The Influence of Plastic Wrap Types on Oxygen Detection Property by Colorimetric Oxygen Indicator Based on TiO_2/Methylene Blue Nanocomposite

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Received: 4 December 2023, Revised: 29 December 2023, Accepted: 30 December 2023

Abstract

The work is focused on the oxygen detection of colorimetric oxygen indicators by covering the indicator surface with different plastic wrap types. The layer of colorimetric detection was composed of titanium dioxides nanoparticles (TiO_2), citric acid, methylene blue (MB) and polyvinyl alcohol (PVA). The precursor suspension was operated at 250 rpm by dry and wet milling process for 30 and 45 min. After that TiO_2/MB composite was coated by the spin coating technique with a spin speed of 3,000 rpm and 5 film layers on a glass substrate. The oxygen indicator with TiO_2/MB composite film was presented in a blue film as indicated initial state. Then, plastic wraps with different types as polyvinylidene chloride (PVDC), polyvinyl chloride (PVC) and polyethylene (PE) were covered on the indicator surface to monitor its physical morphology, optical properties, and oxygen detection. Color changing in bleach and color state and oxygen detection of the indicators with the different plastic wraps were monitored by the snapshots in each hour for the cyan percentage analysis in the CMYK system. Meanwhile, the presence of bleach/color state in the indicators was confirmed by UV-Vis spectrophotometer focusing on the absorption range of MB dye to identify its state. The optimized covering plastic wrap on TiO_2/MB colorimetric indicator was obtained by polyvinyl chloride that showed identical indicator efficiency compared with the original indicator without the plastic wrap owing to excellent oxygen gas flow on its membrane. While the retardation of color changing in the indicator occurred by the polyvinylidene chloride wrap on its surface due to the unique property of blocking oxygen gas transmission.

Keywords: Methylene blue, Titanium dioxide, Nanocomposites, Oxygen indicator, Plastic wrap.

1. Introduction

Oxygen is a fundamental element necessary for life, and it can be found in the Earth environment. However, in certain cases, oxygen can have negative effects, particularly when it is not properly controlled in food production and packaging. Modified atmosphere packaging (MAP) is one of the effective techniques that involves altering the atmosphere inside food packaging by vacuum environment and adding other gases such as carbon dioxide (CO_2) and nitrogen (N_2) to maintain the freshness and crispness of food [1]. In the food industry, oxygen can contribute to the degradation of food over time, especially when combined with factors like temperature and exposure duration. Food spoilage and the development of rancid flavors can occur by the oxidation mechanism after the interaction of food and oxygen molecules in the air. To solve this problem, the usage of oxygen indicators inside the packages is often used to monitor some leakage areas [2]. Oxygen indicators can be

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placed inside food packaging and serve as a visual indicator of damage caused by oxygen exposure. The color change from colorless to colored stated on the indicator surface can be shown after the interaction with oxygen molecules [3]. This oxygen indicator is called a colorimetric oxygen indicator. The level of damaged packaging can be assessed by the intensity of the color change on the oxygen indicator. The colorimetric oxygen indicator is based on a specific mechanism with the compositions of a semiconductor photocatalyst, redox dye, and sacrificial electron donor. The initial mechanism of the indicator started from the creation of electron-hole pairs by the exceeds activated energy than the band gap energy of the semiconductor photocatalyst. Holes react with the sacrificial electron donor, while electrons react with the redox dye, causing a colorless or bleached state. When the oxygen indicator is exposed to an oxygen environment, the presence of hydrogen bonding in the redox dye molecule relates to the product of water molecules. Therefore, the colored state of the indicator is occurred by this reaction.

In the work, the colorimetric oxygen indicator is focused on the effective indicator to monitor damaged packaging because of the cheap, easy notice, and simple process. The semiconductor as TiO_2 nanoparticles, the redox dye of methylene blue (MB), and the sacrificial electron donor of citric acid are the main compositions for the fabrication of the colorimetric oxygen indicator. The prominent properties of TiO_2 nanoparticles are a highly activated photocatalyst under UV illumination [4]. Methylene blue is an effective redox dye that switches between MB chemical structure (blue color) and leuco-MB structure (colorless state) [5]. Citric acid acts as a sacrificial electron donor to generate electrons in the reaction. The performance of TiO_2/MB nanocomposite indicator is studied by the influence of covering plastic wrap on its surface to avoid contamination of TiO_2/MB composite in the packaging. Plastic wrap types are commonly used in food grade, for example, polyvinylidene chloride (PVDC), polyvinyl chloride (PVC), and polyethylene (PE).

2. Experimental

2.1 Materials

As-received TiO_2 P25 nanoparticles were used as a metal oxide precursor. Methylene blue was purchased from LOBA Chemie pharma grade. Citric acid and polyvinyl alcohol were purchased from Ajax Finechem.

2.2 Synthesis of TiO_2/MB nanocomposites

3.00 g of TiO_2 nanoparticles, 0.15 g of citric acid, and 12.5 mg of methylene blue were mixed in a milled pot with the ratio weight of precursor and zirconia balls at 1:10 in a dry milling process at 250 rpm for 30 min. Then, 10 ml of PVA solution (3 wt.%) was added to the milled pot for a wet milling process operated at 250 rpm for 45 min to obtain the blue suspension of TiO_2/MB nanocomposite [6].

2.3 Fabrication of TiO_2/MB nanocomposite film

TiO_2/MB nanocomposite films were fabricated by spin coating technique. TiO_2/MB suspension was coated on a glass substrate with an area of 1 x 1 inch^2 with rotation speed at 3000 rpm and 5 film layers. After that TiO_2/MB nanocomposite films were covered by commercial plastic wraps with an average thickness in a range of 10-20 µm such as PVDC, PVC, and PE wraps due to their availability in the food industry.

2.4 Characterization of TiO_2/MB nanocomposite film and oxygen indicator efficiency

The chemical bonding structure of plastic wrap types was analyzed by Fourier Transform Infrared Spectrometer (FTIR; PerkinElmer Scientific). The optical properties of plastic wrap types and bleached/colored state of TiO_2/MB nanocomposite films were monitored by UV-Vis NIR spectrometer (HITACHI, model UH1450). The bleached state of the TiO_2/MB indicators was operated under UV lamps with a maximum wavelength of 395 nm and 20% intensity. For oxygen detection, the TiO_2/MB indicators covered with different plastic wrap were placed in air ambient at room temperature. The appearance of the indicators under oxygen detection was monitored by a real-time camera.

3. Results and discussion

3.1 The characteristics of plastic wraps

FTIR spectra of different plastic wraps as PVDC, PVC, and PE are shown in Fig. 1 to confirm their chemical bonding. In the case of PVC and PVDC wrap, similar spectra patterns were obtained due to the same composition of vinyl chloride monomers. However, the difference of PVC and PVDC wrap is the copolymer of vinylidene chloride (approximately 90%). The wavenumber in a range of 400 to 800 cm^{-1} corresponded to vibrational C-Cl stretching, while the vibrational of C-C stretching, C-H bending, and C-H stretching was related to the wavenumber in 900 to 1,300 cm^{-1}, 1,300 to 1,500 cm^{-1}, and 2,800 to 3,100 cm^{-1}. The amount of peak position in the wavenumber at 400 to 800 cm^{-1} of PVDC wrap is more increased than PVC wrap because of two functional groups as C-Cl in the monomer.

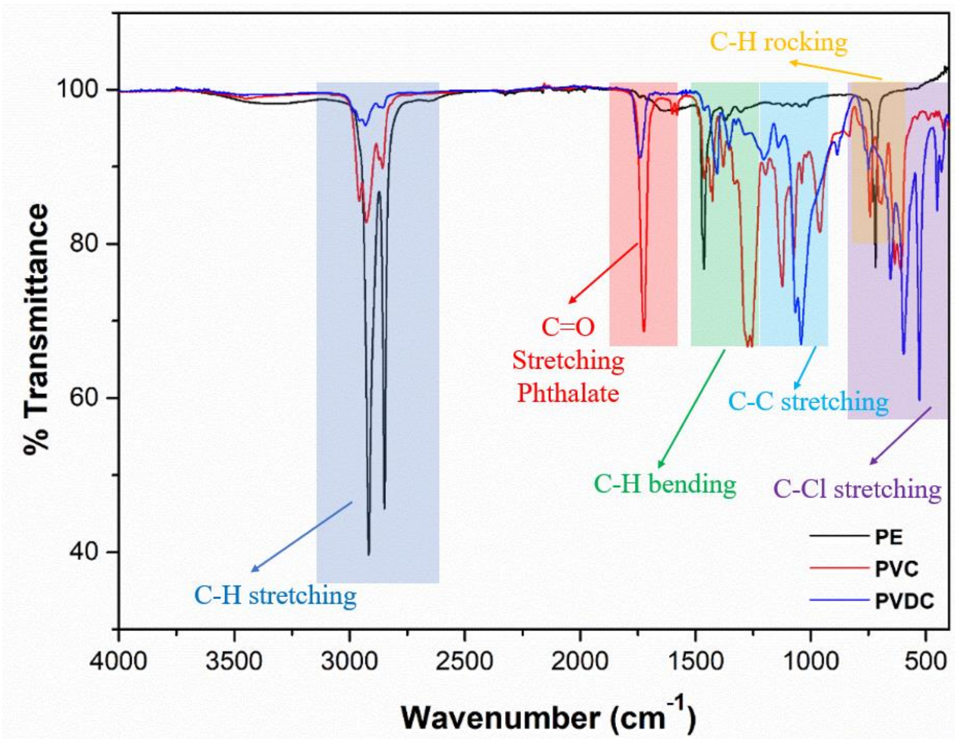

Fig. 1. FTIR spectra of PVC, PVDC, and PE plastic wrap

Meanwhile, the difference between PVDC and PVC wrap in the FTIR spectrum occurs at the wavenumber in 1,700 to 1,800 cm^{-1} relating to the vibrational of C=O stretching in PVDC wrap. For PE wrap, the vibrational groups of C-H rocking, C-H bending, and C-H stretching are located at the wavenumber at 600 to 800 cm^{-1}, 1,300 to 1,500 cm^{-1}, and 2,800-3,100 cm^{-1}. The prominent peaks in the range of 2,800 to 3,000 cm^{-1} are identified as the phthalate groups owing to enhancing elongate and toughness properties of plastic wrap fabrication in industrial production [7].

The optical property of transmission spectra of different plastic wraps is depicted in Fig. 2. High transparency of each film occurred in UV and visible regions. Therefore, the activation under UVA irradiation can transmit and react on the surface of the oxygen indicator to a bleached/colored state. The highest %T in UV and visible region is PE wrap with a stable transmission of around 85%. PVDC wrap showed some absorption in deep UV wavelength and transmission feature wave in wavelength more than 500 nm due to thin and homogeneous film. Moreover, the spectrum contained a wave-like characteristic in PVDC film corresponded to the existence of the interference between the transmitted rays of different path lengths as a result of multiple reflections in the film [8]. The noticeable absorption of PVC wrap in UV region was obtained owing to UV barrier property in PVC material [9].

3.2 Performance of TiO_2/MB oxygen indicator with the difference of covered plastic wrap

The bleach state timing of TiO_2/MB oxygen indicator covered with PVDC wrap, PVC wrap, and PE wrap under UV activation are shown in Table 1. The bleaching time of the oxygen indicator with PVC wrap is 15.9 seconds. Meanwhile, the indicators with PE and PVDC wrap are in 17.6 and 20.4 seconds. For the bare indicator without plastic wrap, the colorless time is 15.1 seconds due to direct oxygen interaction on the indicator surface. The high bleaching time the indicators with PVDC wrap was obtained from the interaction of UV absorption inside the film under UV irradiation at λ_{max} 395 nm corresponding to %T spectra of plastic wraps in Fig. 2. The intensity of UV rays transmitted to PVDC wrap was reduced thus the induced TiO_2 catalyst under UV activation in bleaching mechanism was decreased leading to high bleached time on the indicator area coving with PVDC warp. To compare bleaching time, the performance of the indicator covering with PVC wrap is shown close to the bare indicator. Therefore, the indicator covered with different plastic wraps can interact with UV light resulting in a colorless feature. The thin layer of plastic wrap on the TiO_2/MB oxygen indicator does not affect on coloration and bleaching of the indicator mechanism under UV irradiation owing to high transmission in UVA region corresponding to transmission spectra of plastic wraps in Fig. 2.

Absorbance spectra of TiO_2/MB nanocomposite indicators covered with different plastic wraps under the initial indicator (colored state) and after UVA irradiation (bleached state) are illustrated in Fig. 3. High absorption in all spectra during 250 to 350 nm is related to TiO_2 nanoparticles [10]. While the optical characteristic peak of methylene blue is assigned as

Table 1 Bleached Time of TiO_2/MB oxygen indicators covered with different plastic wraps

Types of plastic warp	**Bleached time (s)**
Bare	15.1
PVDC	20.4
PVC	15.9
PE	17.6

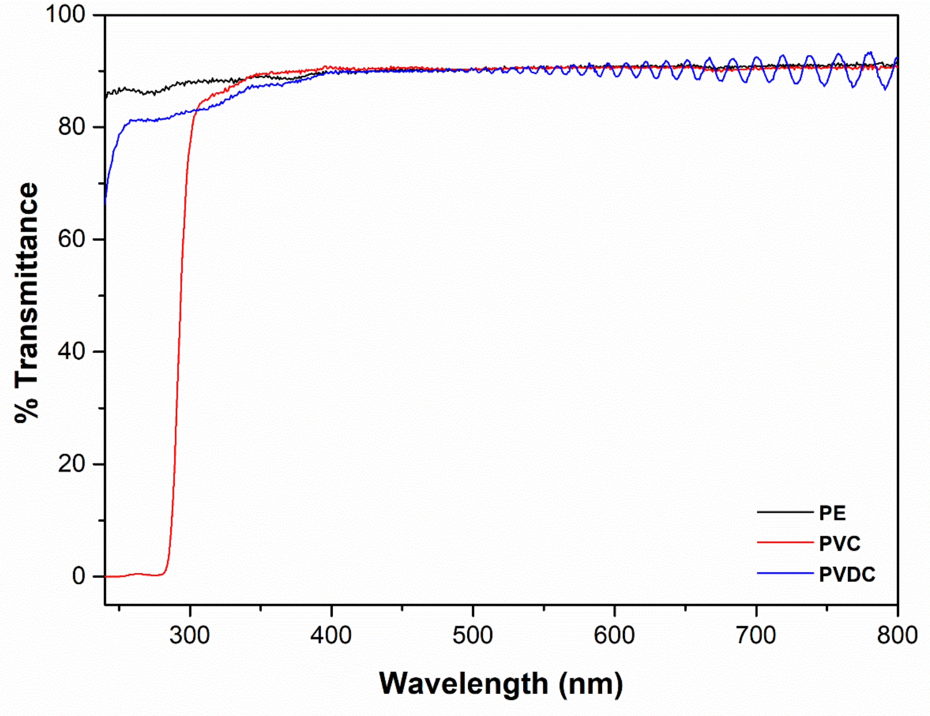

Fig. 2. Transmission spectra of PVC, PVDC, and PE plastic wrap

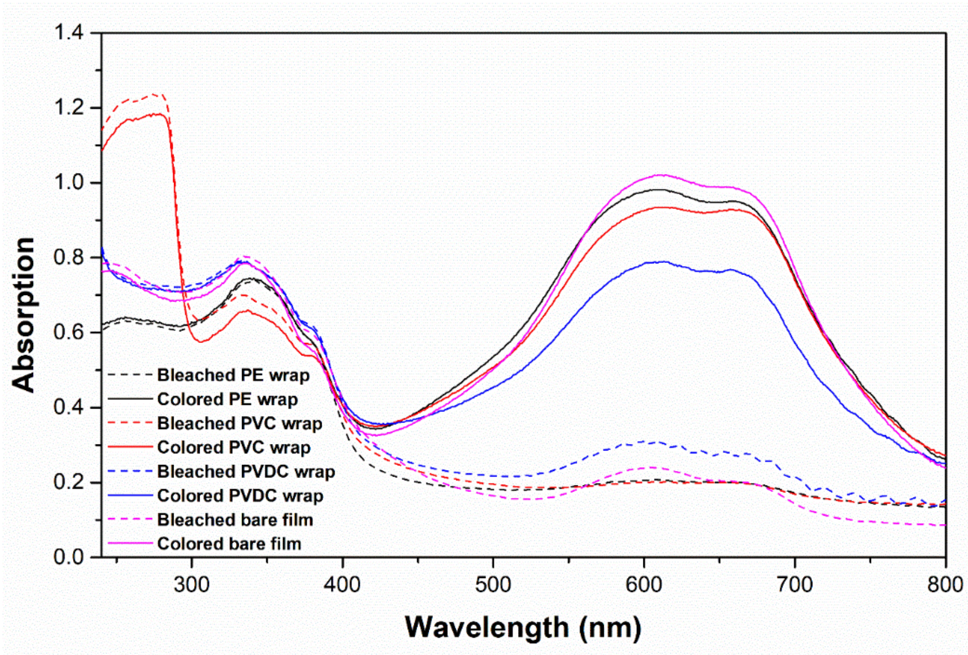

Fig. 3. Absorbance spectra of TiO_2/MB oxygen indicators covered with different plastic wraps under bleached and colored state [solid line; the initial indicators (colored state) and dotted line; the indicators after UVA irradiation (bleached state)]

the prominent peak in a range of 500 to 700 nm [11]. For the initial indicator with blue shading as colored state, high absorption in MB region is obtained at the bare indicator without plastic wrap covering. The indicator with PE wrap showed a similar intensity compared to bare film. Meanwhile, the absorbance intensity of the indicators with PVC wrap and PVDC wrap was decreased due to the influence of the refractive index in the covered film resulting in light propagation into TiO_2/MB layer. However, the peak positions of all samples are still the same patterns. After UVA irradiation or bleached state, the oxygen indicator layer of each condition was in colorless surface relating to the decline of MB absorption. This result can be interpreted as the change of chemical structure from MB to LMB [12]. The absorbance intensity of the indicator covered with PE and PVC wrap was like the bare film. For the indicator covered with PVDC wrap, high absorbance intensity occurred after UV irradiation corresponding to the remaining blue color of MB structure on TiO_2/MB layer. Therefore, the optimized plastic wrap of TiO_2/MB nanocomposite indicator was PE and PVC due to the same absorbance spectra and intensity.

Absorbance spectra of TiO_2/MB oxygen indicators under oxygen detection in air ambient for 300 min covered with different plastic wraps are depicted in Fig. 4. The initial state with the blue color of TiO_2/MB indicator is shown at the top line in each figure. The bleached color on the indicator after UVA treatment is labeled as 0 min relating to the bottom line in each figure. Then the bleached TiO_2/MB indicators were placed in air ambient at room temperature to monitor their color change under oxygen attraction on the surface of TiO_2/MB layer.

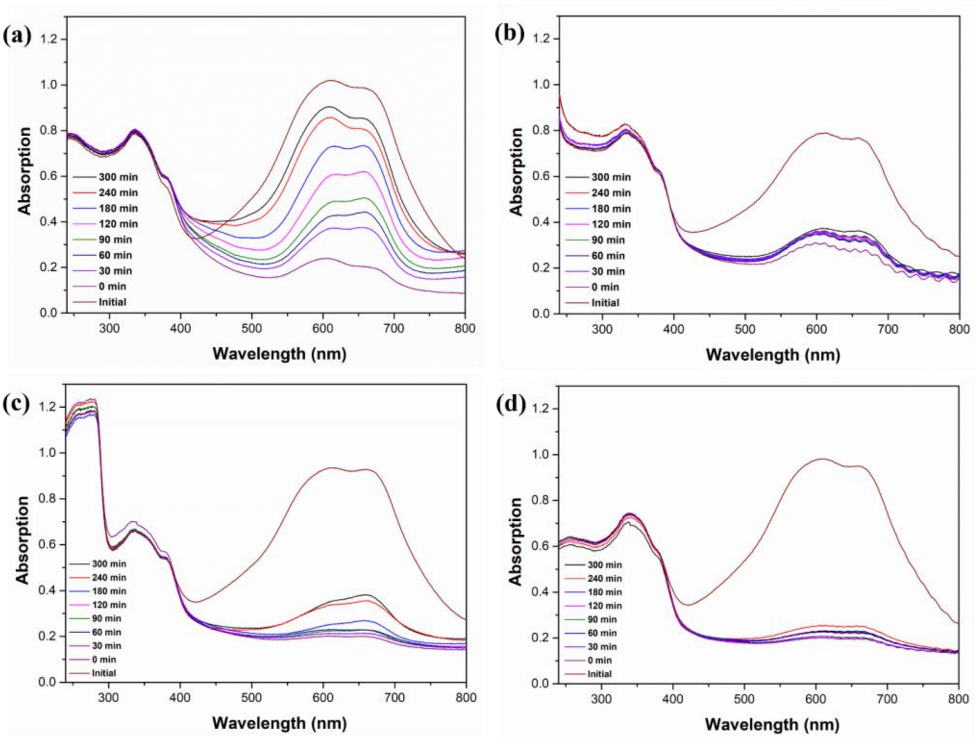

Fig. 4. Absorbance spectra of TiO_2/MB oxygen indicators in oxygen detection in air ambient for 300 min covered with different plastic wraps (a) bare film, (b) PVDC wrap, (c) PVC wrap, and (d) PE wrap

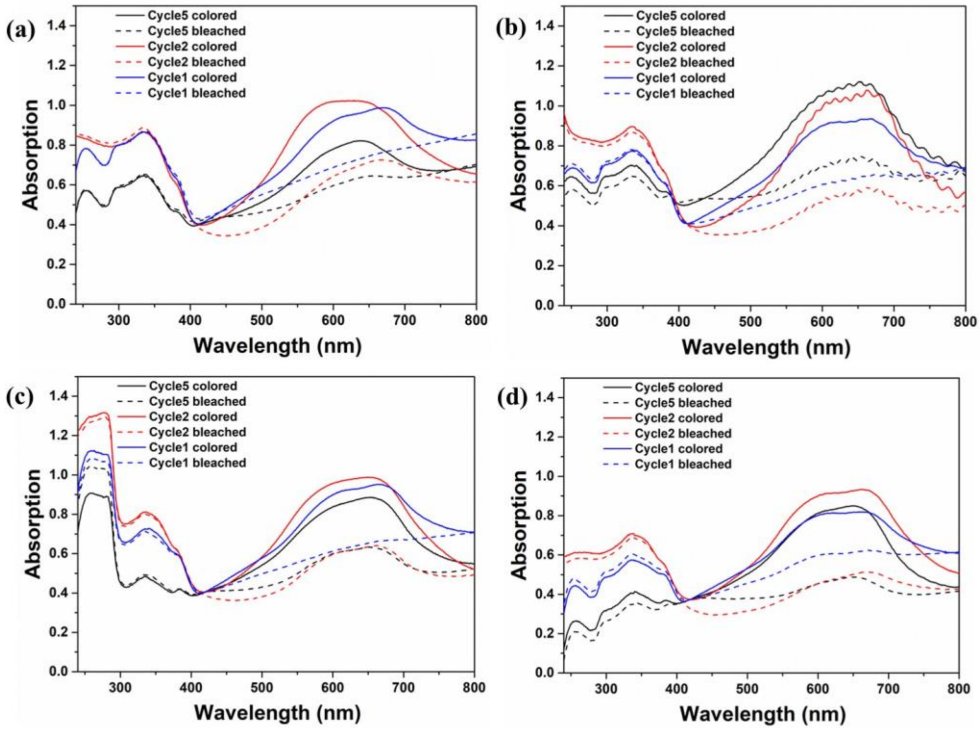

Fig. 5. The evaluation of TiO_2/MB indicator performance with the reused cycles in air ambient covered with different plastic wraps (a) bare film, (b) PVDC wrap, (c) PVC wrap, and (d) PE wrap

The oxygen test on all samples of TiO_2/MB indicators was operated for 300 min and measured absorbance intensity at 30 min. In Fig. 5(a), the absorption intensity of MB region in the bare TiO_2/MB indicator under oxygen detection was significantly increased depending on the prolonged period of oxygen detection. For the coving of plastic wrap on the indicator, absorbance intensity depending on time changing slowly occurred that corresponded to the blue color changing due to the retardation of oxygen gas on the indicator surface. After oxygen detection for 300 min, the color changing from colorless to blue occurred by the indicators covered with PVDC and PVC wrap in Fig. 5(b) and 5(c). Meanwhile, the intensity of PE wrap on the indicator in Fig. 5(d) was almost stable owing to the unique property of blocking oxygen gas.

The performance of the TiO_2/MB oxygen indicators with different covering plastic wraps under oxygen gas detection was monitored by the photographs at different times as depicted in Table 2. This part is studied to the maximum of blue shading under oxygen on the indicator surface. The fastest blue recovery of the oxygen indicator occurred by the bare TiO_2/MB indicator because oxygen gas could directly interact with the indicator under air ambient. The time for oxygen indicator discoloration in blue color was complete in 48 h. In the case of coving plastic wraps, the color state of the indicators with PVDC wrap was slowly changed due to the excellent barrier of oxygen gas and completely blue shading in 72 h. Meanwhile, the recovery time of the blue shade on the indicator with PE wrap was less than the indicator with PVDC film depending on low barriers to oxygen gas transmission. The blue recovery time of the covering PVC wrap on the indicator was shown in 48 h like the bare TiO_2/MB composite film. Good performance of covering PVC film on the oxygen indicator occurred

Table 2 The performance and cyan percentage of the TiO_2/MB oxygen indicators with different plastic wraps under air ambient

Type of plastic wrap	Cyan intensity percentage of oxygen indicator									
	0 min	30 min	1 hrs	2 hrs	4 hrs	8 hrs	12 hrs	24 hrs	48 hrs	72 hrs
Non-wrap	3%	8%	12%	20%	41%	69%	81%	86%	90%	
PVDC	4%	4%	4%	5%	6%	11%	19%	39%	70%	75%
PVC	3%	6%	7%	14%	23%	44%	51%	78%	82%	
PE	12%	14%	16%	17%	20%	31%	39%	55%	74%	79%

from the high gas permeability and clarity layer relating to the interaction of large amounts of oxygen molecules on the activated area on the indicator [13]. Therefore, the covering of PVC wrap on TiO_2/MB indicator showed similar performance with the absence of plastic wrap on the oxygen indicator.

The repeatability of TiO_2/MB indicators covered with different plastic wraps was tested under 5 cycles monitored by absorbance spectra under colored/bleached state as presented in Fig. 5. The difference of colored and bleached states of TiO_2/MB oxygen indicator without plastic wrap was decreased after more reused cycle as seen in Fig. 5(a). Thus, the lower efficiency of the indicator occurred due to the influence of the interaction between the oxygen molecules and TiO_2/MB composite relating to some destructible areas on the indicator surface. Meanwhile, the stable performance of TiO_2/MB oxygen indicator at more reused cycles was obtained by the covering of plastic wraps as depicted in Fig. 5(b)-5(d). The same spectra patterns in colored and bleached states of the indicator covered with plastic wraps were obtained. These results can be interpreted that TiO_2/MB nanocomposite layer with plastic wrap covering was still stable and durable for the repeatability on oxygen indicator application.

4. Conclusion

The performance of TiO_2/MB oxygen indicators was related to the influence of covered plastic wraps such as PVDC, PVC, and PE wrap. More bleached and colored time in UV irradiation and oxygen detection was obtained by coving the plastic wrap on the indicator surface due to obstructing the gas molecule transfer with the thin plastic film layer. While fast reaction of indicator efficiency occurred on the bare film without plastic wrap because of the direct contact of oxygen molecules on the active area. The optimized plastic wrap on TiO_2/MB indicator was obtained at PVC wrap because of the appearance of similar absorbance spectra in the bleached/colored state compared with the bare oxygen indicator. This phenomenon can occur through excellent oxygen gas transfer in PVC film property.

Acknowledgment

This work has been supported by the KMITL Research and Innovation Services (KRIS) in 2021 with grant No. RE-KRIS-FF65-36. The authors would like to thank College of Materials Innovation and Technology, King Mongkut's Institute of Technology Ladkrabang (KMITL) for laboratory research and JASTIP fund for milling machine support.

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