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The design and fabrication of a bis(2,4,5-trichloro-6-carbo-butoxy-phenyl)oxalate-based chemiluminescent signaling system

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The present study focused on the synthesis of bis(2,4,5-trichloro-6-carbobutoxy-phenyl)oxalate and the peroxide component for the manufacture of a novel chemiluminescent system for night signaling. The minimum luminous flux necessary was established and the processing parameters for the manufacture of the plastic cover of the chemiluminescent system were set. The tests performed after 12 months from the vials filling with the chemiluminescent components returned satisfactory results in terms of light emission and mechanical stress.

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1. Introduction

In order to use chemiluminescent mixtures (CLM) for lighting/signaling systems, the applicable regulations and the practical requirements were necessary to identify. The recommended light levels in different workspaces and activities, accordingly to the International Organization for Standardization (ISO 8995-1:2002 - Lighting of work places) [1], are given in Table 1. In the illumination levels column from Table 1, the first is the minimum allowable value and the latter value is optimal for the visual comfort.

Table 1. Recommended light levels [1]

No.	Activity / visual task	Illumination levels (lx)
1	Circulation areas	20-50
2	Circulation areas, storage	50-150
3	Working areas where visual tasks are only occasionally performed	100-200
4	Tasks with simple visual requirements	200-500
5	Tasks with medium visual requirements	300-750
6	Tasks with difficult visual requirements	750-1500
7	Tasks with special visual requirements	1000-2000
8	Tasks with very special and exacting visual requirements	> 2000

Given the applications of CLM-based lighting/signaling systems, the illumination level provided should be considered. This level must be correlated with other factors that take into account other parameters, such as: eye sensitivity, atmospheric attenuation, color, contrast, etc. In order to establish the minimum value for necessary luminous flux of CL signaling systems, the regulations and documentations in marine signaling lights were used here. This field is well documented due to the particular importance of marine signaling lights for navigation. The outcomes from diagrams and formulas have been checked and confirmed practically in different weather conditions.

Accordingly to IALA (International Association of Marine Aids to Navigation and Lighthouse Authorities), the nominal range of a signal light is the distance where this light produces a $2x10^{-7}$ lx illumination intensity at the observer's eye level, at night conditions. This is indeed a practical illuminance value for viewing aid-to-navigation lights at night against a dark background, which was agreed in 1933 at the International Technical Conference of Lighthouse Authorities. At 0.2 mlx, a light can be detected, light color is discernable, and flash duration is discernable too [2]. The required 0.2 mlx illumination intensity at the observer's eye level corresponds to a situation with no background lighting. In most real situations, the lights are viewed against a background that does have lights, this reducing the luminous range. Also, the recommended method for the compensation of the background lighting is to use different values for the required illuminance. Two different values should be used as a replacement for 0.2 mlx: 2 mlx, for minor background lighting, and 20 mlx, for substantial background lighting.

The atmospheric conditions influence directly the visibility limits, which are defined by transmittance (100% is represented by a perfectly clear atmosphere that does not exist in real conditions). Due to the fact that weather conditions vary from one region of the world to another, the visibility limits of maritime lighthouses are given as arbitrary standards corresponding to a meteorological visibility of 10 nautical miles (18.5 km), related to a 74% transmittance. The common outdoor day and night light levels can be found in Table 2.

The illuminance (E) can be calculated using Allard's law [1,4],

$$E(d) = \frac{I \cdot 0.05^{\frac{d}{V}}}{3.43 \cdot 10^6 \cdot d^2} \qquad (1)$$

where d is the distance, I is the luminous intensity, and V is the meteorological visibility. If the light appears as a point source, the luminous range (D) is defined as the maximum distance at which a light can be seen at the observer's eye (formerly known as threshold). At the maximum distance, E is reduced to the value E_t at the observer's eye.

$$I = (3.43 \cdot 10^6) E_t D^2 (0.05)^{-\frac{D}{V}} \qquad (2)$$

Table 2. Outdoor light levels [3]

No.	Condition	Illumination (lx)
1	Sunlight	107,527
2	Full daylight	10,752
3	Overcast day	1,075
4	Very dark day	107
5	Twilight	10.8
6	Deep twilight	1.08
7	Full Moon	0.108
8	Quarter Moon	0.0108
9	Starlight	0.0011
10	Overcast night	0.0001

Using the formulas for determining the night luminous range for a CLM-based lighting/signaling system, it results that a source with a $5.65 \cdot 10^{-2}$ lm luminous flux, is visible even for a 55% transmittance and an important background lighting, from 165 m distance and from 205 m for a 74% standard transmittance.

The average useful duration of a CLM-based lighting/signaling system is the amount of time until illumination decreases below 5% of the initial value. This means that, for the same lighting/signaling system, the initial luminous flux is ~1.10 lm, and the afferent luminous range is 655 m, for a 74% standard transmittance.

Taking into consideration the fact that regulations regarding practical applications of CLMs are not set, it can be stated that the minimum luminous flux that ensures a 200-m light range for a 74% standard transmittance is sufficient for reaching our goals regarding the lighting / signaling system. These values are consistent with those found at major manufacturers of light sticks. Thereby, the minimum luminous flux, necessary for the manufacture of CLM-based lighting / signaling system, is $5.65 \cdot 10^{-2}$ lm.

The operating principle of "cold light" generating devices (CLM-based lighting/signaling system) consists in mixing the two solutions: CL reagent (oxalate component) and peroxide solution as oxidizing reagent. The chemical energy resulted from the reaction determines the fluorescent excitation that emits light while it returns to fundamental state.

2. Materials and methods

2.1 Components of the CL lighting / signaling system

The CLM was prepared taking into account the practical requirements of the lighting / signaling systems, that components are kept separated and combined only when it is necessary to produce light. The reagents were mainly purchased from Aldrich, and used without further purification. The volumetric ratio used in the CL mixture has been chosen as 3:1 between oxalate and peroxide components.

2.1.1 Preparation of oxalate component

The synthesis protocol was previously detailed in [5]. In brief, 21.6 grams of bis(2,4,5-trichloro-6-carbo-butoxy-phenyl)oxalate (TCCBPO) and 80 mL of dibutylphtalate (DBP) were placed in a 100 mL brown flask equipped with magnetic stirrer, thermostatic heating bath, thermometer and condenser fitted with a calcium chloride drying tube. The mixture was stirred for 60 min. at 80 °C and then cooled to room temperature. Subsequent, 0.3840 grams of 1-chloro-9,10-bis(phenylethynyl)anthracene and 1.1485 g of PEG 200 were added. The volume was completed to 100 mL with DBP and the mixture was stirred for 20 min. at 60 °C; finally, the mixture was cooled to room temperature.

2.1.2 Preparation of peroxide solution

0.2048 g sodium salicylate and 50 mL solution dimethyl phthalate: t-butanol 4:1 (v/v) were placed in a 100-mL volumetric flask equipped with magnetic stirrer. 6.4 g hydrogen peroxide was slowly added. Additionally, 40 mL solution of dimethyl phthalate: t-butanol 4:1 (v/v) were added and the solution was stirred for 60 min. at room temperature. The stirring bar was removed and additional solvent solution completed to 100 mL.

2.1.3 Glass vial

The glass vial housed inside the light stick is made of a special N16B glass tube produced by Schott-Rohrglas GmbH. The glass chemical composition allows the CLM storage for a year without significant degradation of the components. The main chemical components of N16B glass are (in weight %) SiO_2 (68.5), B_2O_3 (2), Al_2O_3 (7.5),

Na_2O (16), CaO (3.5), MgO (1) and Zn (1.5). The N16B glass belongs to the hydrolytic class 3, acid class 2 and alkali class 2, its coefficient of linear thermal expansion is $8.7 \cdot 10^{-6}$ K^{-1}, and its given working point is at 725 °C.

N16B glass tubing with a 6 ± 0.15 mm outside diameter and a 0.8 ± 0.04 mm wall thickness, has the subsequent stress maximum values: longitudinal stress: 5.0 MPa, and edge stress: 6.0 MPa.

2.1.4 Plastic vial

The light stick's plastic vial was produced from transparent granular low-density polyethylene (LDPE) with 6 mm average diameter and 0.910 ÷ 0.925 g/cm^3 density. The granules were dried before use for 90 min. at 65 °C. The main technical properties of LDPE used for the manufacture of the light stick's plastic vial are presented in Table 3.

2.2 Injection molding

The molding machine is presented in Fig. 1. The light stick dimensions were set as: inner volume = 11.85 cm^3; length = 149.7 mm; maximum outer diameter = 18.2 mm; average wall thickness = 1.5 mm. The processing conditions allowed the use of high injection rate, 600 bar injection pressure and 60 bar backpressure. The molten plastic was allowed to cool at the contact with the interior mold surface and the cooled products were extracted. A 1.5% plastic contraction was considered for the mold design, taking into consideration the processing conditions, the polymer rheology and the wall thickness.

Table 3. LDPE technical properties.

No.	LDPE technical properties	M.U.	Values
1.	Density	g/cm^3	0.910 ÷ 0.925
2.	Specific volume	cm^3/g	1.09 ÷ 1.11
3.	Refractive index (N_D)	-	1.51
4.	Transmittance	%	translucent ÷ opaque
5.	Shore hardness	^{o}Sh·D	45 ÷ 53
6.	Deflection temperature under load, 1.8 MPa	°C	30 ÷ 40

2.3 Plastic material investigation

Morphostructural investigations of the light stick's plastic vial were performed using Scanning Electron Microscopy (SEM); morphochemical investigations were performed by Energy-Dispersive X-ray spectroscopy using a Bruker AXS X-ray spectrometer (EDX).

In order to prevent thermal degradation of LDPE, as well as for the acquired microphotographs quality enhancement, the samples were coated by sputtering on their surface of a very thin gold layer; additionally, the macromolecular framework of the polymer may be extra degraded by the low electrical conductivity of the material. The gold layer was sputtered on the plastic vial samples in argon atmosphere using a SPI Module^{TM} Sputter Coater equipment (SPI Supplies, Westchester, USA). The thickness of the gold layer was ~120 Å nm for a deposition time of 40 s and a 3 Å/s current.

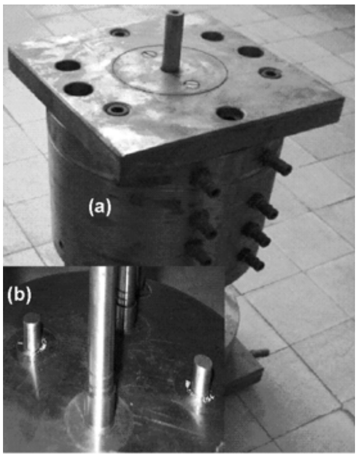

Fig. 1. The plastic vials and plastic caps injection molding equipment (a) and its particular construction elements (b).

2.4 Light stick fabrication

The light stick manufacture involved several steps, as following: a. preparation of the CLM solutions (peroxide component-solution and oxalate component-solution); b. manufacture of the glass vials from special N16B glass tube; c. glass vial loading with 2 mL of peroxide solution; d. closing the glass vial by welding; d. loading the LDPE vial with 6 mL of oxalate component; e. placing the glass vial into the light stick's plastic vial; f. closing the light stick's plastic vial with a cap; g. packaging the light stick in order to protect it from light exposure.

2.5 CL determination equipment

The CL compositions were evaluated in terms of illuminance using an Extech HD 450 detector sensor (Extech Instruments Corporation, Nashua, USA) and its dedicated software, and a B&W case (Fig. 2). For the determination of the average luminous flux emitted by the light sticks, tests were replicated 10 times for: the first samples were bent in the filling day, the second 10 were tested at 90 days since filling, and the latter 10 were submitted to tests after one year (360 days) since filling.

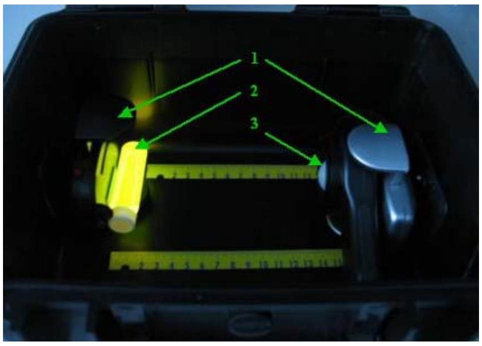

Fig. 2 B&W case: 1. Fixing systems, 2. 10 ml vials with CL composition, 3. Extech HD 450 sensor.

3. Results and discussion

3.1 The design and the fabrication of the lighting/signaling device - Concrete and theoretical approaches

The main reasons for choosing to use LDPE as fabrication material for the light stick's plastic vial were its very low cost, its excellent chemical resistance and very good processing characteristics, its high resistance against mechanical shocks, very low water absorption, recommended for long time CLM preservation, and translucent - accordingly to polymer crystalline properties and material thickness, better flexibility and transparency versus high-density polyethylene (HDPE) [6].

LDPE was processed by injection molding, the vial obtained having a translucent and flexible structure, suitable for long time preservation and for CL reaction. The 8-cm^3 CLM necessary volume was calculated taking into account the transmittance ratio for LDPE and the glass layers, and also the characteristics of CLM that have to ensure a $5.65 \cdot 10^{-2}$ lm luminous flux at the end of lighting/signaling system useful life.

The lighting/signaling system's dimensions were determined taking into account the loading ratios for glass and LDPE vials, and also the functionality considerations, in order to ensure the glass vial breaking and a good mixture of the CLM components.

Tests were performed in order to determine the optimum processing temperatures for injection molding. Two injection programs were used to obtain the light stick's plastic vial under different conditions. The processing temperature values are presented in Table 4.

A significant number of studies were conducted on fracture propagation in LDPE in various liquids, using the concepts of fracture mechanics, thermally activated polymer chain microsites motion, liquid diffusion through fractures and capillary open microfractures [7-10], or in the microdefects structure that have as outcome the influence of yield light emission [11]. According to this, the structural analyses have been performed on the samples that are coming from different places of the manufactured material; also, the material fabrication was performed in agreement with the conditions presented in Table 4.

Table 4. The injection molding temperatures

No.	Mould temperature (°C)	Nozzle temperature (°C)	Cylinder temperature (°C)		
			Area III	Area II	Area I
1.	40	170	190	170	150
2.	40	190	210	190	170

3.2 The LDPE morphostructural and morphochemical analysis

In order to reveal the depth and surface structure of stick's plastic vial we have performed detailed SEM and EDX investigations (Fig. 3 and 4).

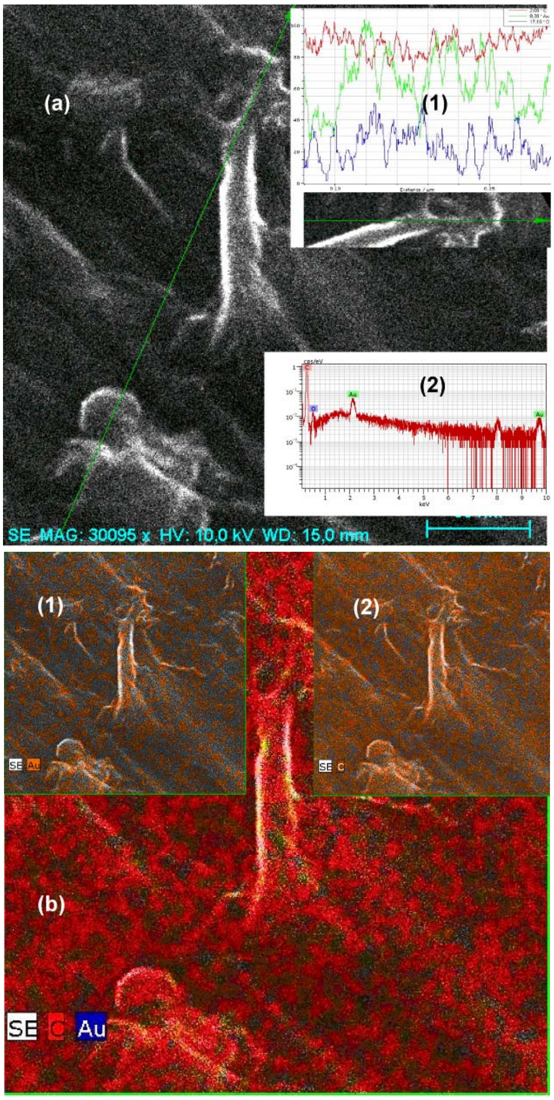

Fig. 3. Linear profile surface microanalysis (a) and corresponding chemical mapping (b) in the case of a LDPE sample

The main approach was to acquire useful information for the understanding of material three-dimensional morphologic distribution; the SEM has a good focus depth owing to differential emission of secondary electrons coming from the material phases of the material. Besides, the EDX investigations allow the identification, through chemical mapping, as well as quantifying of the material phase in the sample, according to the chemical structure.

Based on the characteristic X-ray spectrum (Fig. 3a(2)), it can be observed that the chemical elements engrafted into the chemical morphostructure of the vial are only C, O and Au. This suggests that during sputtering process secondary oxidation processes take place, as a consequence of high energy Au ions contact within the framework of vials polymer structure; besides, this can be a possible explanation for the presence of O and Au on the microsurfaces investigated (Fig. 3a(1)). The linear profiles distribution of O and Au (Fig. 3a(1)) show that O distribution is at the interface of Au and C; also, these experimentals suggest that, indeed, hot Au may lead to the formation of different oxygen-speciated chemical compounds.

Furthermore, from a morphological point of view, Au microlayer presents a discrete structure with an islet-based pattern distribution; therefore, the metal microislets were formed as a consequence of polymer heat transfer which induces the formation of extra metal nucleation microsites.

Microanalysis acquired data statistics on microsurfaces (Fig. 4a(2)) show that C:Au ratio rank 75-100% (weight ratios). The material phase transition between neighbored Au islets are mixed material phases that contain both organic and metal phases; most likely, this state was induced by the diffusion of high energy metal ions into the plastic polymer, at molecular level; also, the average of C concentration on the mixed material phases is ~89%.

The microfracture propagation process may be influenced or initiated by the CLM presence and the mechanical stress occurs when the cap is introduced in the light stick's plastic vial. The microfracture initiation rate is correlated with the solvent molecules diffusion in the polymer, the process requiring a slight polymer swelling, necessary for these liquids to influence the microfracture initiation. Also, comparing the SEM microphotographs in Fig. 4a and Fig. 4b, one may observe that the dimensions of topological weaknesses are below 20 nm; moreover, in can be seen that the dimensions of swellings that are pointed in the inner microchanneling structure of the fractures have the same magnitude order as those placed on smoothed polymer microsurfaces.

The representation of the morphostructural perimeter parameters, length and compactness (Fig. 5) was performed following the methods proposed earlier by Iordache et al. [12]. The compactness quantifies the roundness deviation in the case of real elementary segmented objects; these geometrical operators are linked by relation Round = P^2 / 4DA. In Fig. 5d is given the surface distribution of the elemental segmentation belonging to the microfractured LDPE. A large number of microchannels that have a dendrite-like distribution can be seen. The main peaks of perimeter values distribution of microfractured LDPE are at 6.4, 10.6, 16.72, 23.27, 31.71 and 43.40 nm, respectively; moreover, the main peaks of compactness values distribution in the case of microfractured LDPE are at about 1, 1.53, 2.1 and 3 respectively.

Furthermore, the microphotograph in Fig. 4a(3) sustains the assumption of liquid microfractures initiating.

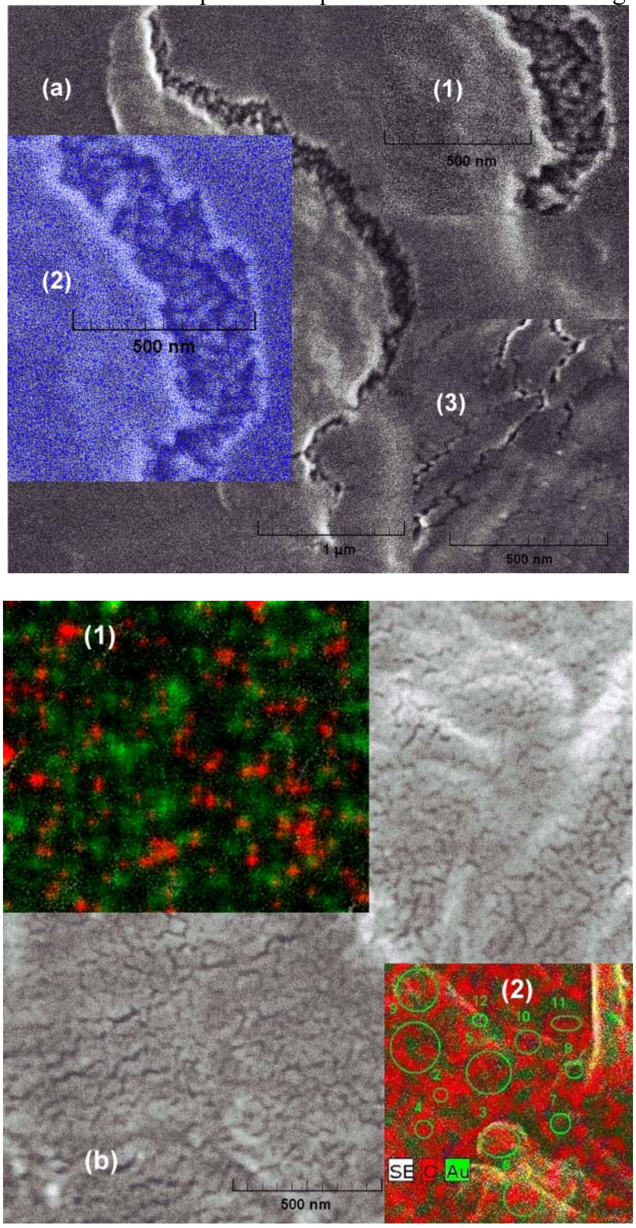

Fig. 4. Microphotographs of microfractured LDPE (a) at different magnifications (a(1)), elemental morphostructural segmentation (a(2)); microfractures distributed on a wide field of view (a(4)). Microphotographs of LDPE free of microfractures and associated chemical mapping of Au and C statistical distribution (b).

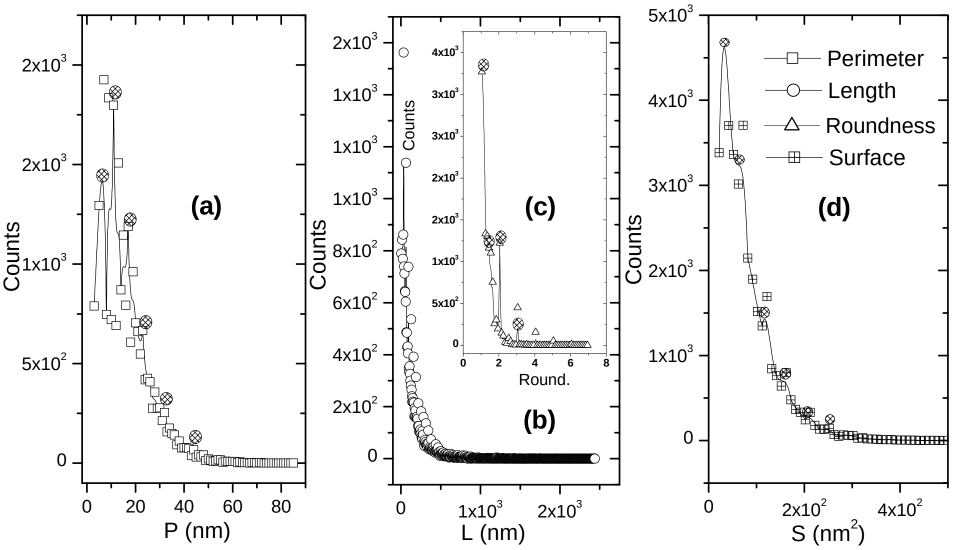

Fig. 5. Graphical representation of morphostructural perimeter, length, surface and compactness parameters belonging to the elemental segmentation of the objects from Fig. 6b

These evidences suggest that the topography of swellings presents strong deviations from roundness; moreover, according to real measurements performed on the SEM microphotographs, it is most probable that real values of surface swellings to be distributed at 23.27, 31.71 and 43.40 nm eigenvalue respectively.

Secondly, in the case of LDPE without microfractures, we have found that the main peaks of microsurfaces values distribution are placed at 34.34, 65.38, 117.58, 155, 305 and 250 nm^2 respectively; as mentioned above, a remarkable correspondence between the real dimensions of smoothed polymer microsurfaces and the dimensions of swellings coming from microchannel fractures can be observed.

The presence of the microfracture initiating agent into the structure of polymer framework increases the macromolecular chains mobility, together with a glass temperature decrease; as a consequence, finally the polymer framework breaks.

3.3 The use and functionality of the light stick

The use of the light stick is very easy: when the plastic vial is bent, the glass vial breaks, the two solutions flow together, the CL reaction initiates and starts to emit light (Fig. 6a). The plastic vials obtained and their customization caps are illustrated in Fig. 6b. Experiments were performed in order to determine the ratio between the transmittance of the light stick's plastic vial and the transmittance of the glass vials. Equal volumes of CLMs were placed in the both types of vials. The experiments were performed at illumination levels in the range 0.2 ÷ 10.3 lx. A value was determined at 0.72; in completion, that was determined as transmittance ratio between LDPE and the glass layers.

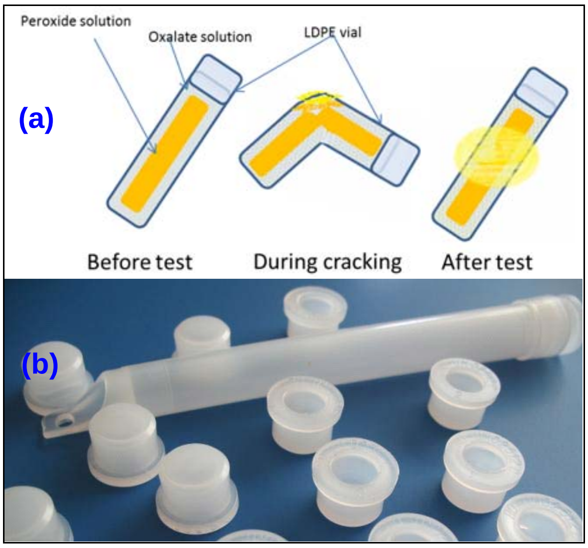

Fig. 6. The working principle of the light stick (a) and the final product (b)

It has been observed that microfractures appear in the LDPE structure (Fig. 4a), after 60 days from CLM filling; this process was observed in 40% of the vials fabricated in agreement with the conditions mentioned in Table 4 (no. 1). Also, the microfractures found in the semi-crystalline polymer are revealed as a well-defined region with a width between less than 1 μm and a few micrometers length; the semicrystalline polymer phases contain irregularities formed by the microfibers and microholes orientation; the microfibers and microholes densities are ~40-60% related to the unaffected material. Most likely, the formed microfractures may lead further to the formation of other microfractures in the LDPE light stick's plastic vials body.

Good results were obtained during the manufacture of the plastic vials following the procedure from Table 4, no. 2. The depth and the surface structure analyses did not reveal microfractures. In Fig. 6b is given the structure of the light stick's plastic vial. The LDPE structure was proven to be unitary and free of fractures. The plastic vials maintained their integrity for over 12 months since CLM filling. The light sticks, on their turn, gave satisfactory results in terms of luminous flux versus time. In Fig. 7 the graph containing the light emission during 6 hours since bending of the three sample groups (the day of filling, 90 days from filling, and 360 days from filling) is presented.

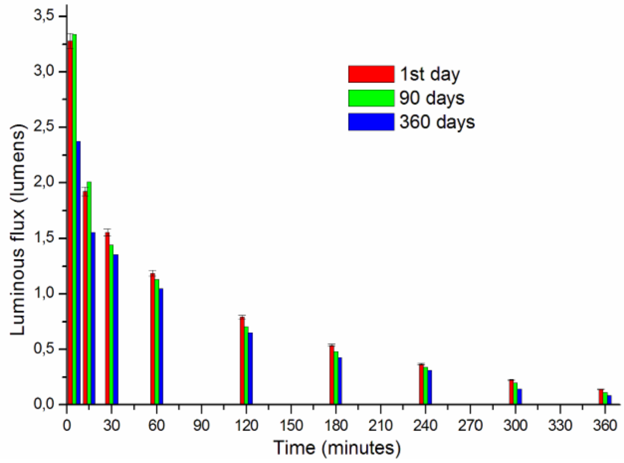

Fig. 7. The light sticks functioning - luminous flux evolution during 360 minutes since breaking.

4. Conclusions

In this paper, the minimum luminous flux necessary for the manufacture of CLM-based signaling system, accordingly to the standard night visibility limits, was established.

The following results have been obtained: (1) The manufacture of a novel signaling system based on a new enhanced polymer-CLM was presented in detail. Moreover, the preparation and the processing of the two CLM components, which have to be kept separately and combined only when it is necessary to produce light, was presented. (2) An injection mold for the light stick's plastic vial and its customization cap was fabricated. Additionally, the properties and the main advantages of using LDPE for the light-stick were investigated. (3) Detailed morphostructural and morphochemical investigations of vials were performed. The liquid microfracture initiations rate is mainly correlated with the polymer swelling ratio; in this respect, a complete quantification of plastic polymer microsurface morphology was performed. The outcomes of the morphostructural investigations were completed and confirmed by morphochemical investigations. (4) Complete investigations were performed in order to determine the ratio between the transmittance of light stick's plastic vial and the transmittance of glass vials. The light stick was tested after one year and the light emitted agreed the standard parameters.

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