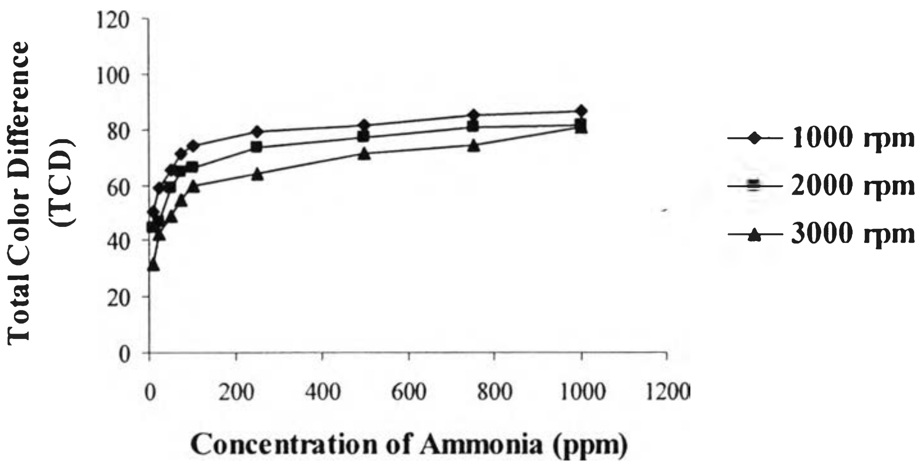


(D)

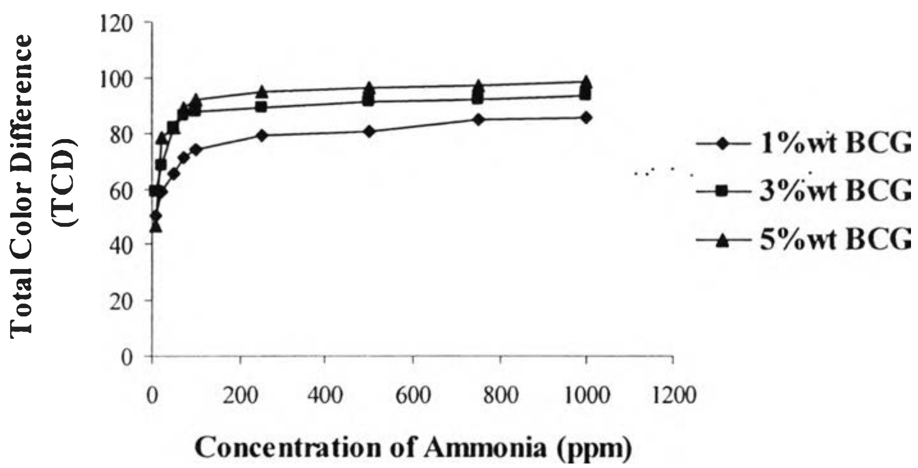


(E)

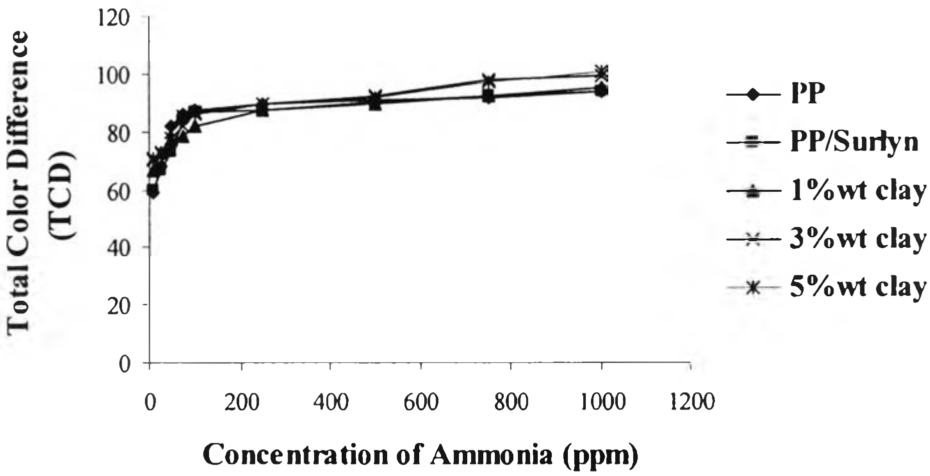
Figure 5.4 Changes in Hunter color values for BCG indicator response to increasing ammonia concentration after standing at 12 hr during storage at room temperature: (A) PP, (B) PP/Surlyn, (C) 1%wt clay, (D) 3%wt clay, and (E) 5%wt clay.


120
100
80
60
40
20
0
Total Color Difference
(TCD)
0
200
400
600
800
1000
1200
Concentration of Ammonia (ppm)
1000 rpm
2000 rpm
3000 rpm

(A)


120
100
80
60
40
20
0
Total Color Difference
(TCD)
0
200
400
600
800
1000
1200
Concentration of Ammonia (ppm)
1%wt BCG
3%wt BCG
5%wt BCG

(B)



(C)

Figure 5.5 Changes in TCD values of the indicator films to increasing ammonia concentration after standing at 12 hr during storage at ambient temperature: (A) Vary Thickness, (B) Vary %wt BCG, and (C) Vary %wt clay.

C. Sensor Response to TVB-N

All sensors indirect contact with the tissue samples responded to the increasing volatile basic amines generated by spoilage with a very distinct color change from yellow to blue for BCG type films. Sensors were monitored at every 3 h until no further Hunter color values change was observed. The changes in Hunter color values for BCG indicator of packaged films upon direct contact of the TVB-N during storage at room temperature are investigated in Figure 5.7, 5.8, and 5.9. Prior to the first stage, Hunter *L*, a, and *b* decreases slowly. Thereafter, steadily changed remain constant at the final stage.

The TCD values (ΔE) of BCG indicator films for fresh fish packaging during storage at ambient temperature are calculated and depicted in Figure 5.10. The TCD value also changes continuously with the response of the indicator films. The TCD values significantly increased with time when fresh fish became spoiling.

The responses of the sensors spin-coated at 1,000, 2,000 and 3,000 rpm, the change in color is not different for 1000, 2000, and 3000 rpm. However, 1000 rpm film sensor was selected for further preparation due to many research choose this thickness according to thicker sensor contain more dye content, so color change can be more enhanced. The spin-coated sensor using 1%, 3%, and 5%wt BCG, the data indicated that 3 and 5%wt BCG were similar in TCD range. Moreover, response of 5%wt BCG is nonlinear or variable in TCD data as shown in Figure 5.8 (B). So, 3%wt BCG was selected for next step preparation due to saving cost and correlates with information done by standard ammonia. Additionally, responses of the spin-coated sensor by adding 1%, 3%, and 5%wt clay show that 5%wt clay provide a small color change to choma meter than those coated. So, it can be concluded that when increase clay content in nanocomposite pH sensor not only improve mechanical properties but also provide extent shelf live of fish due to improvement of oxygen barrier properties of packaging.

By combining result of both sensor response to standard ammonia and TVB-N testing, the nanocomposite pH sensors at 1000 rpm added with 3%wt BCG and 5%wt clay content were selected as the most suitable sensor for fish packaging as show is Figure 5.6.

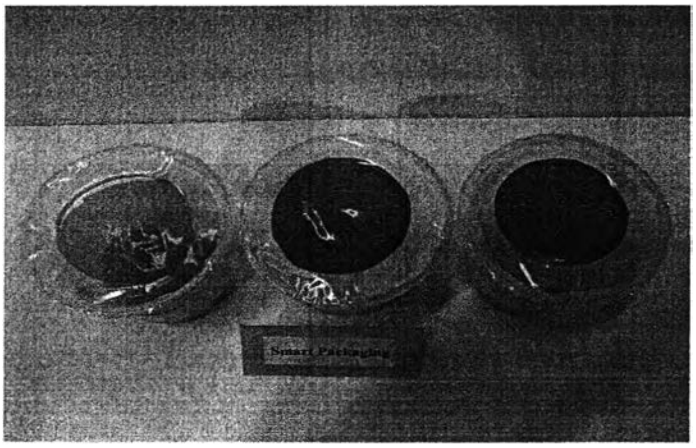
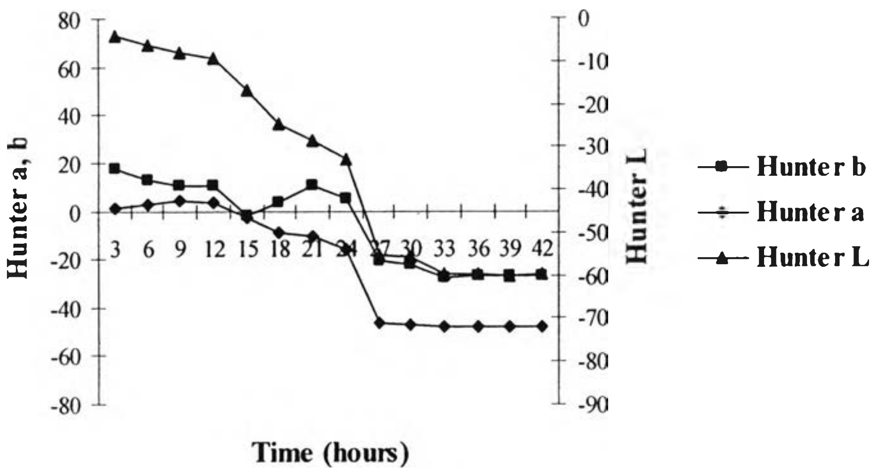
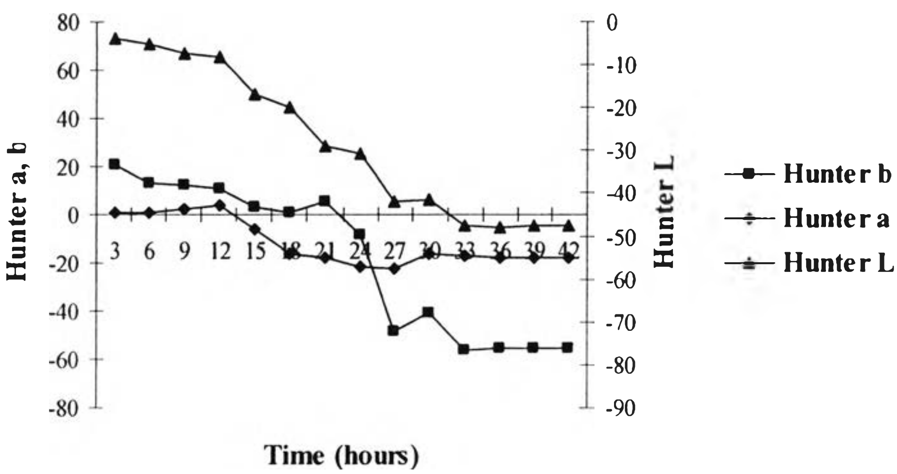


Figure 5.6 Color change of smart packaging using spin coating speed 1000 rpm, 3%wt BCG, and 5%wt clay with 20g of fish meat at ambient temperature


80
60
40
20
0
-20
-40
-60
-80
Hunter a, b
3 6 9 12 15 18 21 24 27 30 33 36 39 42
Time (hours)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Hunter L
Hunter b
Hunter a
Hunter L

(A)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Hunter a, b
3 6 9 12 15 18 21 24 27 30 33 36 39 42
Time (hours)
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-10
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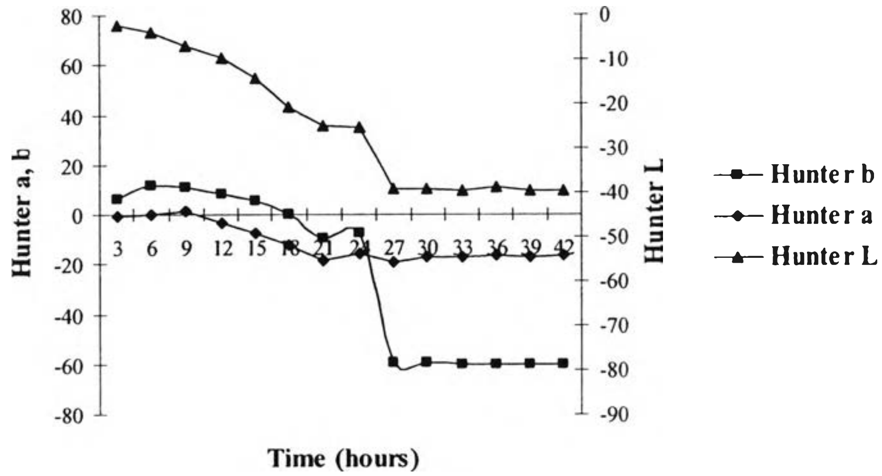
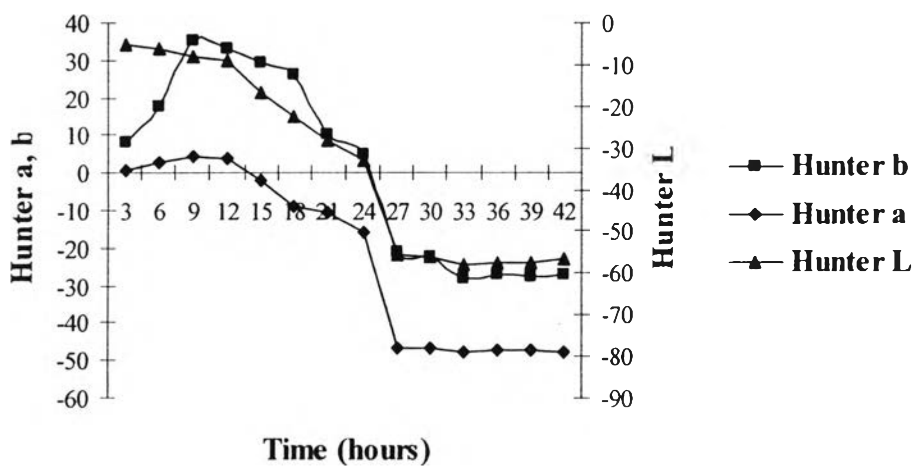
-30
-40
-50
-60
-70
-80
-90
Hunter L
Hunter b
Hunter a
Hunter L

(B)

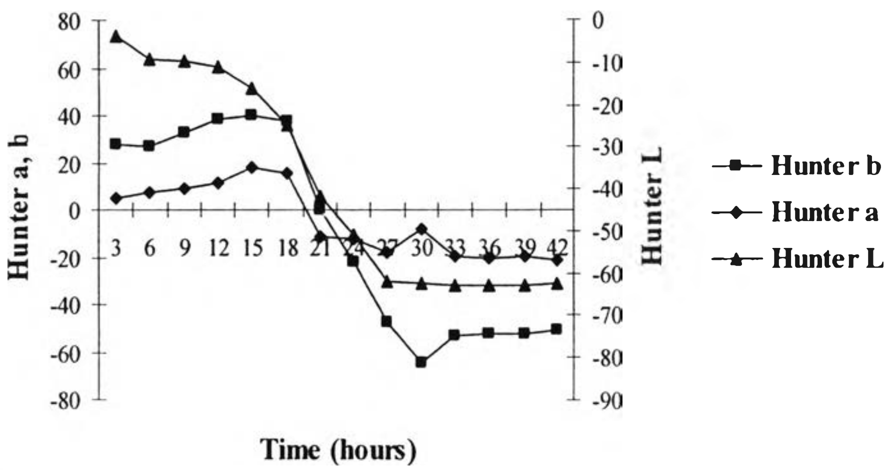


(C)

Figure 5.7 Changes in Hunter color values of the BCG indicator films in barramundi fish during storage at ambient temperature: (A) 1,000 rpm, (B) 2,000 rpm and (C) 3,000 rpm.



(A)



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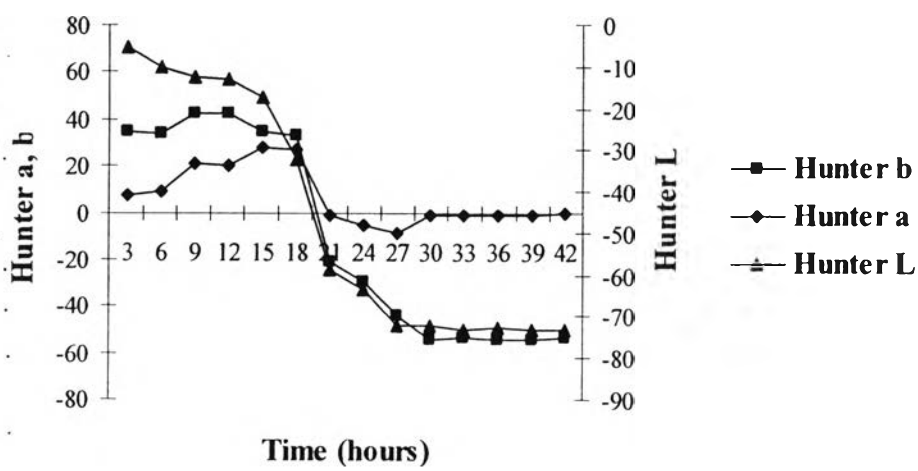
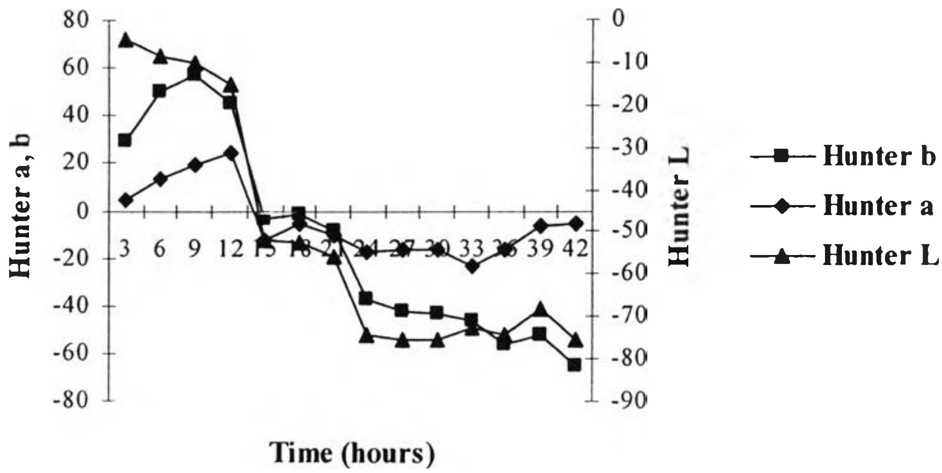
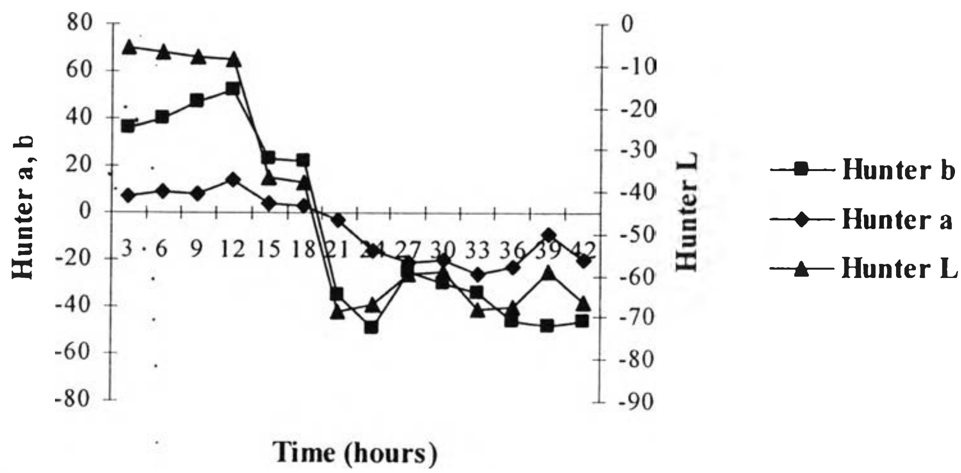


(C)

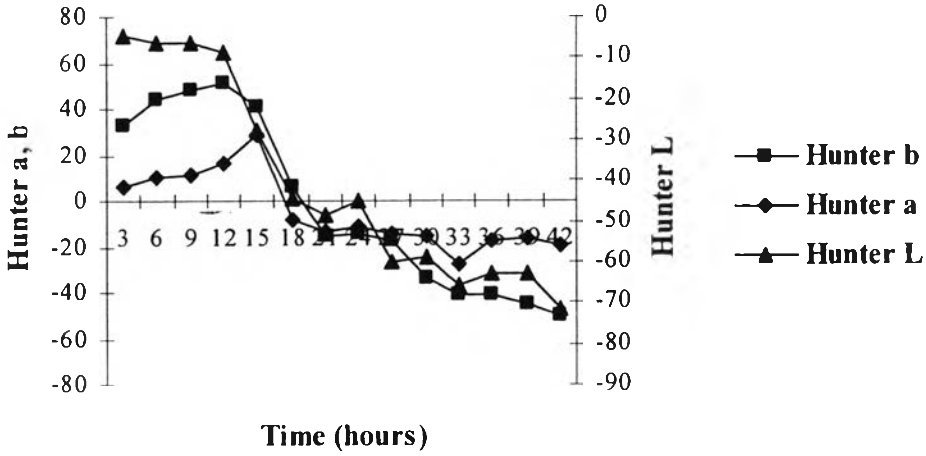
Figure 5.8 Changes in Hunter color values of the BCG indicator films in barramundi fish during storage at ambient temperature: (A) 1%wt BCG, (B) 3%wt BCG and (C) 5%wt BCG.


Hunter a, b
Hunter L
Time (hours)
Hunter b
Hunter a
Hunter L

(A)


Hunter a, b
Hunter L
Time (hours)
Hunter b
Hunter a
Hunter L

(B)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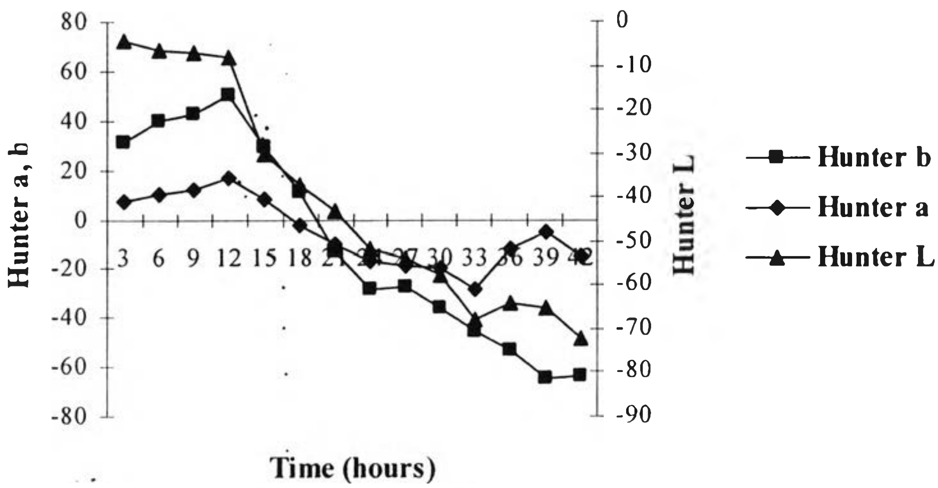
-80
Hunter a, b
3 6 9 12 15 18 21 24 27 30 33 36 39 42
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Hunter L
Time (hours)
Hunter b
Hunter a
Hunter L

(C)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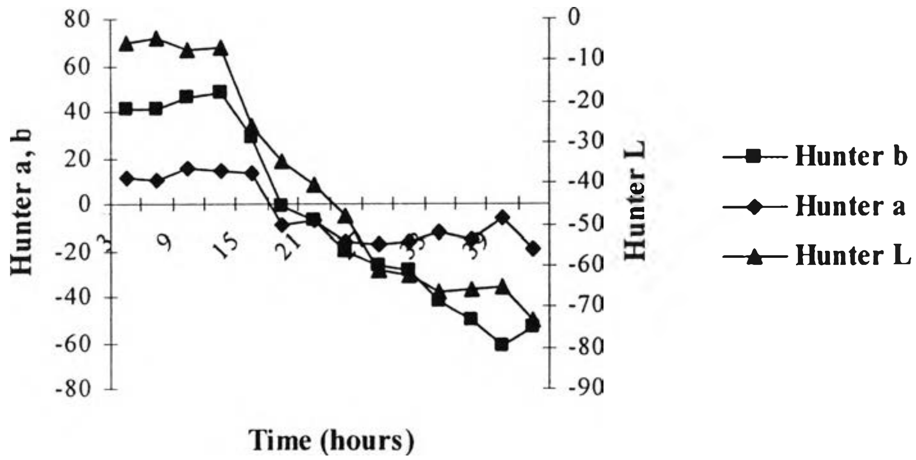
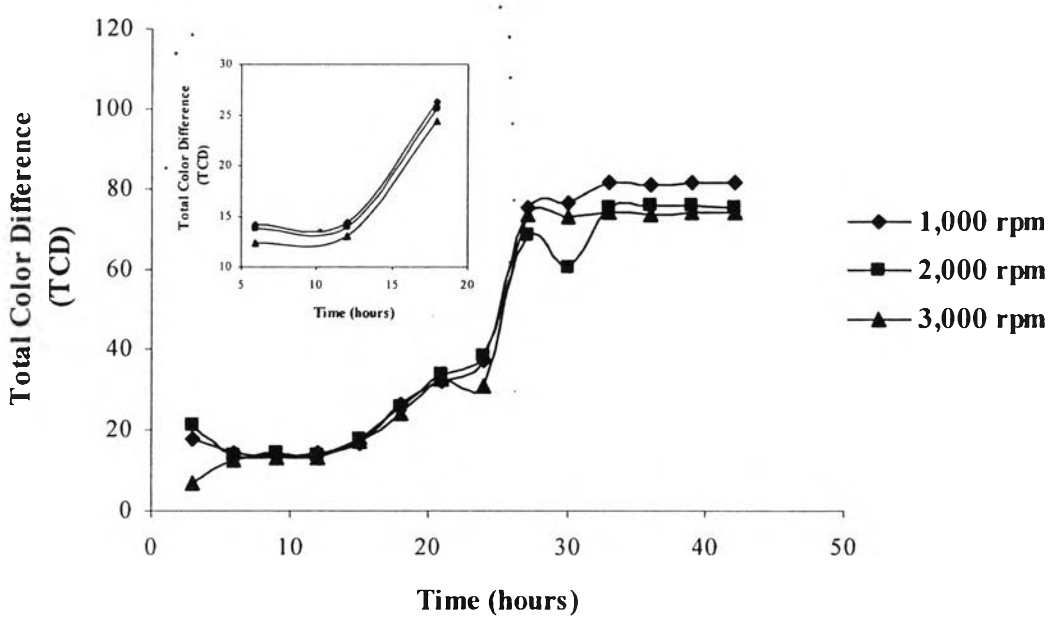
-40
-60
-80
Hunter a, b
3 6 9 12 15 18 21 24 27 30 33 36 39 42
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
Hunter L
Time (hours)
Hunter b
Hunter a
Hunter L

(D)

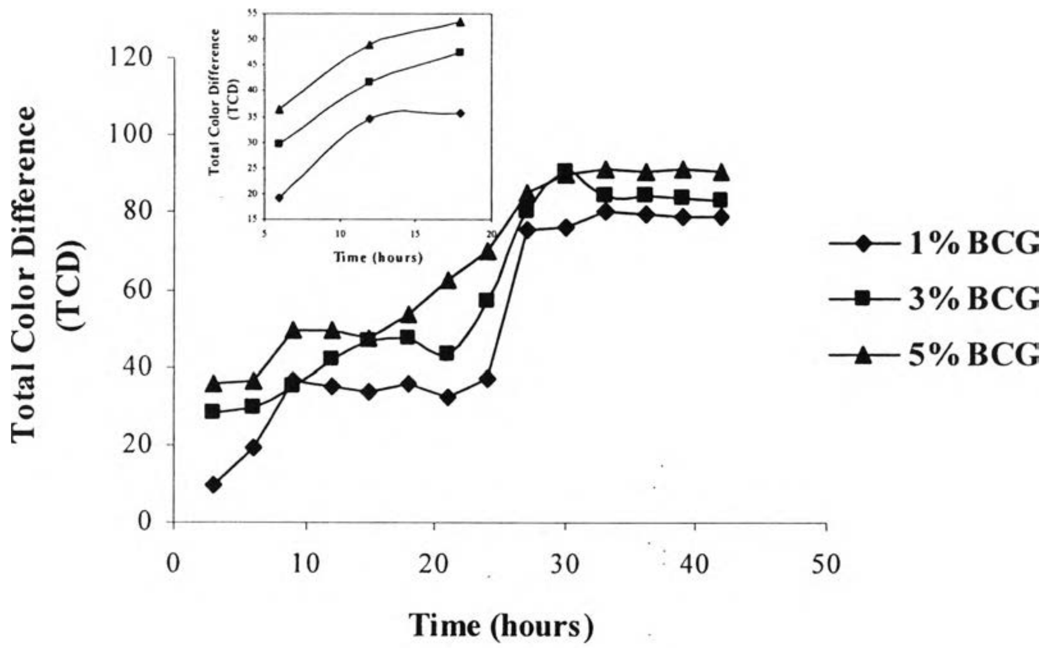


(E)

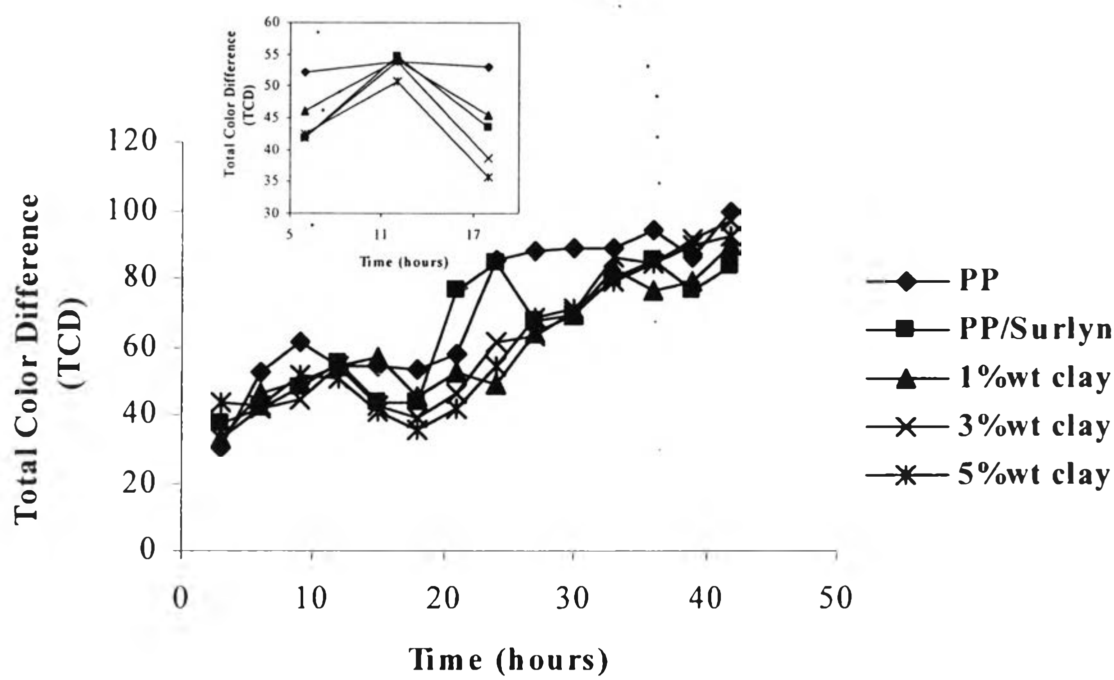
Figure 5.9 Changes in Hunter color values of the BCG indicator films in barramundi fish during storage at ambient temperature: (A) PP, (B) PP/Surlyn, (C) 1%wt clay, (D) 3%wt clay, and (E) 5%wt clay.



(A)



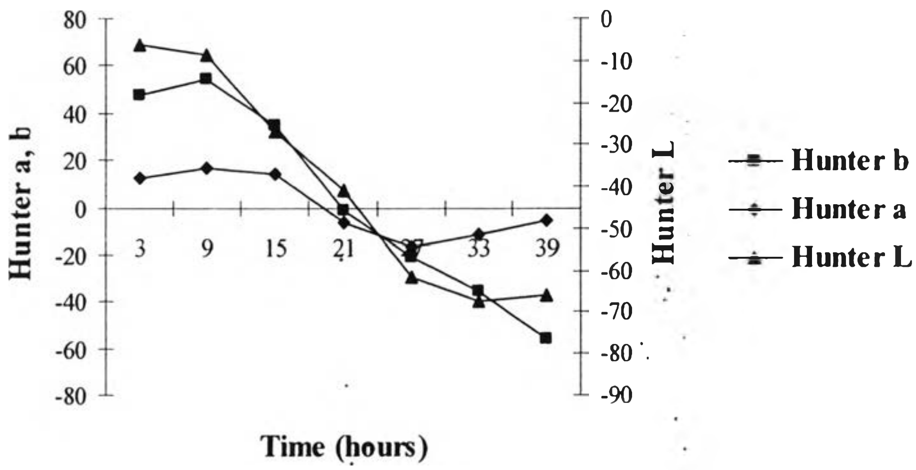
(B)



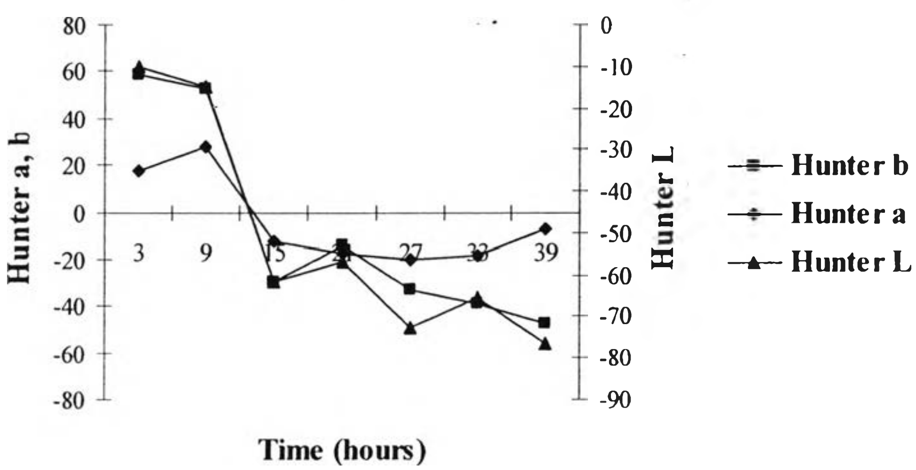
(C)

Figure 5.10 Changes in TCD values of the indicator films in the barramundi fish during storage at ambient temperature: (A) Vary thickness, (B) Vary %BCG, and (C) Vary %clay.

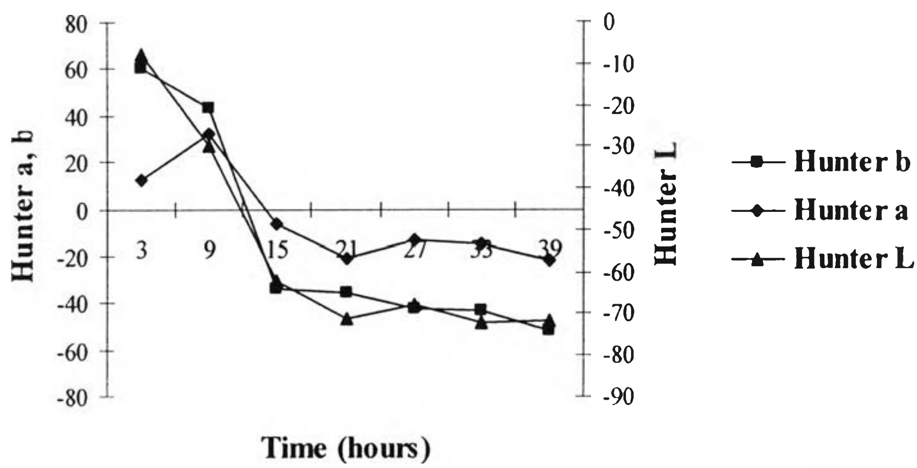
In order to investigate the effect of fish tissue amount to the change of sensor color, the varying of fish tissue amount were done at 20, 40, and 60 g. The result showed that 60 g of fish tissue gave the most intense color change of sensor. This can be implied that the more fish tissue amount the more sensor color change because of more production of TVB-N after spoilage of fresh fish. The changes in Hunter color values for BCG indicator response to increasing TVB-N during storage at room temperature is shown in Figure 5.12.



(A)



(B)



(C)

Figure 5.11 Changes in Hunter color values of the BCG indicator films response to increasing TVB-N during storage at ambient temperature: (A) Fish meat 20 g, (B) Fish meat 40 g, and (C) Fish meat 60 g.

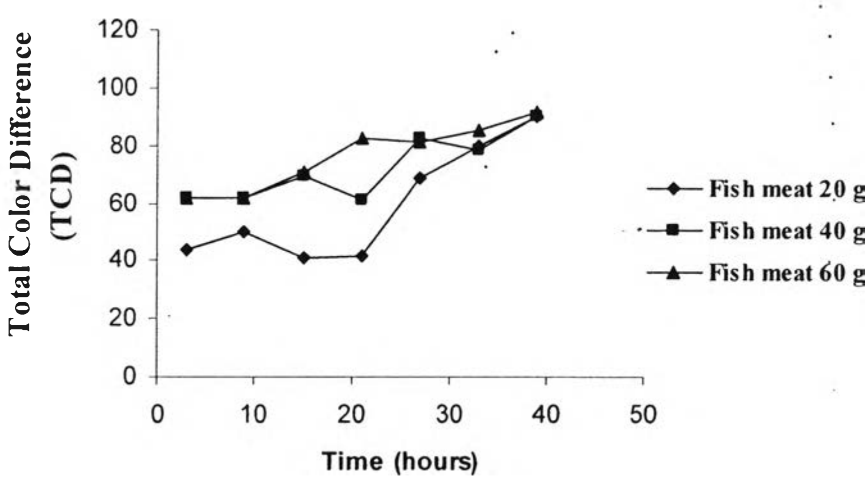


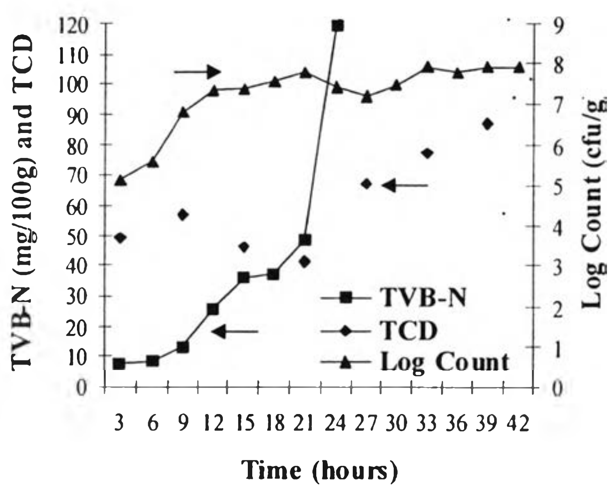
Figure 5.12 Changes in TCD values of the indicator films response to increasing TVB-N during storage at ambient temperature.

D. Correlation of the Nanocomposite pH Sensor Response to Fish Spoilage

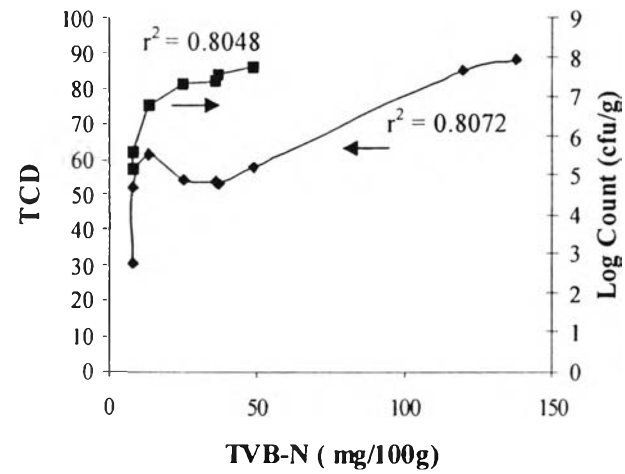
The main purpose for the application of the nanocomposte pH sensor film to fresh fish packaging is to provide an easy and reliable method to evaluate the degree of the fresh fish spoilage in non-destructive way during distribution and retail sale.

The TVB-N and APC values of fresh fish are hence compared with the TCD values of the indicator as illustrated in Figure 5.13.

Information of the Barramundis' shelf-life could be reported based on the criteria of the level of 10^7cfu/g from Aerobic Plate Count (APC) and level of 30-35 mg/100g from Total Volatile Basic Nitrogen (TVB-N) technique. By these measurements the end shelf-life of our Barramundi fish stored at room temperature was about 12 hours. From this correlation of the nanocomposite pH sensor response to fish spoilage could be obtained. From figure 5.13 APC level of 10^7cfu/g and TVB-N level of 30-35 mg/100g at 12 hours demonstrate TCD value about 50 which is easily detected by eye. This position was the threshold of fresh fish spoilage. Figure 5.13 also show that the correlation of log APC, TVB-N, and time are rather linear as well as that correlation of TCD and time from 0-12 hr. So, this suggests that the BCG film sensor can be used to monitor the freshness of fish meat with time.



(A)



(B)

Figure 5.13 Correlation of change in microbial populations and TVB-N of fish meat, allowed to spoil at room temperature and sensor response of 5%wt BCG spin-coated at 1000 rpm onto 5%wt clay nanocomposite films, of meat samples of 20 g during storage time at room temperature: (A) curve of aerobic plate count (APC), TVB-N, and TCD values with time and (B) curve of aerobic plate count (APC) and TCD values with TVB-N.

E. Leaching Studies

The leakage of the indicator dyes incorporated into the nanocomposite indicator films observed by UV-vis spectrometer in form of calibration curve at 615 nm is shown in Figure 5.14. The amount of BCG leaked to water is just only 0.63 ppm/42.4 mg of nanocomposite sensor which not exceeds the limitation of residual bromine is 4-10 ppm by U.S. food and drug administration (FDA). The result implies that when the sensor disc attached with nanocomposite film using laminating machine at 160°C. It can prevent the leakage of the water soluble dyes because improvement of adhesion between dye and PP/Clay nanocomposite by heating.

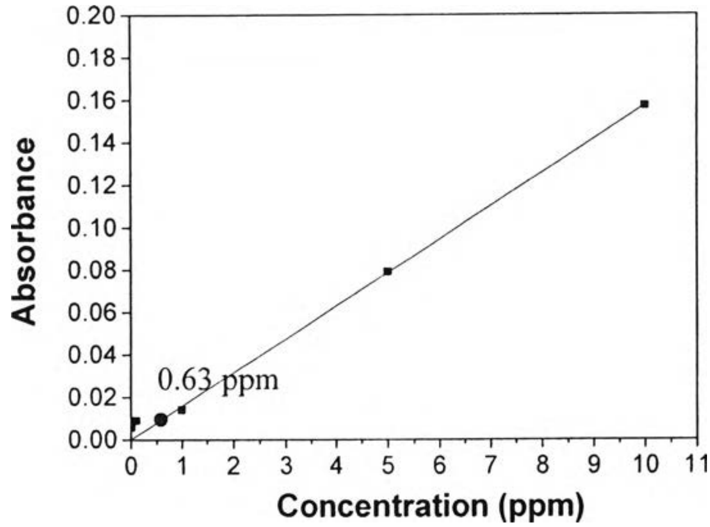


Figure 5.14 The leakage of the indicator dyes incorporated into the nanocomposite pH sensor film.

5.5 Conclusions

The color changes of the developed nanocomposite indicator film properly represent the fresh fish spoilage. The suitable choice of pH sensor disc was fabricated by using a spin-coater at 1000 rpm and 3%wt BCG. Since at these condition sensor could provide a more intense color change observed by human eyes and chroma meter. Then, they were attached onto an appropriate PP/clay nanocomposite films at 5%wt nanoclay using a laminating machine (at 160°C). At this level clay content, sensor color would be change slower than other clay content. According to oxygen barrier properties of nanoclay composite, the higher nanoclay contents the longer extent shelf life of fresh fish.

Additionally, Fish spoilage was assessed for APC and the color changes of the pH sensor were measured and expressed as Hunter values and then total color difference (TCD). The TCD value would be increase with time during fish spoilage as well as in standard ammonia investigation. The TCD values about 50 of BCG type indicator which signify fish begin spoilage during stored at room temperature. The color of the pH sensor turned from an initial yellow to a final green for BCG type. The color changes of the developed pH sensor properly represented the degree of spoilage of the fresh fish with very small amount of indicator leakage. The pH sensor could be employed as an effective smart packaging technology.

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