

A STUDY OF USING POLYCARBONATE AS A REUSABLE RADIOCHROMIC INTEGRATING DOSIMETER FOR THE DETERMINATION OF HIGH DOSES OF IONIZING RADIATION

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Abstract. *The aim of this research is to study the use of polycarbonate as a reusable radiochromic integrating dosimeter for the determination of high doses of ionizing radiation in the (range of 0.1 to 10 kGy). The region of the linear dependence of the optical density of polycarbonate samples on gamma radiation dose, as well as the fading of the radiation effect and the possibility of accelerating this fading by annealing have been explored. To determine the effect of oxygen concentration on changes in optical density and the rate of oxygen diffusion into the polycarbonate, some samples were stored in a pure oxygen atmosphere, produced by electrolytic dissociation of distilled water using a fuel cell.*

Key words: *Annealing, fading, optical density, photocolourimetry, polycarbonate samples, radiochromic effect*

1. INTRODUCTION

Significant radiation-induced changes in solids can be used in dosimetry for high doses by determining changes in the optical density of the irradiated material. The determination of dosimetric monitored changes is usually carried out by spectrophotometry or photocolourimetry, i.e. by the transmission measurement of optical density changes at various wavelengths of an incident source.

For polymers, the changes in optical density first occur in the ultraviolet spectral region. At higher doses these modifications extend into the region of light. The useful property of polymers is their low atomic number, which is closer to that of biological tissue. Consequently, there is low energy dependence at dose calibrations for use with tissues. The disadvantage of these materials may be a significant variability of the response not only for the same material from different manufacturers, but also for different production batches from a single manufacturer.

One-time usability is the common indicator of all these transparent polymeric materials. Irreversible changes occur inside the polymer after the irradiation and the dosimeter, which is made with such materials, is no longer usable.

In this work, we focused on the study of the possibility to use one of the previously overlooked polymers – polycarbonate (PC) – as a reusable radiochromic integrating dosimeter for the determination of high doses of ionizing radiation. The region of linearity of optical density of polycarbonate samples as a function of gamma radiation dose must be

sufficiently explored, together with fading of the studied material, and the possibilities of accelerating fading by annealing.

Polycarbonate is a much cheaper alternative than the commonly used alanine dosimeters. The EPR (Electron Paramagnetic Resonance) method used to evaluate (deducting) of the dose, makes the dosimetric use of alanine more expensive. The PC dosimeter response is a linear of dose ranging from 0 Gy – 100 kGy with a resolution of 100 Gy.

Polycarbonate is characterized by considerable radiation resistance related to the preservation of mechanical properties (up to hundredfold in comparison with the PMMA) [3], the mechanical and dimensional stability in the temperature range of -50 to 140 °C. The glass transition temperature of PC is 150 °C. From this temperature the polymer starts to soften quickly and gas bubbles, which scatters light and degrades optical properties, appear inside.

Polycarbonate can be used as an integrating dosimeter for high doses of ionizing radiation for various industries: in biology (sterilization of surgical instruments, sterilization of waste water, sterilization of foodstuffs, treatment of antiquities attacked by woodworm organisms, bacteriological research) or industry (defectoscopy, geological exploration (carotage), industrial irradiation of materials – photopolymerisation (polymer crosslinking), the study of the degradation of physical and chemical properties of materials exposed to high doses of radiation).

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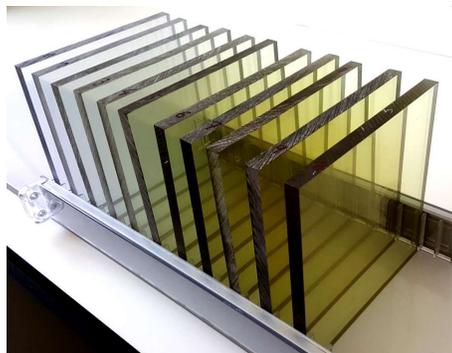


Figure 1. Polycarbonate samples irradiated at different doses

2. EXPERIMENTAL PART

2.1. Sample preparation

For these experiments, polycarbonate plates of MAKROCLEAR without surface treatment were purchased from the manufacturer of technical plastics OMNIPLAST Ltd. We chose the thickness of the plates to be 1 cm in order to have better detectability of changes of the optical properties after irradiation. Test samples of 140x140 mm were cut from the received plates by water jet saw and subsequently irradiated in an industrial PRAZDROJ irradiator based on a high activity ^{60}Co emitter.

The dose rate where the samples were irradiated was determined by repeated measurements using alanine integrating dosimeters and found to be 350 Gy/h. Two sets of samples were prepared and the response of each series to irradiation was studied.

Various samples were exposed for a short period of time (in the order of hours) to attain high doses in the range of 0.5 – 10 kGy in the cobalt radiation room. After the exposure the optical density of the samples was measured at regular intervals.

2.2. Optical density (OD)

The optical density was measured with a specially designed densitometer equipped with planar LED lamp of 250 x 250 mm exposure area, with a high surface homogeneity of the luminous flux of 2000 lm and the chromaticity corresponding approximately to the black body radiation at 4000 K. As a detector we used a digital luxmeter SONEL LXP-10A, which measures intensity in the range of 0.001 – 400 000 lx, with the resolution of 0.001 lx and sampling frequency of 1.3 s^{-1} . The detector was the sensor LP-10A with a silicon photodiode. The measurement uncertainty is around 2%.

The light source was further covered with the aperture defining the light field to 200 x 200 mm, into which color filters of the same dimension could be inserted. The samples were then placed on top of these filters. The light detector was installed light-tight into the top cover of the densitometer and after its closing it was in a precisely reproducible position at 1 mm above the sample surface.

For our experiment filters transmitting radiation of wavelengths between 450 nm (blue), 570 nm (yellow), and 640 nm (red) were selected.



Figure 2. The optical densitometer for spectrophotometric analysis of the irradiated samples

2.3. Radiochromic phenomenon

During the irradiation of the polycarbonate, colorization (a radiochromic response) occurs, in which the optical density of the polymer gradually increases with the dose.

The physical and chemical principle of the radiochromic response is the formation of color centers due to changes in the optical absorption properties. The radiochromic response is caused by the disintegration of the molecules of the polymer (photodegradation) [1], and both radicals and ionic processes contribute. A typical process is the pairing of free radicals [4], [5].

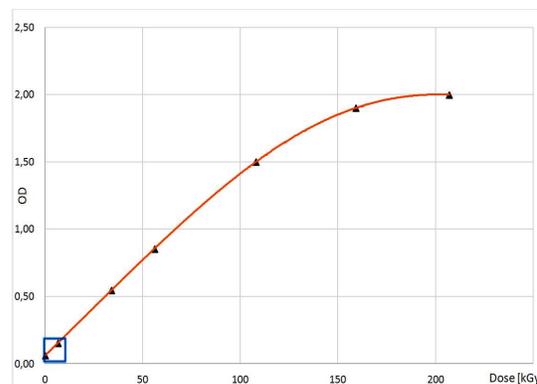


Figure 3. Radiochromic response curve of the PC dosimeter irradiated up to 200 kGy, shown for 550 nm

In reference [6], the changes of optical density of PC samples irradiated at doses up to 200 kGy, when the OD saturation occurs, were studied. It is clear from Figure 3 that the dependence of OD on dose was linear up to 100 kGy. This material is an easily used, inexpensive and readily available integrating dosimeter up to that level of irradiation with high-energy photons.

Long-term studies of the fading of PC samples irradiated with such a high dose showed that the colorization effect was irreversible [5] – the samples even after annealing remained permanently orange-

colored, and their OD converges with time to approximately 0.3. In this work we focused on the study of optical responses of PC dosimeters in lower dose ranges, which is approximately indicated by a blue square in Figure 3. Long-term observations suggested that the PC samples, which did not receive the dose higher than about 10 kGy, can be completely regenerated and can be reusable, such as thermoluminescent dosimeters (TLD).

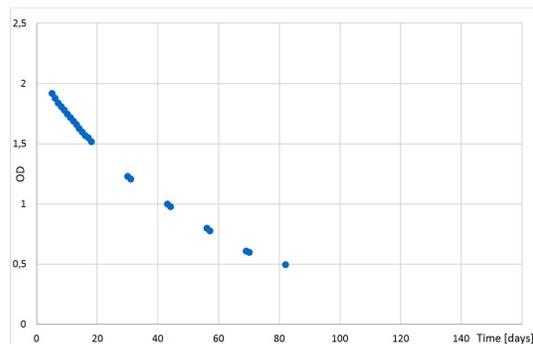
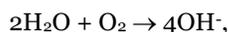
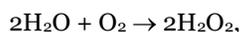


Figure 4. The time dependence of fading of the PC dosimeter irradiated up to 200 kGy, shown for 550 nm

2.4. Fading

The research performed with other clear carbon-based polymers, such as the already mentioned PMMA [3], revealed that after the termination of irradiation a series of reactions involving atmospheric oxygen occurs inside the polymer. This results in a slow gradual regeneration of optical properties of the material, i.e. in the exponential decrease in the optical density – fading. The cause of that is the "bleaching" of color centers due to oxygen diffusing into the material from the surface. During the irradiation microscopic bubbles of gas, such as H_2O , CO_2 , CO , CH_4 , form radiolytically in the material. Namely, H_2O reacts with air oxygen in reactions



and at the same time the formed hydrogen peroxide and the hydroxyl ion then attack the color centers and degrade their absorption properties in the visible region of the electromagnetic spectrum. Fading can be also accelerated by water vapor diffusion from the surrounding environment into the material. It can be increased by storing in a humid environment and also in the environment with high oxygen content. According to published studies the rate of regression in pure oxygen atmosphere is about doubled compared to storage in dryness and ten times higher compared to the storage in nitrogen atmosphere.

As will be shown in following paragraphs, our study has shown the influence of oxygen on the acceleration of fading also for the PC samples. In comparison with the PMMA samples, where fading is approx. 2% per week, the PC samples regenerate in the air much faster.

In the reference [1], the authors came to the same conclusion as in our work – linear dependence of OD

on the dose. They provide a viscosimetric and thermogravimetric evidence of the dose-proportional reduction in molecular weight, which are the same results as we are currently observe by the method of the NMR spectroscopy, and will be published in some of the forthcoming publication. The authors, unlike us, do not perform measurements in the region of visible light, but in the medium ultraviolet area (UV), where the non-irradiated PC also absorbs extremely. The authors worked with liquid samples (polycarbonate dissolved in chloroform), which may behave quite differently. The fading of irradiated samples was researched, but the authors perform the measurements of fading only at three various time points (0, 10 and 20 days), and intersect points with a straight line, contrary to our results. These authors next state, that the fading was relatively insignificant one week after irradiation. Our results on the contrary show, that the fading is an exponential function of time, and the most severe changes of OD occur in the order of hours to a few days after irradiation.

2.5. Annealing

For the repeated use of polycarbonate integrating dosimeters annealing can be used. This method allows to accelerate the time development of fading, e.g. by heating the sample at a higher temperature, or by exposing the sample to intense light radiation, etc. Due to the easy controllability and reproducibility of annealing conditions it is advantageous to choose the former option.

Suitable conditions for annealing of polycarbonate samples turned out to be keeping them at a temperature of 100 °C for several tens of minutes (at temperatures around 150 °C irreversible disruption of the optical properties of the sample already occurs due to the formation of gas bubbles in the sample). According to our results published in reference [4], the PC sample can get old in just 30 minutes of annealing by an equivalent of 12 days at room temperature.

2.6. The measurement process

Approximately within one hour after the removal from the cobalt irradiation units, each sample was measured by the optical densitometer both in white light and in each of the four color channels. Subsequently, the measurements were repeated at regular time intervals of approximately 24 hours, for the following 9 days. Thus, we obtained 10 time measurements, each of which included white light plus the four color channels.

The samples were placed into an electric furnace then, in which they were kept at a constant temperature of 100 °C for 30 minutes. After their removal, the optical density of the samples was re-measured and plotted in graph. The annealing was repeated for the total of three times with an interval of 7 days between annealing, so that the samples had sufficient time for the re-absorption of oxygen.

3. RESULTS

For brevity, we present the summarized results of those measurements only for 640 nm, in which the samples recovered the most quickly.

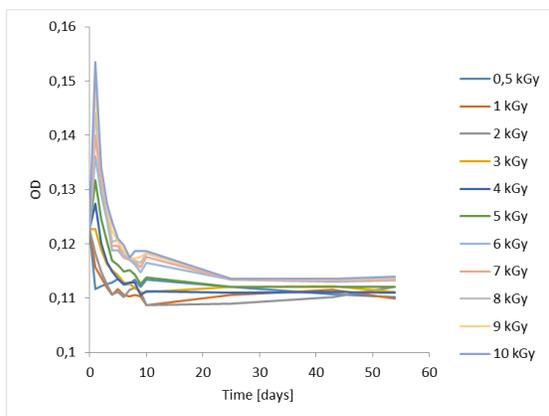


Figure 5. The dependence of $OD(t)$ of the samples irradiated by different doses, shown for 640 nm

In Figure 5, the dependence of optical density with time ($OD(t)$) for each of the samples irradiated with different doses.

After each annealing we present the period of time calculated as an estimate of the time for regeneration of the sample without annealing, according to the results in reference [6].

3.1. Reusability of the dosimeters and the effect of the influence of oxygen concentration

To verify the reusability of dosimeters we choose the sample which was irradiated with a dose of 10 kGy and then stored at room temperature and in the darkness for one year. The densitometer verified that the optical density of this sample no longer differs significantly statistically in the monitored spectral regions from the optical response from the non-irradiated samples cut from the same plate.

This sample (see the blue points in Figure 6) was re-irradiated with a dose of 10 kGy together with the reference one, so far non-irradiated (see the red points in Figure 6). Subsequently both samples were stored in pure oxygen atmosphere produced by electrolytic dissociation of distilled water using a fuel cell. The samples were tested for optical density at regular time intervals of 24 hours.

Currently, the repeatability of ingestion is experimentally verified on at least 4 cycles of samples irradiated with different doses up to 10 kGy.

From the graph, it is further shown that the equalization of OD for both samples occurred as early as 24 hours after the end of the exposure. Therefore, we recommend letting that time pass before recording the doses from the integrating PC-dosimeters.

The optical response of the repeatedly irradiated and for the first-time irradiated samples in longer time intervals appeared to be almost identical. Even after several repeated annealings, in between which both

samples were kept for a period of 7 days in a pure oxygen atmosphere to replenish the consumed oxygen in the samples, there were no statistically significant deviations in OD of both samples in any of the studied spectral channels.

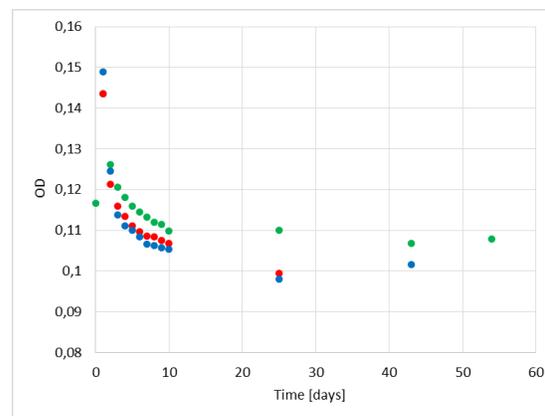


Figure 6. Comparison of the time development of fading of the samples stored in pure O_2 atmosphere – the sample repeatedly irradiated with a dose of 10 kGy (blue points) and the sample irradiated for the first time with the same dose (red points) – with the reference sample also irradiated with a dose of 10 kGy, but maintained at the atmospheric oxygen concentration of 21% (green points), shown for 550 nm.

The influence of the concentration of ambient oxygen on the changes in optical density and the rate of diffusion into the sample, have been studied with respect to the time changes of OD of the samples irradiated with the same dose and kept at the atmospheric oxygen concentration of 21% (see the yellow points in Figure 6). The figure shows that the difference in the speed of fading is clearly apparent, especially in 455 nm and 575 nm. However, already the first annealing has shown that the increased concentration of oxygen inside the samples heated at temperature of 100 °C leads to faster recovery of the optical properties in comparison with the sample stored at 21% O_2 concentration. This change was observable in all studied spectral channels.

From Figure 6 it is clear that, after repeated annealing, a convergence of OD for all 3 studied samples to the value of OD of non-irradiated samples, i.e., to the gradual complete regeneration of the samples, occurred.

4. CONCLUSION

This study demonstrates the reusability of radiochromic PC dosimeters for the dosimetry of doses in the range of approximately 0.1 to 10 kGy. At the same time it proved the influence of elevated oxygen concentration on fading and annealing.

Currently the chemical dosimeters based on alanine or radiochromic dosimeters B3 are used by default for the determination of high doses. Compared with both of the above-mentioned types of dosimeters, PC dosimeters are several times cheaper, including the cost of their evaluation. In comparison with B3 films,

for the PC the OD dependence on the dose is linear at a minimum of 100 kGy. The dosimetric comparisons were performed only with alanine dosimeters. We performed four comparative measurements and the results ranged from 10% to 20%.

In the reference [2] the authors state a linear OD dependence on the dose, in line with our results. Galante *et al.* states about 15% variation coefficient, which is in line with our results – comparison PC versus Alanine. They perform the measurements in a near UV area, as the reference [1].

The follow up work will focus on the exploration of the optical response of PC dosimeters on irradiation with lower doses from 100 Gy to 1 kGy in more detail.

Further research will be oriented on the study of long-term regeneration of differently irradiated samples and the efficiency of different methods of annealing, as the irradiation from intense light, ultraviolet radiation (UV), etc., or a combination of several different methods.

Subsequently, the dependence of the optical response of the PC dosimeters on the energy of gamma radiation, or the response of the PC dosimeters on the irradiation of other kinds of ionizing particles, such as neutrons will be explored.

Last but not least, we would like to investigate radiation-induced physicochemical changes of PC dosimeters and their time evolution during the fading and annealing on the molecular level using Raman spectroscopy or NMR (Nuclear Magnetic Resonance).

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