



Monitoring time and temperature by methylene blue containing polyacrylate film

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ABSTRACT

The redox characteristic of methylene blue in polyacrylate film has been investigated for applications in monitoring time and temperature. This monitoring capability is based on a color change from colorless to blue under exposure to air. The oxidation process is controlled by the air diffusion which is affected by the chemical structure of the polyacrylate. The activation energy of diffusion, which was calculated by Arrhenius equation, goes up with increasing the rigid structure of the polyacrylate. The results correlate well with the glass transition temperature of different polyacrylates. The unique feature of the methylene blue to change color under oxidation, can be used for the fabrication of low cost visual sensors for monitoring time and temperature.

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1. Introduction

Visual time monitoring that is based on color transition has found many applications in different fields of science and technology. There are a number of time–temperature integrators used in food and pharmaceutical industry which help to determine safe storage period and freshness of the products [1–6]. Time indicating devices are also widely used in manufacturing passes and permits [7,8]. Many time indicators are based on dye diffusion [6,9–11] or on reaction of a reduced dye with oxygen [5,7,12,13]. Methylene blue (MB) is one of the most common redox dyes. The easy reduction of MB to leuco methylene blue (LMB) and its re-oxidation (Fig. 1) have extensive use throughout industry. For example, the commercial colorimetric oxygen indicator is based on this reaction [14–20]. The working principle of the oxygen indicator is based on the fast oxidation of colorless LMB in the presence of oxygen to blue MB. The reduction of MB can occur as a result of an electrochromic reaction using various reducing agents. One system, The Ageless Eye[®] oxygen indicator [19,20] (Mitsubishi Gas Company) uses MB, glucose and alkali for the reaction. Upon anaerobic condition MB is reduced by glucose to leuco form, which can be readily re-oxidized by O₂ with color change. The reduction of MB can also occur as a result of electron and proton transfer from a sacrificial electron donor (SED)

under ultraviolet (UV) irradiation (photochromism) [21,22]. Mills and coworkers [23] reported a novel UV-activated oxygen indicator based on nanoparticles of titania for electron transfer and reduction of MB by triethanolamine using UV light (315–380 nm). This oxygen indicator is successfully used in food and pharmaceutical packaging. Finally, the redox reaction of MB has found wide applications in optical storage media with limited access [24]. In this technology CD and DVD disks with optical transparent LMB coating are produced. The transparent coating allows access to the data when LMB reacts with oxygen and turns into colored MB, now limiting data access. The reversible reaction of reduction and re-oxidation of MB is also widely used in data recording industry and holography [25,26].

The opportunity of this and other similar dyes in the applications of sensors and data storage is very promising. Polymers are ideal carriers for presenting the dye molecule in a convenient and useful form. Therefore, the more comprehensive knowledge about the mechanism and kinetics of the above mentioned reactions in polymer media can open new ways of their usages. In most cases, attention has been paid to investigate the reduction kinetics of MB to leuco dye [21,27,28]. The oxidation of LMB blue is very fast under sufficient amounts of oxygen. However, if LMB is situated in polymer media, the oxidation speed will be slowed down in air due to a diffusion process. Therefore, the investigation of diffusion-kinetics of LMB oxidation is important for future development and inventions. In particular, oxidation within an extended period can be used for “time monitoring”. The principle of oxidative color transition can be exploited for the development of visual

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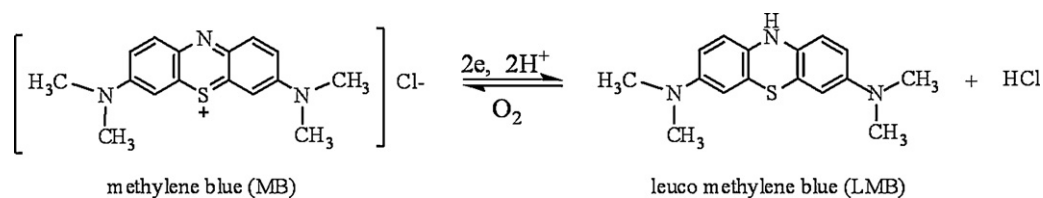


Fig. 1. Reduction and re-oxidation of MB.

time–temperature integrators and other apparatuses connected to time duration and changes of oxygen concentration. Therefore, the oxidation of MB in different polyacrylates that is accompanied by color transition can be used for monitoring of time and temperature.

2. Experimental

2.1. Materials

The methylene blue (MB) used in this work was obtained from Acros Organics (Belgium), photoinitiator: 2,2-dimethoxy-2-phenyl acetophenone – benzil dimethyl ketal (DBK) – from Ciba Specialty Chemicals (Switzerland), 2-Hydroxyethyl methacrylate (HEMA) was obtained from Sigma–Aldrich. Ethoxylated (15) trimethylolpropane triacrylate (EO(15)TMPTA), tetraethylene glycol diacrylate (TEGDA), propoxylated (2) neopentyl glycol diacrylate (PO(2)NPGDA), ethoxylated (3) bisphenol A diacrylate (EO(3)BPADA), tricyclodecane dimethanol diacrylate (TCDDA), tris (2-hydroxy ethyl) isocyanurate triacrylate (THEICTA), polyethylene glycol (400) diacrylate (PEGDA), ethoxylated (9) trimethylolpropane triacrylate (EO(9)TPTA), highly propoxylated (5.5) glyceryl triacrylate (HPO(5.5)GTA) were obtained from Sartomer Co. (USA). The chemical structures of used acrylates are shown in Table 1. All chemicals were used as received without any purification.

2.2. Preparation of leuco methylene blue based polymer films

The compositions for LMB contained polymer films consists of 1 g of 1% solution of MB in HEMA, 2 g of HEMA, 3 g of other acrylate monomer (depending on composition) and 0.24 g of BDK.

The mixture of MB, acrylates and photoinitiator was stirred for about 10 min to obtain a blue solution. Then a 100 μm blue thin film was placed on the glass substrate using a draw down rod. The samples were UV irradiated for about 5 min in a nitrogen atmosphere. During that time two concurrent reactions take place: acrylate polymerization and photobleaching of methylene blue. After that, thin (around 100 μm) colorless acrylate film was obtained. All UV radiations were conducted using UV light, provided by 4-watts UVGL-25 Mineralight[®] lamp (UVP, Inc., San Gabriel, CA), $\lambda = 365 \text{ nm}$.

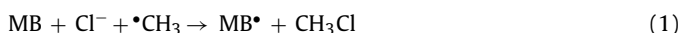
2.3. Measurements

The rate of oxidation of LMB to MB was followed by the change of absorbance measured by a Perkin Elmer Lambda 35 UV/VIS Spectrometer. Scans of the UV/VIS spectrum of the thin polymer films were taken over the range of 300–800 nm. The oxidation was carried out at 277, 298, 308 and 318 K under an air atmosphere in darkness.

Glass transition temperature was determined by differential scanning calorimeter (Diamond DSC, PerkinElmer). The samples were scanned by a ramping rate of 10 $^{\circ}\text{C}/\text{min}$ from 50 to 100 $^{\circ}\text{C}$ or 150 $^{\circ}\text{C}$ and the furnace was heated and purged by N_2 with a flux of 20 ml/min.

3. Results and discussion

The MB containing polyacrylate films were prepared by UV polymerization of a mixture of acrylates monomers and benzil dimethyl ketal (BDK) photoinitiator. The photoinitiator under UV irradiation ($\lambda_{\text{max}} = 365 \text{ nm}$) is able to undergo a photocleavage reaction with the generation of free radicals [29] (Fig. 2), which initiate polymerization of acrylates. At the same time, the radical formed from benzil dimethyl ketal is able to reduce MB. The detailed reaction mechanism of photoreduction of MB has been published recently [30]. The main reaction involves an interaction of MB with active electrophilic methyl radical which was generated from the photocleavage of BDK (Eq. (1)).



As a result of this interaction, the semi-reduced MB radicals are generated. Further reduction of semi-reduced methylene blue radical leads to the formation of leuco dye. Thus, the UV irradiation of MB/acrylate solution containing photoinitiator BDK leads to two parallel processes: polymerization of acrylates and reduction of MB. This is how the colorless polyacrylate films containing LMB are obtained. Upon contact with oxygen, leuco dye readily oxidizes to MB that entails color transition from colorless to blue. The oxidation of LMB (Eq. (2)) occurs in solid media which is preceded by the diffusion of air. If the rate of reaction is limited by the diffusion, the diffusion-kinetic will regulate the rate of reaction.



According to Fick's Second Law, the concentration change within the diffusion volume with respect to time is shown in Eq. (3).

$$\frac{\partial C}{\partial t} = \frac{D \partial^2 C}{\partial x^2} \quad (3)$$

where C is the oxygen concentration [mol m^{-3}], t is time [s], D is diffusion coefficient [$\text{m}^2 \text{ s}^{-1}$], x is the distance [m]. The diffusion coefficient does not depend on the oxygen concentration, so the average value of distance squared X^2 of diffusion with time (t) is determined by Eq. (4):

$$X^2 = 2Dt \quad (4)$$

If the thickness of diffusion layer and the diffusion time are known, then the coefficient of diffusion can be determined:

$$D = \frac{X^2}{2t} \quad (5)$$

Diffusion in the samples runs deep into the film along the distance X . Thin films have been obtained on glass substrate, so the air diffusion occurs from one side of the film; therefore distance X is equal to film thickness. For the films without substrate, air will diffuse from two sides of the film. That is why X in such samples is equal to 1/2 of the film thickness.

The time of diffusion is defined from spectrophotometric measurements. As soon as oxygen penetrates into polymer matrix, it reacts with LMB and colored dye (MB) appears, according to Eq. (2). The presence of MB is determined by absorption spectra. The typical result of spectrophotometric measurements is illustrated in

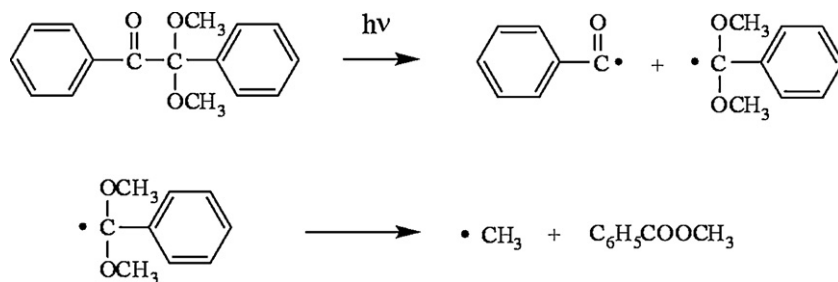


Fig. 2. Photocleavage reaction of benzil dimethyl ketal.

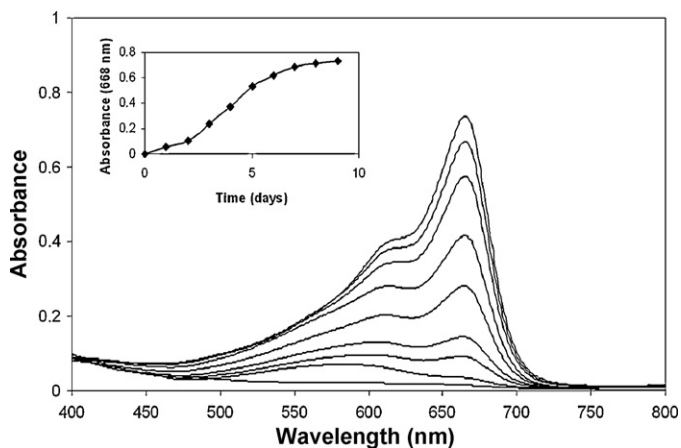


Fig. 3. Absorption spectra of LMB oxidation by O_2 , incorporated in polyacrylate (HEMA/TCDDA) thin film (thickness 10^{-4} m, $T = 298$ K).

Table 2
Diffusion coefficient of air into LMB containing polyacrylate thin films at different temperatures.

T (K)	Diffusion coefficient ($m^2 s^{-1}$)		
	HEMA/EO(15)TMPTA	HEMA/EO(3)BPADA	HEMA/TCDDA
277	1.39×10^{-13}	1.39×10^{-13}	4.13×10^{-15}
292	2.31×10^{-13}	2.31×10^{-13}	7.23×10^{-15}
308	2.78×10^{-13}	2.78×10^{-13}	9.65×10^{-14}
318	3.47×10^{-13}	3.47×10^{-13}	1.16×10^{-14}

The temperature dependence of the diffusion coefficient was defined by Arrhenius's equation:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad \text{or} \quad \ln D = -\frac{E_a}{RT} + \ln D_0 \quad (6)$$

where E_a —the activation energy of the diffusion, D_0 —frequency factor, $\ln D_0$ —an integration constant. Arrhenius plots ($\ln D$ against $1/T$) for different polyacrylate compositions as shown in Fig. 5. The activation energies E_a of oxygen diffusion in each polymer binder, D_0 and correlation coefficients of calculation are summarized in Table 3.

The differences in the activation energy for three polyacrylate film are possible due to the difference in the crosslinking density and rigidity of the polyacrylates. The high crosslinking rigid films have lower diffusion rate than that of low crosslinking flexible films

Table 3
Activation energy, integration constant and correlation coefficient of oxidation of leuco methylene blue in polyacrylate media.

Polyacrylate	E_a (kJ mol $^{-1}$)	D_0 ($m^2 s^{-1}$)	r^2
HEMA/EO(15)TMPTA	17.43529	2.66×10^{-10}	0.9851
HEMA/EO(3)BPADA	19.75656	7.88×10^{-11}	0.9901
HEMA/TCDDA	20.17974	2.59×10^{-11}	0.9938

[31]. The polymers with high crosslinking density and rigid structure exhibit high glass transition temperature. Therefore, diffusion coefficient of polymer is dependent on its glass transition temperature. To prove this, the following experiments have been carried out.

The rate of oxidation of LMB in ten different polyacrylate matrixes at $25^\circ C$ was measured. The polymer binder for LMB was a mixture of two acrylates: 50% of HEMA and 50% of an acrylate listed in Table 1. The diffusion properties of the polyacrylates depend on the chemical structure of monomer and its T_g , functionality and molecular weight per one active functional group. All of these

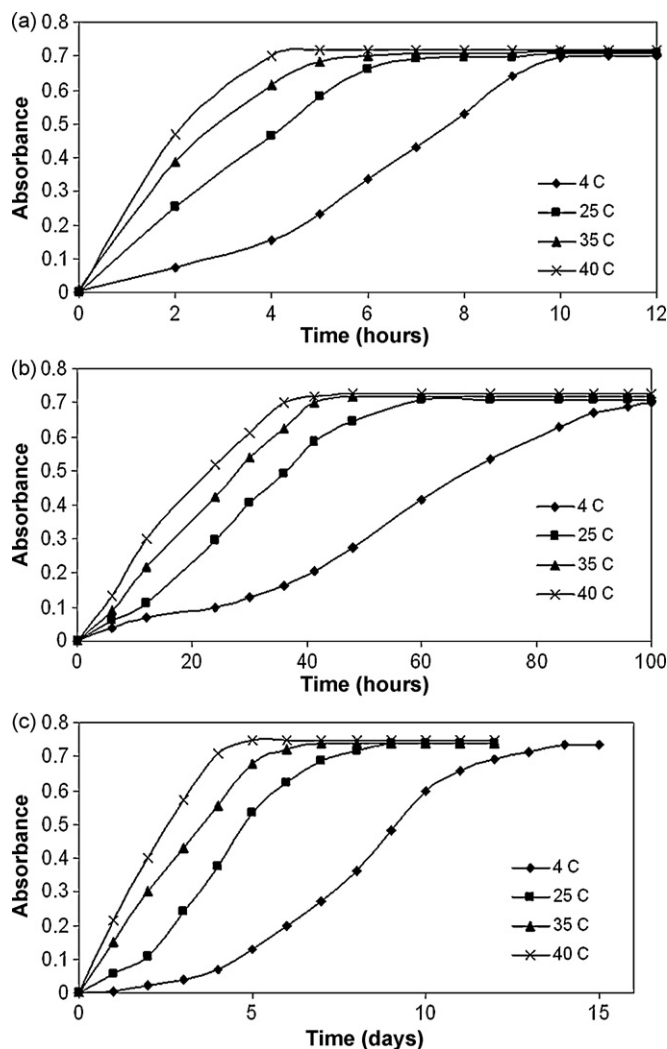


Fig. 4. Kinetic curves of LMB oxidation in different polyacrylate matrixes: (a) HEMA/EO(15)TMPTA, (b) HEMA/EO(3)BPADA, (c) HEMA/TCDDA.

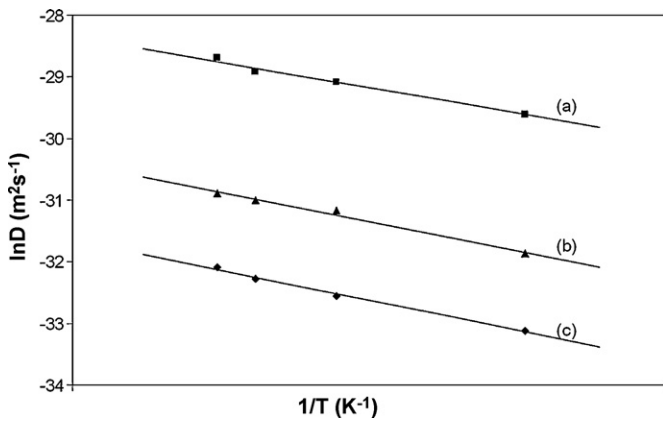


Fig. 5. Arrhenius plot for LMB oxidation in different acrylate compositions: (a) HEMA/EO(15)TMPTA, (b) HEMA/EO(3)BPADA, (c) HEMA/TCDDA.

Table 4
Glass transition temperature of the polyacrylate samples.

Sample	T_g (°C)
HEMA:EO(15)TMPTA	9.8
HEMA:PEGDA	-5.5
HEMA:EO(9)TPTA	10.4
HEMA:HPO(5,5)GTA	48.2
HEMA:TEGDA	17.2
HEMA:PO(2)NPGDA	46.4
HEMA:EO(3)BPADA	44.5
HEMA:TCDDA	96.1
HEMA:THEICTA	112.3

parameters are also summarized in Table 1. The glass transition temperatures of the polyacrylate sample are given in Table 4. As was expected, the rate of LMB oxidation in different polyacrylate matrixes is entirely dependent on the glass transition temperature of polymer. The relationship between the time of LMB oxidized in the polymer film (10^{-4} m in thickness) and the glass transition temperature of the polyacrylates is given in Fig. 6. A linear relationship is obtained with a correlation coefficient of $r^2 = 0.9387$

The air diffusion coefficient of each polyacrylate at 25 °C was calculated by Eq. (5) using its measured diffusion time. Then, the relationship between the glass transition temperature of each polyacrylate and its air diffusion coefficient was plotted (Fig. 7). The correlation presents a bend at 25 °C which is the temperature of the test. In other words, the air diffusion coefficient of each polyacrylate at measured temperature correlates well with its glass transition temperature. If the glass transition temperature of polyacrylate

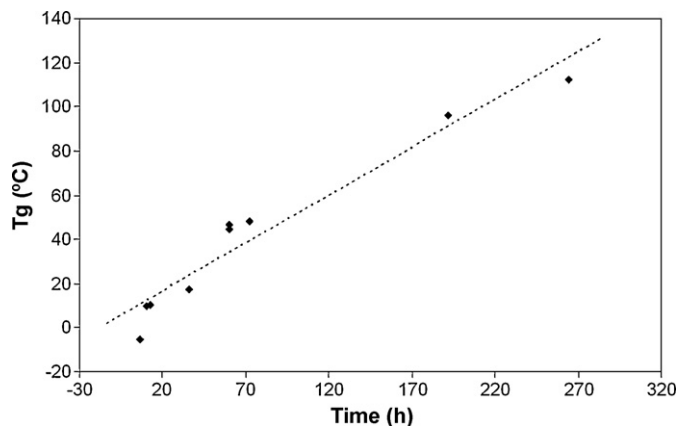


Fig. 6. Time of color transition in polyacrylate thin films (100 μm) versus their glass transition temperature.

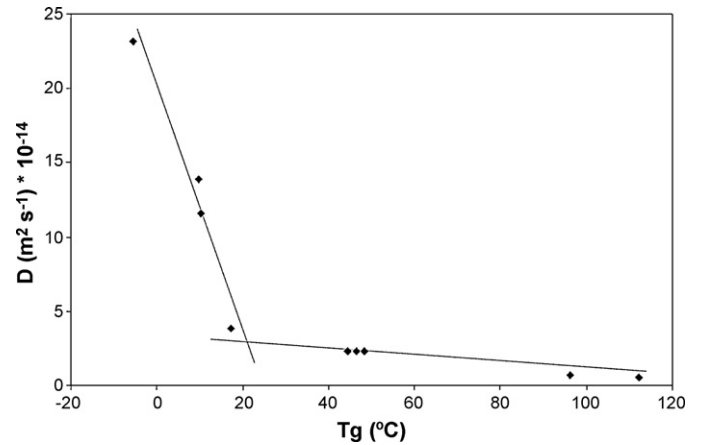


Fig. 7. The relationship between glass transition temperature of polyacrylates and their diffusion coefficient at 25 °C.

is lower than environmental temperature, its diffusion coefficient will be very high with low activation energy of diffusion. When the temperature of the environment is higher than that of the glass transition of polyacrylate, its air diffusion rate will be very fast.

The time–temperature relationship of LMB oxidation in polyacrylate thin films (HEMA/EO(15)TMPTA, HEMA/EO(3)BPADA and HEMA/TCDDA) is given in Fig. 8. Thus, the complete oxidation of LMB in HEMA/EO(15)TMPTA ($T_g = -32$ °C) film with the thickness 10^{-4} m is limited to a few hours. At the same time, the complete oxidation in polyacrylates with higher T_g can last few days. The color of the films during the oxidation changes gradually (Fig. 9). This feature can be exploited in many future applications mentioned previously (data recording industry, time sensors and time–temperature integrators).

MB is light sensitive. In case of air exposure of the film containing LMB, the rate of color change is different in the dark or light conditions, because the oxidization and photobleaching occur simultaneously in the light. Fig. 10 shows that the amount of MB formed decreases with increasing light intensity. This result limits the utility of time and temperature sensors based on the technology of color change of photoreduced MB in polymer in lighted situations. However, the problem can be solved by using a control standard in parallel with the sensor made from the film containing photoreduced MB. The control standard is made of the sensor with completely oxidized blue film. When a fresh sensor is placed next to the control standard in the light, both films are exposed to the

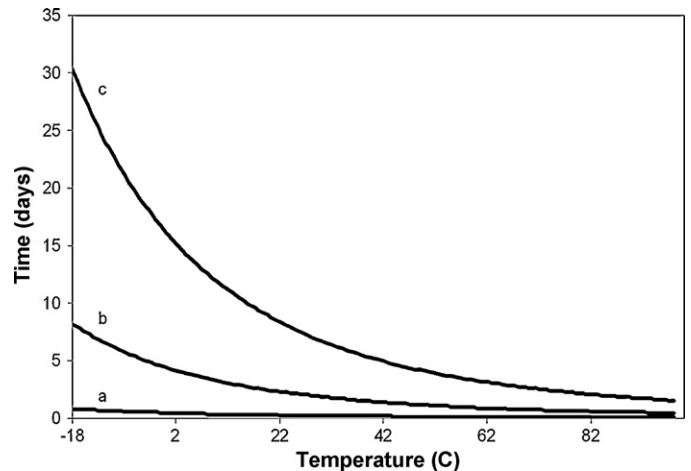


Fig. 8. Time–temperature relationship of LMB oxidation in polyacrylate thin films (100 μm): (a) HEMA/EO(15)TMPTA, (b) HEMA/EO(3)BPADA, (c) HEMA/TCDDA.

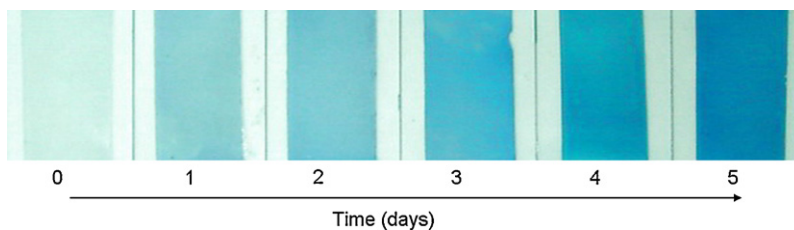


Fig. 9. Gradual color transition in HEMA/TCDDA/MB 100 μm film.

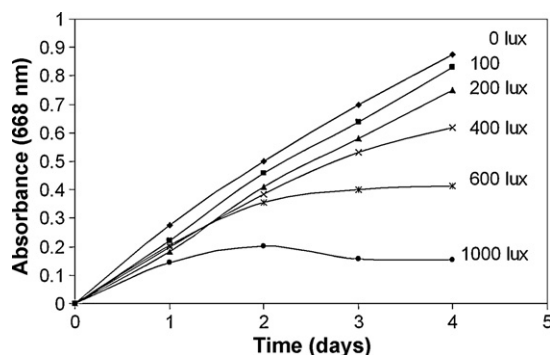


Fig. 10. Kinetic curves of LMB oxidation in HEMA/TCDDA polyacrylate matrix at different light levels, illuminated by fluorescent lamp.

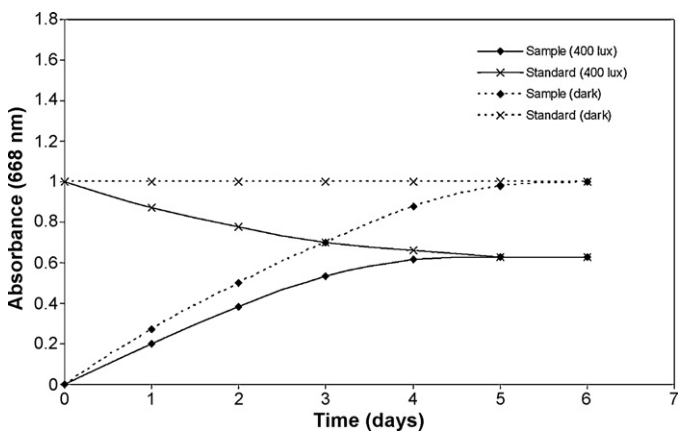


Fig. 11. Kinetic curve of LMB oxidation in HEMA/TCDDA polyacrylate sample in dark or in 400 lux illuminance as compared with the standard.

air simultaneously and the degree of photobleaching will be the same for both films. Thus, we can still observe the extent of color changing with respect to the time in the light. Fig. 11 shows the same duration of the time can be obtained either in dark or light condition when the control standard was used together with the sensor.

4. Conclusion

The LMB based polyacrylate films are very promising materials for application as sensors and for data storage. The polymer matrix has a tendency to slow the oxidation rate in air with a gradual color transition. The rate of oxidation of LMB in polyacrylate can be described by diffusion-kinetics. The diffusion coefficients and activation energy of diffusion have been calculated for different polyacrylate matrixes. The time–temperature relationship of LMB oxidation in polyacrylate matrixes has been determined for the manufacture of time–temperature integrators, oxygen sensors and etc. The diffusion coefficient of air into polymer matrix correlates well with the glass transition temperature of the polymer

at specific measuring temperature. The time of LMB to reach full oxidation is a linear relationship that depends on the glass transition temperature of polyacrylate. This result is very useful for the selection of appropriate polyacrylate matrix for the required time of color transition. The principle of gradual color transition can be used in the manufacture of time–temperature integrators, and other apparatus related to the elapsed time.

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