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Characterization of fatigue resistance in photochromic composite materials for 3D rewritable optical memory applications

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ABSTRACT

Fatigue resistance of the photochromic diarylethene molecules 1,2-bis[2-methylbenzo[b]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene embedded in three different acrylic polymers is studied upon multiple coloration–decoloration cycles. The resistance to photofatigue is found different in the three polymeric materials when one-photon excitation was used for the reversible photoconversion experiment. In particular, the photochromic molecules lose their photoisomerization ability faster if they are embedded in poly(methyl methacrylate) (PMMA) with respect to poly(ethyl methacrylate-co-methyl acrylate) (PEMMA) and poly(ethyl methacrylate) (PEMA). We propose several explanations based on the physico-chemical properties of the matrix and the photochromic molecules. In the case of two-photon excitation, which is necessary for 3D optical writing, the fatigue resistance is found to be poorer than in the one-photon case. The accelerated photodegradation can be assigned to the non-linear nature of interaction between the polymeric composite material and light.

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1. Introduction

Materials based on photochromic molecules are becoming very promising candidates for the fabrication of compact and cheap photoswitchable devices such as optical memories. However, to be a successful candidate for practical applications, a photochromic material should fulfill a number of requirements, among which high sensitivity, fast response, thermal stability, and resistance to photochemical fatigue, i.e., loss of performance in photochromic conversion over time due to chemical degradation of the material [1]. Many organic photochromic molecules were proposed for optical memory applications [2–13]. Not many of them, though, are thermally stable in both isomeric forms and highly resistant to photochemical fatigue. Some of these molecules, despite being effective photoswitches, can be only used for write-once-read-many (WORM) memories as it was demonstrated by Liang et al.

[4], but they are not appropriate for many writing–reading–erasing operations since these compounds lose their photochromic performance after a few repetitive cycles of irradiations [14,15]. Better candidates for rewritable memory applications seem to be the novel highly thermo- and photostable photochromic molecules of the diarylethene family [2,16–20] introduced by Irie and Mohri [21]. However, up to now there are only few reported experimental studies concerning the fatigue properties of the diarylethenes (DAE). Irie in his review [10] describes experimental studies of fatigue in several diarylethene derivatives upon multiple ring closing–opening cycles by measuring the absorbance of the closed-ring isomers both in solutions and in different polymers. In particular, the photochromic diarylethene molecule investigated also in the present work (see Fig. 1(a)), in methylcyclohexane solution was reported to last an extraordinary high number of cycles ($>1.3 \times 10^4$) before recording a decrease in the absorbance to 80% of the initial value. This indicates an extremely low quantum yield for side product formation [10]. Hoshino et al. [22] investigated refractive index changes of the same diarylethene in solid co-polymer of fluoroethyl methacrylate and methyl methacrylate films and reported a noticeably good photostability of the diarylethene in the polymer films after hundreds of irradiation cycles by monitoring the absorbance in the visible (VIS) spectral range. They reported a decrease of the optical density to 80% of the initial value after about 300 cycles. The authors concluded that photodegradation was caused by UV irradiation upon the ring-closure reaction, rather than by the visible irradiation, which did not lead to formation

Abbreviations: DAE, diarylethene; PMMA, poly(methyl methacrylate); PEMA, poly(ethyl methacrylate); PEMMA, poly(ethyl methacrylate-co-methyl acrylate); WORM, write-one-read-many; VIS, visible; NA, numerical aperture.

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Fig. 1. Chemical structure of the two photochromic isomers of the 1,2-bis[2-methylbenzo[b]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene. Lower panel shows a photograph of two spin-coated samples, containing the open-ring (left) and closed-ring (right) isomers.

of side products. In the work of Jeong et al. [23] a series of diarylethenes and their substituted analogs were investigated in order to obtain photochromic switches with excellent fluorescent properties. The authors tested the fatigue property applying UV light from a lamp source to various diarylethenes in ethyl acetate solution and observed that the absorbance of the diarylethene, investigated in our work, decays to 80% of the maximum value after about 340 min of continuous UV irradiation. The decrease of the absorbance was attributed to formation of byproduct of the closed-ring isomer. It should be pointed out that experimental conditions are of great importance when fatigue resistance is being tested. Since some experiments are performed in solutions and other in polymer films, interactions of photochromic molecules with the surrounding environment can affect the photo-physical properties of the molecules and therefore their fatigue. It is also important to keep in mind that the fatigue property can be defined differently depending on the desired application. It can be the ability to detect absorption/fluorescence of the initial isomeric form many times for WORM memories or the ability to convert reversibly from one isomeric form to the other many times for multiple write–read–erase memories. For these reasons, in this work we present an experimental study on the photoinduced degradation of a common diarylethene molecule (Fig. 1(a)) incorporated in three polymeric matrices upon multiple light irradiation cycles (writing–erasing cycles). The study was performed in three widely used acrylic polymers that can be good candidates for the preparation of solid photochromic films for optical memory devices. The fatigue resistance was defined as the number of repeatable UV–VIS laser irradiation cycles that the photochromic films can undergo before the intensity of absorbance/fluorescence spectra of the closed isomeric form reached a certain threshold (80% of its maximum value). The examined systems were successfully tested also for 3D optical data storage, using two-photon laser excitation for the writing into the bulk of the photochromic polymer materials, although in this case the fatigue resistance of the embedded photochromic molecules was strongly reduced.

2. Experimental procedure

2.1. Sample preparation

The samples for the fatigue resistance measurements were prepared by mixing 1,2-bis[2-methylbenzo[b]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene (TCI, 97% purity)

with PMMA (poly(methyl methacrylate), MW = 120,000, Sigma–Aldrich), PEMMA (poly(ethyl methacrylate-co-methyl acrylate), MW = 88,000 [24], PARALOID™ B-72, Rohmihaas) and PEMA (poly(ethyl methacrylate), MW = 515,000, Sigma–Aldrich) in chloroform or toluene. 300 μ l of prepared polymer-photochromic solutions were deposited on 1 mm thick quartz slides and spin-coated (1000 rpm, 1.5 min). The concentrations of the photochromic molecules into the prepared films were 5 wt%, 10 wt%, and 15 wt%. The thicknesses of the polymer-photochromic films measured with a profilometer (XP-2, Ambient Technology) varied between 1.6 and 2.7 μ m in all three polymers.

For two-photon writing into the depth of the films, samples were prepared from identical polymer-photochromic solutions by drop-casting on a glass cover slip. The prepared films were covered by a 1 mm thick microscope slide after drying and baking in the oven at 70 °C for 1–2 h. The film thickness has been determined as 30–100 μ m by profilometry. The two-photon fatigue experiment was carried on the surface of spin-coated samples as described above.

2.2. Optical setup for one-photon fatigue measurements

The coloration–decoloration cycles in the one-photon experiment were performed using a CW He:Cd laser (λ = 325 nm, I = 36 mW/cm²) causing the ring closure of the A isomer, and a diode laser (λ = 561 nm, I = 16 mW/cm²) inducing a ring-opening reaction of the B isomer. The photoinduced changes in the molecules were monitored with a compact UV-VIS spectrometer (AvaSpec 2048, Avantes) by recording absorption spectra every 20 cycles. The data acquisition and data evaluation was performed a home-made Lab-view software. The number of “operative” cycles was extracted by plotting the maximum absorption intensity at 528 nm as a function of the number of cycles.

2.3. Optical setup for two-photon fatigue measurements

The writing–reading–erasing experiments were performed by means of a commercial inverted confocal microscope (Olympus, FV 1000) coupled with a Ti:Sa pulsed laser (Spectra Physics, Mai Tai, ~100 fs, 80 MHz) tuned at 720 nm in order to write information within the volume of the medium. The exposure time on the sample during writing was 60 s. The fluorescence of the written images was retrieved with single photon excitation at 405 nm and collected in

the spectral range of 575–640 nm which is the range of the fluorescence emission of the colored closed form. The written information was erased with a wavelength of 515 nm. The maximum erasing time was 5 min.

In the two-photon fatigue test, the photoconversion rate of DAE molecules was monitored by collecting the induced fluorescence signal in the same spectral channel used above (575–640 nm). In this case we used an air objective (10 $\times$, 0.4 NA) of the microscope giving intensity at the sample of 1.6 MW/cm². The intensity of the reading/erasing laser beam at 515 nm was 43 kW/cm².

2.4. Thermal analysis

Thermal analysis was carried out using a Perkin-Elmer Pyris Diamond Differential Scanning Calorimeter (DSC) previously calibrated with an indium standard. Polymer-photochromic solutions were drop casted in standard aluminum pans (Perkin-Elmer) and dried first at room temperature (final samples weight $\sim$ 5 mg) and then directly in the DSC during the first cycle. To determine glass transition temperature two consecutive cycles were performed (20 $^{\circ}$ C/min) using the half C_p value. To preserve the polymers and photochromic molecules from thermal degradation and to reassess solvent evaporation, samples of PEMMA, PEMMA/DAE, PMMA, PMMA/DAE were heated up to 150 $^{\circ}$ C (holding for 30 min), whereas samples PEMA and PEMA/DAE were heated up to 100 $^{\circ}$ C (holding for 60 min). Details about drying and measurement cycles are described in the Supplementary data. Prior the DSC measurements, thermal degradation rates were checked with thermal gravimetric analyzer (TGA) (Q500, TA Instruments) by putting the powders ($\sim$ 10 mg) of PEMMA, PEMA, PMMA and DAE in platinum sample pans and heating from 25 $^{\circ}$ C to 600 $^{\circ}$ C at 20 $^{\circ}$ C/min. The purge gas was N₂ (60 ml/min).

3. Results and discussion

3.1. Absorption and fluorescence characterization

Fig. 1(a) shows the molecular structure of the two photochromic isomers of 1,2-bis[2-methylbenzo[b]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene. The photocyclization reaction is driven by irradiation of the open form A with UV light ($\lambda < 400$ nm), whereas the cycloreversion reaction is initiated by irradiation of the closed form B with VIS light ($\lambda = 400$ –580 nm). The photochromic reaction of the diarylethene in solid polymer results in coloration of the initially transparent into reddish-colored films, as shown in Fig. 1(b). At room temperature the coloration is stable in the dark.

In Fig. 2 absorption and fluorescence spectra of the two isomeric forms of 10 wt% of DAE in PEMMA matrix are shown. The spectral amplitudes of the B-isomer were multiplied for easier viewing. Change in the hosting polymeric matrix did not change significantly the absorption and fluorescence spectra of the films. For the photoconversion between the two photochromic isomers in the cycle experiment, continuous laser light of 325 nm for the coloration and 561 nm for decoloration was used, denoted as empty circles in Fig. 2(a). In the same picture we marked the wavelengths used in the optical memory experiment as 360 nm and 515 nm (filled circles) for data writing and erasing, and 405 nm for data reading (gray triangle). The 405 nm irradiation does not initiate the cycloreversion reaction in the samples because of the much smaller absorption of the A isomer at this wavelength. On the contrary, the 405 nm light could be absorbed by the B isomer leading to the fluorescence emission of the closed form.

Fig. 2(b) shows fluorescence spectra of the A (solid line) and B (dashed line) forms of 10 wt% of DAE in PEMMA matrix. The spectral amplitudes of the fluorescence for A and B isomers were

Fig. 2. Absorption (a) and fluorescence (b) spectra of the A (gray solid line) and B (black dashed line) forms of DAE in PEMMA polymer films prepared in chloroform. The fluorescence spectra of A and B forms were measured using excitation wavelengths of 325 nm and 500 nm, respectively.

significantly different with a ratio $I(A):I(B)=7$. For this reason the fluorescence spectrum of the B form was scaled for better visibility. Well separated absorption and fluorescence spectra of the two photochromic forms allowed selective excitation for the writing–reading–erasing experiment.

3.2. Thermal characterization

In order to determine the T_g of the pure polymers and the composites, thermal analysis of all samples was performed by differential scanning calorimetry. Prior the DSC, thermal stability of the polymers and of the photochromic compound was investigated by TGA (Supplementary data, Fig. S1–S3). Thermal stability of all the samples differed slightly. For this reason, the heating temperatures for the DSC analysis were adjusted to avoid thermal decomposition of the material (Supplementary data).

The results obtained by DSC are presented in Table 1. Comparing T_g values for powders of the polymers (first row in Table 1) and dried drop-casted pure polymeric samples (second row, value on the left), we found identical values for the PEMMA (38 $^{\circ}$ C) and PMMA (108 $^{\circ}$ C) polymers. For the PEMA drop-casted samples, the T_g value was lower than for a powder due to remaining solvent as described above. Comparing only drop-casted samples (second row of Table 1) with and without the DAE, we obtained similar values of T_g for the PEMMA (36 $^{\circ}$ C/38 $^{\circ}$ C) and the PEMA (40 $^{\circ}$ C/39 $^{\circ}$ C) polymers. In PMMA samples the T_g was higher in pure polymers than in doped ones by 7 $^{\circ}$ C. The similarities in T_g for pure and doped polymers may indicate that the interactions between the photochromic molecules and the hosting matrices are minimal and do not strongly affect the thermal behavior of the composites. Slight decrease of the T_g for doped samples can be due to a plasticizing effect of the matrix due to the photochromic molecules [9]. The measured T_g values of the composites rule out strong interactions, such as

Table 1Parameters of all investigated materials: T_g , molecular weight, and the fatigue given in number of “operative” cycles.

Sample	PEMMA/PEMMA + 10 wt% DAE	PEMA/PEMA + 10 wt% DAE	PMMA/PMMA + 10 wt% DAE
Powder samples, T_g [°C]	38/–	59/–	108/–
Dried samples, T_g [°C]	38/36	40/39	108/101
Molecular weight	88,000	515,000	120,000
Number of “operative” cycles	550	450	220

formation of chemical bonds, between the polymers and photochromic molecules.

3.3. One-photon fatigue characterization

The capability of performing multiple coloration–decoloration cycles without loss of performance is crucial parameter for a photochromic material to be suitable for various applications. In this contribution the fatigue resistance property for the DAE in three acrylic polymer matrices was investigated. In order to determine the dose of irradiation necessary for photochromic conversion and to estimate its efficiency, an absorption saturation experiment was carried out. The optical absorption in the visible spectral range ($\lambda_{\max} = 528$ nm) was monitored as a function of increased irradiation time using 325 nm laser light. The irradiation continued until the saturation of absorption at 528 nm ($A \rightarrow B$ isomerization) was reached. Fig. 3 shows the normalized absorption values, $A_t - A_0/A_{\text{sat}}$, for different UV irradiation time, where A_t is the absorption amplitude at a given irradiation time at 528 nm, A_0 is the absorption amplitude of the as prepared sample at 528 nm, and A_{sat} is the saturation absorption value at the same wavelength. The saturation absorption of the B isomer is reached in a similar way for all matrices. After about 20 s of total UV irradiation time the values of absorption at 528 nm reach 95% of the maximum value, and therefore this irradiation time was chosen as the UV dose for the following cycling experiment.

For the back photoconversion the samples were irradiated with VIS laser light of 561 nm until the absorption at 528 nm ($B \rightarrow A$ isomerization) almost fully disappeared (Fig. 3). The back photoconversion rate was found to be very similar for all polymer matrices. We will discuss the similarities in the photoconversion rates for different polymers in the end of Section 3.3. For the following cyclic fatigue experiment the dose of the VIS irradiation was set to 40 s, since after this irradiation time the absorbance at 528 nm reaches a minimal value.

The photoinduced fatigue resistance property of the three polymeric composites with 10 wt% of DAE prepared after spin-coating of their chloroform solutions was investigated upon multiple

irradiation cycles with the chosen UV and VIS doses and it is presented in Fig. 4. The normalized absorption intensity, $(A_1 - A_i)/A_1$, at 528 nm is plotted versus the number of UV–VIS irradiation cycles, where A_1 is the absorption amplitude after the UV irradiation of the first cycle, and A_i is the absorption amplitude after the UV irradiation of the i -th cycle. A significant reduction of the visible absorption was observed already after several hundreds of repetitive coloration–decoloration cycles. The number of cycles, corresponding to absorbance decrease to 80% of its maximum value, is defined as “operative” number of cycles for applications. In Fig. 4 the operative numbers of cycles are marked with vertical dashed lines. Despite similar conversion efficiency of the DAE isomers in the different hosting matrices, it can be seen that the fatigue curves for the three polymers show a different decay. The most rapidly decaying curve was obtained for the PMMA polymer, with the estimated number of operative cycles arriving to 220. For the PEMA and PEMMA polymers the number of operative cycles was 450 and 550, respectively. It was also observed that the fatigue curve for the PEMMA polymer is characterized by an initial rise in the first 40 cycles, indicating that the A to B conversion efficiency increases with increasing number of cycles. This effect could be attributed to the variation of the free volume of the PEMMA polymer, which is characterized by a low T_g and, therefore, by high mobility of polymeric chains. The latter facilitates the rearrangement of the photochromic molecules with respect to the chains during the first irradiation cycles [22].

The overall fatigue resistance of the tested photochromic materials estimated from our experiments was found to be poorer than the one previously reported by Irie [10] for the DAE in liquid environment and is comparable to the one found by Hoshino in a co-polymer of fluoroethyl methacrylate and methyl methacrylate [22]. In our experiment, the three acrylic polymers have different glass transition temperatures and molecular weights. The poorest fatigue resistance was obtained for the DAE embedded in PMMA matrix, characterized by the highest T_g (101 °C) compared to the other examined polymers. It was reported earlier that in rigid hosting matrices, with high T_g , molecular motions related to the

Fig. 3. Peak value of the absorbance band in the visible spectral range (528 nm) as a function of the irradiation time for photocyclization and cycloreversion processes.

Fig. 4. Fatigue resistance curves of the DAE in PEMMA, PMMA, and PEMA polymers prepared in chloroform. The vertical dashed lines indicate the crossing points at which the number of “operative” cycles was determined.

photochromic isomerization can be restricted [25,26]. Photochromic compounds that are unstable at room temperatures (e.g. azobenzenes, spiropyrans, and spiroxazines) demonstrate faster fading rates as the T_g values of their polymer matrices decrease [25,27]. Photochromic reaction in such compounds is typically accompanied by a large molecular motion, requiring a sufficient volume inside the hosting polymer. Since the available free local volume in a polymer is inversely proportional to its glass transition temperature, such large motions are facilitated in polymers with low T_g [25]. In contrast to the previously mentioned thermally activated photochromic compounds, the diarylethenes do not require a large space for photo-cyclization reaction. Nevertheless, the matrix rigidity may affect the photophysical properties of the molecules, and therefore we propose the following hypotheses to explain our findings.

A diarylethene in several polymeric matrices at a single-molecular level was investigated by Fukaminato et al. [28]. Non-exponential histograms for the fluorescence turn ON/OFF times were found in the polymers with high T_g values (Zeonex, Arton and PMMA). This result was ascribed to the matrix rigidity and to the disability of molecules to freely move in the polymer matrix. The authors suggested that the polymeric chains work as a steric hindrance leading to a modification of the molecular potential energy surface, in contrast to what observed for molecules in a less rigid environment. The number of switching cycles was estimated to be around 100 [28]. We assume that the low number of cycles reported in the work of Fukaminato et al. could be associated with the steric hindrance of the polymer surrounding the molecules. The photochromic diarylethene used in the present work is of a smaller size, and the effect of the matrix rigidity may still affect, but less drastically, the photochromic reaction of the DAE.

An alternative scenario to explain our experimental results on fatigue is related to the isomerization in the open form. It is known that the transparent open-ring form of DAE has two isomers (parallel and anti-parallel) [10]. Both isomers coexist in the ground state of the ring-opened diarylethene, but only the anti-parallel isomer undergoes the photochromic reaction. The isomerization between the parallel and anti-parallel forms, in contrast to the photochromic reaction, is accompanied by a large molecular rearrangement. The effect of the matrix rigidity and of the free local volume available might be more prominent. More rigid polymer matrices might prevent or slow down the isomerization between the parallel and anti-parallel forms, in contrast to a solution or a soft polymer, and provide trapping conditions for one of the two forms. Our data seem to agree with this scenario assuming that the parallel isomer (non photoactive) gets stabilized more efficiently in the PMMA upon multiple cycling, and, accordingly, fewer and fewer molecules undergo the photochromic reaction. This could lead to the absorption decrease in the visible spectral range. The photophysics of the parallel isomer was so far poorly investigated. Ishibashi et al. [29] reported a detailed spectroscopic investigation of the DAE with the time-resolved methods on the femtosecond-to-microsecond time scales. They found that the anti-parallel (photochromic) isomer is characterized by a fast sub-picosecond transient dynamics describing the cyclization process. The parallel (non photochromic) isomer is characterized by a significantly slower excited-state dynamics with the lifetimes of 150 ps and ca. 1 μ s. The slower component was assigned to the lifetime of a triplet state [29]. The long-lived triplet state found in the parallel isomer might lead to accelerated photodegradation of this isomer and possibly to the decreased total number of available molecules. In this case the absorption intensity in the visible spectral range (528 nm) could gradually decrease upon repetitive cycles.

Both of the described scenarios could explain the difference in the fatigue for the studied polymeric matrices (Fig. 4). It should be

noted that the both effects are accumulative, and therefore become prominent with repeated cycles (fatigue curves in Fig. 4). If only one UV–VIS photoconversion cycle is applied to the samples, as the one presented in Fig. 3, the effects of the matrix on photoconversion rates are negligible and therefore cannot be observed at our experimental conditions.

We have additionally tested the fatigue of the composites prepared in toluene and we found out that the fatigue behavior is independent of the preparation solvent (see Fig. S4).

Finally, in order to exclude possible molecular aggregation effects on the fatigue, the measurement were also performed for 5 wt% and 15 wt% of DAE in the host matrix (Supplementary data, Fig. S5). The amount of DAE in the matrices was kept low to assure good mixing of the two compounds. In the range of the tested concentrations by weight, no major variations were observed in the fatigue curves. We conclude that the molecules in our experiment were dispersed homogeneously and inter-molecular interactions do not influence the fatigue behavior.

3.4. Application for 3D optical memory and two-photon fatigue characterization

The above presented results demonstrate that the studied photochromic polymeric composites can be satisfactory candidates for 2D optical memories, since, especially the ones with low T_g , can undergo hundreds of cycles without apparent fatigue. On the other hand, since for large volume storage, 3D-writing is essential, we studied the same composites as candidates for 3D optical memory media, first demonstrating their viability for this application and then performing tests of writing–reading–erasing cycles. This demonstration is given in Fig. 5(a), where each letter is written separately using two photon absorption, by scanning the selected region of interest with ultrashort pulses of the infrared laser light. The written images were visualized by acquiring the fluorescence from the photoconverted area upon 405 nm excitation. The spectral range for fluorescence acquisition was chosen to be 575–640 nm in order to match the emission of the B form (see Fig. 2(b)). Inhomogeneities in the fluorescence intensity in the pictures are due to reduced efficiency of the two-photon process outside the central part of the field of view because of aberrations rather than inhomogeneities of the samples. The lower panel of Fig. 5(a) shows the erasing effect of the lower half of the image obtained by scanning with the 515 nm laser. The writing–reading–erasing procedure was successful for all three samples under the used experimental conditions, and this demonstrated that all three polymeric matrices can be used as media for optical memories.

As a demonstration of the 3D character of this storage application, it has to be noted that the image shown in Fig. 5(a) and its corresponding analogs obtained in the other polymeric matrices, were not realized at the surface of the drop-casted sample but some tens of micrometers inside the bulk. In fact, in the image acquisition by fluorescence detection, by shifting the focal plane of the objective by 5–10 μ m above or below the position of the photoconverted letters, no fluorescence signal could be obtained in all samples, thus demonstrating the vertical confinement of the photoconverted region. This vertical confinement is better demonstrated in Fig. 5(b), where a cross section of the drop-casted sample along the z-direction shows a series of vertically aligned photoconverted spots throughout the depth of the sample. The sizes of the laser spots have FWHM of 8.7 μ m in the longitudinal direction, and of 2.2 μ m in the transversal one [30]. The displacement along the vertical direction between the spots was 5 μ m. The picture reported shows a sequence of 16 spots. Up to around 20 spots were obtained in some samples, their number being limited only by the thickness of the samples obtained with the drop-cast method.

Fig. 5. (A) Fluorescent images of the DAE-PEMMA samples obtained by two-photon writing ($\lambda_{\text{wr}} = 720 \text{ nm}$), one-photon reading ($\lambda_{\text{read}} = 405 \text{ nm}$) and one-photon erasing ($\lambda_{\text{er}} = 515 \text{ nm}$). The erasing was applied to a bottom half of the image. (B) Optical section of the photoconverted molecules in a laser spot taken in XY and XZ planes. (C) Fluorescence emitted by the spin-coated DAE-PEMA samples after the 1st, 10th, and 20th writing cycle (left to right).

A qualitative demonstration that the materials can sustain the repetitive photoconversion process upon two-photon excitation, is performed by repeating a sequence of writing-erasing on the same area and then monitoring the emission of the specific area (Fig. 5(c)). For this particular test, on the spin-coated samples of DAE molecules dispersed in the three polymers we choose square areas of $62 \mu\text{m}$ in size. These areas were irradiated in the above described confocal microscope and photoconversion to the closed form was induced by two-photon absorption process. The photoconversion rate of DAE molecules was monitored by collecting the induced fluorescence signal in the same spectral channel used above (575–640 nm). The irradiated area was continuously scanned in this condition in order to reach a photoconversion level of the photochromic molecules around 90% of the saturation value, in analogy with what was done for the fatigue tests with one-photon excitation. Fig. 5(c) shows the intensity of the fluorescence recorded from the irradiated areas after the 1st, 10th and 20th writing cycles for the PEMA/DAE sample. The fluorescence is still detectable after 20 cycles but its intensity decreases significantly compared to the intensity after the first writing. This indicates a more rapid photodegradation of the photochromic material under the two-photon excitation. Possible explanation for this observation could be that the two-photon absorption process requires high laser intensities, compared to the one-photon process, possibly leading to thermal modification of the hosting matrix. Moreover, another side effect of the non-linear writing process could be a faster photodegradation of the matrix or of the photochromic molecules, induced by a small fraction of higher-order multiphoton absorption processes. To help to understand the difference in the fatigue between

one-photon and two-photon excitations, additional experiments, such as excited-state dynamics measurements, might be needed, but are out of the scope of the present manuscript.

4. Conclusions

We demonstrated experimental data on fatigue resistance of photochromic diarylethene molecules embedded in three acrylic polymers prepared by simple blending. The photoinduced fatigue is one of the crucial parameters for rewritable data storage devices and it was determined as the number of coloration-decoloration cycles at which the absorbance/fluorescence of the closed-ring photochromic isomer decreases to 80% of its initial intensity. The fatigue was tested for one- and two-photon excitations. For the case of one-photon excitation, our data show that the best fatigue resistance in polymer-photochromic materials can be obtained using polymers with lower T_g . In particular, the samples prepared with the PEMA and PEMMA polymers displayed better resistance to photodegradation with respect to PMMA. For 3D memories, two-photon excitation is needed for writing. In this case, our study on fatigue showed significantly different results compared to the one-photon excitation. The high laser intensity of the two-photon excitation may lead to additional thermal and photochemical processes involving both, the photochromic molecules and the polymeric matrices. The fatigue therefore was found to be strongly reduced in comparison with the one-photon excitation and it was similar for all the studied composites. The presented data on the number of “operative” cycles presented are comparative and can be very useful in choosing the proper combination of polymer-photochromic materials for applications, such optical memories, demonstrated herein.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.mseb.2013.03.009>.

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